Engine Coolant Testing

Fourth Volume

Roy E. Beal, editor

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Foreword

The Symposium on Engine Coolant Testing was held 5–7 November 1997 in Scottsdale, Arizona. Committee D15 on Engine Coolants sponsored the symposium. Roy E. Beal, Amalgamated Technologies, Inc., presided as symposium chairman and is editor of this publication.

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Overview

The Fourth Symposium on Engine Coolants demonstrated many advances and changes in the technology of coolants and their testing procedures. A gradual globalization of coolant formulation is occurring in parallel with the world production of specific vehicles that meet the demands of several disparate markets. There are still important differences in the direction of technology in the United States, Europe, Japan, and the rest of the world. There is now a more widespread acceptance that usefully constructed coolants should be used in any location. New engine designs demand coolant fluid discipline. Organic acid basic inhibitor technology is the growth area with continued interest in propylene glycol as a substitute for the more commonly used ethylene glycol. The new work is in extended life coolants. Major vehicle manufacturers are now recommending 10 years or in some instances life of vehicle coolants. These factors will slow the total volume of coolant required somewhat, but the total world vehicle population is increasing at the same time. There is continued interest in the development, management, and quality control of the modern engine for both OEM and after-market, which is the main purpose of ASTM D15 Committee as the standards body responsible for guiding a consensus towards agreed levels of technical competence to serve an increasingly sophisticated vehicle market.

The first symposium was held in Atlanta, Georgia, in 1979, and papers presented were published in STP 705, which is still a practical, as well as historical volume. Rapid changes in material usage with more aluminum radiators and cylinder heads required inhibitor package modifications and new tests, covered in the second ASTM Engine Coolant Testing conference in 1984. A hot surface protection standard had been developed and propylene glycol was introduced. Electrochemistry was highlighted and heavy duty vehicles received attention. Presented papers were published in STP 887.

A third ASTM Engine Coolant Symposium followed in 1991 which was truly international in character with presentations from Europe, Japan, and the United States. Organic acid based inhibitors were introduced, work on sebacic acids, and typical alkaline phosphate silicate formulas prevalent at the time in the United States were covered. Cavitation of diesel engine liners and protection, pump seal evaluations, and recycling of coolant were other major areas presented. Papers can be found in STP 1192, the third volume in the Engine Coolant Testing Series. A look at all three volumes as a compendium reveals an excellent collection of technology in the field and together with this fourth book, makes the most comprehensive review of the engine coolant world past and present with a brief look at its possible future.

The symposium opened with papers on organic acid inhibitor technology lead by Tom Weir who covered testing of organic acids by examination of the effectiveness of thirty organic acids using electrochemistry, glassware, and galvanic methods. In general, aliphatic monoacids provide good aluminum alloy protection, but are antagonistic to solders. Aromatic monoacids can be good on steels and cast iron. Longer chain acids tend to provide better protection. Several organic acids with good overall performance were identified.

The composition of incipient passivating layers on heat rejecting aluminum in carboxylate and silicate inhibited coolants was the title of the Wagner et al. paper, where correlation with ASTM D 4340 weight losses was reported. X-ray photoelectron spectroscopy identified the compositional differences between the coolants on 319 aluminum alloy surfaces under heat rejecting conditions. Silica was the primary layer in silicated coolants with hydrated alumina formed in the organic acid coolant family. The role of the carboxylate inhibitors is suggested as a promoter of highly protective forms of hydrated alumina on converted metal surfaces, where the silica layer is purely exogenous. Mixtures of the two coolants produced increased corrosion and less protection, especially at lower 25% glycol levels, where low levels of cross contamination produced significant loss of protection. Clearly, contamination is to be avoided until a protective layer is created on the surface of the components involved with either the silicated or carboxylic inhibited packages.

Fleet test evaluations of fully formulated coolants for heavy duty application were compared with a standard supplemental coolant additives (SCA) filter charge program. Ethylene glycol based coolant with phosphate-silicate, nitrited carboxylic acid technology and a phosphate-free low silicate formula in propylene glycol were investigated by Aroyan and Eaton. Results demonstrated that a nitrited carboxylic acid inhibited coolant was similar in performance to the more conventional coolant inhibitor approach in both ethylene and propylene glycol bases. All technologies were providing acceptable protection in a 66 fleet test program.

The overall performance of conventional coolant inhibitor technology compared to the newer organic acid technology has not been previously reported and was investigated by D. E. Turcotte et al. The depleting nature of silicates during service has led to a conservative coolant change recommendation of 30 000 to 50 000 miles (48 279 to 80 465 km) in automobiles. Laboratory bench, engine dynamometer, and vehicle service studies were made with the two inhibitor families. A new electrochemical test was introduced to examine passivation kinetics on aluminum alloy surfaces. Results show that silicate coolants act more quickly and passivate aluminum surface faster than the organic acid coolant. Dynamic erosion/corrosion tests tend to favor silicate technology. Both silicate and organic acid coolants provide equally long service life when adequately formulated. The main advantage of organic acid technology appears to be meeting chemical limitations imposed by some global coolant specifications.

Bartley et al. studied the depletion of tolyltriazole in testing and in service, in extended life coolant using organic acid coolant technology. Electrochemical polarization experiments indicate that the tolyltriazole forms a surface layer on copper alloys that is very protective. Laboratory tests and radiators retrieved from field tests demonstrate the effectiveness of the tolyltriazole inhibitor in conjunction with organic acid inhibitor packages. Simulated rapid coolant aging was achieved by adding finely divided powders of aluminum, iron and copper to the coolants exposed in glassware at about 105°C in air under atmospheric pressure. Results from analyses of periodically withdrawn samples correlated well with service experience. Good copper protection is achieved with tolyltriazole depletion matching laboratory and field observations.

The wide range of metals used in vehicle engine and cooling circuits requires careful consideration of the chemical complex that forms an inhibitor package. Beal reviewed corrosion aspects of the metals involved, preferred protection processes, and likely contaminants in water that reduce coolant effectiveness. Information was gathered from the general corrosion literature as it pertains to coolant, and some of the current standards for testing were discussed. The desire for longer life engine coolants emphasizes the need for newer test methods to simulate these requirements and provide needed protection.

Predictive tools for coolant development enhance experimental studies. Gershun and Mercer have defined an accelerated aging procedure for modeling fleet test results. The program objective was to predict coolant composition effects after 100 000 miles (160 930 km) or more. Cooling system metals used, their respective surface areas and coolant conditions were utilized. Degradation products, inhibitor depletion, reduction in pH and the presence of corrosion products in solution were monitored. Test coolants were evaluated by ASTM D 1384 glassware and ASTM D 4340 hot surface tests. The test procedure developed produces coolant that compares favorably in composition, physical properties and performance with fleet test fluid. A rapid evaluation of the effectiveness of a coolant inhibitor package after 100 000 miles (160 930 km) can be performed using the procedure and is useful in the selection of competing formulas.

Rapid electrochemical screening and correlation with ASTM D 1384 glassware tests was reported by Doucet et al. The objective was to identify promising coolants more quickly, to accelerate testing and reduce coolant evaluation time and cost. Some success was claimed with a triad galvanic corrosion rate test providing the best correlation. Other tests were promising, but further work is needed.

Elastomers are very important, since most cooling systems involve several hoses under the hood. However, there are presently no standard ASTM elastomer evaluation procedures for coolant compatibilities. A session devoted to this subject was well received. Long-term service of elastomers was studied by Bussem et al. Aging effects do occur that influence physical and chemical properties over a long time period. The authors identified FEPM materials as the elastomer of choice at present for engine coolant application. Greaney and Smith used high temperature, short time immersion testing to determine the usefulness of a variety of elastomers and plastics in coolant, covering hoses, radiator tanks, and water pump seals. All of the materials tested showed some degradation after exposure to diluted or concentrated coolants with both ethylene and propylene glycol bases. Currently used inhibitor packages covered conventional, hybrid and organic acid technologies, which all similarly influenced the chosen elastomers. Evaluations included immersion tests, overflow bottle effects, post fluid analyses, tensile properties, and physical values.

Degradation of EPDM hoses by electrochemical attack was studied by Vroomen et al. covering the influences of engine coolant composition or behavior in service conditions. EPDM has been used for over 25 years, and a service problem was identified with cracking failure in hoses. Investigation had primarily explored factors involved except for the coolant. Using a laboratory test with a stainless steel holder and specimens under mechanical strain, an electrical current is forced through the essentially insulating material by having the specimen serve as the anode, and the holder is the cathode. Sulfur cured hoses are more susceptible than peroxide cured hoses to the cracking phenomenon. Collectively, these papers provide a direction to understanding the needs of a test protocol for nonmetallic materials and their response in coolants.

Heavy-duty coolants for diesel and larger trucks have particular operating requirements. Carr assessed the validity of conductivity measurement to estimate total dissolved solids and determined that it gives satisfactory data with controlled dilution. Chen and Kershisnik looked at scale deposits in high heat rejection conditions. Key parameters were evaluated and a quantitative relationship of scale formation, water hardness, and heat flux was observed. Water soluble polymers do prevent scale deposits. Glassware hard-water compatibility tests do not predict scale or deposit formation results demonstrated by the new test procedure. An extended service coolant filter development was covered by Mitchell and Hudgens, depending upon time release concepts that worked actively up to 140 000 miles (225 302 km).

Engine coolant recycling has not become as pervasive as earlier thought possible, but the industry is still growing. Large-scale recovery by distillation was reviewed by Frye et al., claiming that 15 million gal (57 million L) per year are recovered this way. Industry practices are presented with confirmation that ASTM specification engine coolants can be reliably produced by recycling. Reverse osmosis has proved itself as a suitable technology applied to engine coolant recycling. Haddock and Eaton explain the process and their experience. The technique is used in both stationary large plants and for mobile application as described by Kughn and Eaton using similar process equipment. A multistage chemical recycling process is described by Woyciesjes and Frost with extensive fleet testing to prove the method. Excellent protection is demonstrated in heavy-duty fleets. An important caveat is that all recycling technologies do not work as well. General Motors recognized the need for a totally independent assessment of recycled engine coolants and has undertaken an approval program for automotive application. An evaluation of various processes was covered by Bradley with the development of a selection protocol.

Engine coolant testing methods that delineate protection and service capabilities are incorporated into ASTM standards by consensus. McCracken and Beal described some new procedures and proposed changes to existing methods that will strengthen the testing standards including ASTM D 4340, D 3147, D 2809, and D 2570. Possible new dynamic coolant tests are discussed. The importance of silicate stabilization to effective aluminum alloy protection was investigated by Schwartz. Results of experiments illustrate formula dependent behavior. An overview of engine coolant testing in Europe with particular reference to Germany was presented by Brösel. The well known FVV test is undergoing complete revision. A new hot test apparatus has been devised with dynamic recirculation and direct heat transfer simulation. The test comprises a modular approach with various samples in the circuit. The cavitation test is also under revision and final plans are not yet complete. The proposed tests are intended to reflect modern engine conditions for stressful operation to ensure satisfactory coolant formulation for long-service life.

Quality assessment of engine coolant production for specific formulations is vital to a consistent product. Starkey and Couch described manufacturing and quality control considerations to obtain a satisfactory output. Eaton reported on extended service fully formulated heavy-duty engine coolant experience in automobile service. Vehicle tests demonstrated satisfactory coolant performance. A new coolant filter and conditioning system applicable to automotive and truck manufacturers was reported by Wright with field test evaluations.

A successful symposium with good attendance was achieved. Some controversial presentations were made, but were certainly thought provoking for the future of coolant technology. Thanks are expressed to all the authors, the symposium subcommittee, and ASTM staff with special mention of Gloria Collins for her help throughout. The volume extends an excellent series on the progression of the engine coolant industry.

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Organic Acid Inhibitor Technology

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Testing of Organic Acids in Engine Coolants

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ABSTRACT: The effectiveness of 30 organic acids as inhibitors in engine coolants is reported. Tests include glassware corrosion of coupled and uncoupled metals, FORD galvanostatic and cyclic polarization electrochemistry for aluminum pitting, and reserve alkalinity (RA) measurements. Details of each test are discussed as well as some general conclusions. For example, benzoic acid inhibits coupled metals well but is ineffective on cast iron when uncoupled. In general, the organic acids provide little RA when titrated to a pH of 5.5, titration to a pH of 4.5 can result in precipitation of the acid. Trends with respect to acid chain length are reported also.

KEYWORDS: corrosion, organic acids, long-life, coolants, glassware corrosion, electrochemistry, lead, copper, brass, cast iron, aluminum, steel

Inhibition by individual organic acids in coolants is reported to fill the literature gap between single metal inhibition by lone acids and multimetallic inhibition by acid combinations. Literature and patents [*1*] related to coolants provide a selection of organic acids to test for corrosion inhibition performance in ASTM and electrochemical tests. Some literature references (for example, Hersch et al. [*2*] and A. D. Mercer [*3*]) report inhibition by a large number of acids on a range of metals using a one-acid-on-one-metal approach. Others (for example, Maes [*4*] and W. C. Mercer [*5*]) report corrosion results for mixtures of acids either on single metals or the typical metal specimen bundle of ASTM Standard Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384). Patents are invariably concerned with synergistic mixtures of various acids. What is missing is testing of individual acids using typical multimetallic ASTM methods and extensions.

Thirty tested acids fall into three broad categories, aliphatic monoacid, aromatic monoacid, and aliphatic diacid. These acid types appear to provide the best corrosion protection based on literature reports. Also, trends associated with acids within a particular type are investigated. For example, the linear aliphatic monoacids from C_3 to C_{12} are progressively less soluble.

General corrosion of multimetallic specimen bundles and aluminum pitting are the focus of testing. Coupled (as in D 1384) and uncoupled multimetallic bundles are considered. The coupled bundle is used for familiarity and nominal similarity to an automotive cooling system. The uncoupled bundle provides a link between single and coupled metals, is applicable to single metal cooling systems, and identifies coupling effects (in conjunction with the coupled bundle). Aluminum pitting protection is tested electrochemically using complementary procedures. The cyclic polarization procedure is best at measuring what happens as pits initiate and grow. The galvanostatic procedure is best at determining what happens as the pits repassivate. Together, a reasonable picture of the protection mechanism can be formed.

Also, a link from familiar tests and inhibitors to these unfamiliar test methods and organic

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acid inhibitors is provided. Distilled water, ethylene glycol (EG), propylene glycol (PG), ASTM Standard Specification f6r ASTM Reference Fluid for Coolant Tests (D 3585) in EG and PG, and commercial products are tested as benchmarks.

Experimental

Test Methods

Coolants are tested for RA (reserve alkalinity) using ASTM Standard Test Method for Reserve Alkalinity of Engine Coolants and Antirusts (D 1121), general corrosion of coupled and uncoupled metals using a modified D 1384, and aluminum pitting corrosion using FORD Laboratory Test Method BL5-1 ''A Rapid Method to Predict the Effectiveness of Inhibited Coolants in Aluminum Heat Exchangers,'' a galvanostatic method, and cyclic polarization electrochemical methods. These tests are described separately.

RA is measured by titration of 10 mL of coolant in a 10 volume% solution with 0.1 N hydrochloric acid (HCl). Two endpoints are chosen, the D 1121 standard endpoint of pH 5.5 and a lower endpoint at pH 4.5. The intent of the RA measurement is to provide an indication of the buffer to maintain effective pH control of corrosion. Therefore, the titration must go through the buffer region of the organic acids. However, organic acids buffer below a pH 5 [*6*]. pH 4.5 is a compromise between titrating to even lower pH and a titrating to a pH where corrosion is still under control.

The modified D 1384 test efficiently connects typical coolant testing (coupled metal coupons) with literature references (isolated or uncoupled metal coupons). Four beakers in a 2 by 2 array contain a combination of solder (Sn30A or Modine) and coupon coupling (specimens either galvanically coupled or not). Thus the four beakers are: Sn30A with coupled metals, Modine with coupled metals, Sn30A with no coupling of metals, and Modine with no coupling of metals. Teflon spacers are used between metal specimens in the uncoupled bundles. Duplication is insured by the statistical design. Otherwise, test conditions are the same as for D 1384, 33 volume% coolant diluted with corrosive water (100 ppm of chloride (Cl^-), sulfate ($SO_4^=$), and bicarbonate (HCO_3^-)) at 88°C for 2 weeks. General corrosion is measured by weight loss.

The BL5-1 test is performed by polarizing a piece of Al 3003H at 100 $\mu A/cm^2$ for 20 min in 25 vol% coolant diluted with corrosive water to give 100 ppm each of Cl^-, $SO_4^=$, and HCO_3^-. The nonsteady state conditions of the test are important in evaluating the rate of inhibitor action. The test is run in duplicate. Two potentials relate to the tendency of aluminum to undergo pitting corrosion. The first potential, E_{max}, is a fair measure of the likelihood for the protective aluminum oxide (Al_2O_3) coating to break down. The second potential, E_{min}, is a very good measure of the likelihood for the oxide to heal. All voltages are measured against a saturated silver/silver chloride (Ag/AgCl) electrode.

The same solution and cell arrangement are used for cyclic polarization. A voltage scan is begun at -1.0 V and raised at the rate of 3 mV/s to a potential of 2.4 V. The scan is reversed, reducing the potential back to -1 V at the rate of 3 mV/s. Three potentials and a current density measurement are obtained. The first potential, E_c, is an excellent measure of the natural or ''corrosion'' potential of the aluminum in solution. The second potential, E_b, is an excellent measure of the ''break'' potential which Al_2O_3 breaks down. The third potential, E_r, is an approximate measure of the ''repassivation'' potential below which Al_2O_3 is again stable. The maximum current density, J_{max}, obtained during the scan indicates the rate of aluminum weight loss due to localized corrosion.

E_b from cyclic polarization and E_{max} from BL5-1 testing are measures of the same phenomena. However, E_b is obtained under assumed steady-state conditions and is considered a better measure of the ''break'' potential. E_{min} and E_r are nominally measures of the same phenomena.

However, E_{min}, is more sensitive to inhibitors and other coolant conditions because it is not affected by the time the sample undergoes localized corrosion, as in E_r. In either case, higher potentials represent decreased aluminum pitting.

Coolant Blending

Liquid base (either sodium hydroxide (NaOH, 50%) or potassium hydroxide (KOH, 45%)) equal to 95% of the desired total amount was added to 90% of the required amount of PG. The choice of NaOH or KOH depended on solubility, potassium salts being more soluble. The desired acid was added and allowed to dissolve completely. Azoles and antifoam were added, again waiting for complete dissolution. Base (10 weight% in PG) was added to raise the pH to the desired 8.2 to 8.4 range of the concentrate. PG was added to bring the mixture up to 100%. The formulations are given in Table 1.

TABLE 1—*Composition and RA of individual acid coolands (in wt%).*

Acid in Formula	PG	Acid	TTZ	NaOH	KOH	RA @ 5.5	RA @ 4.5
		LINEAR ALIPHATIC MONOACIDS					
Propionic	91.527	4.000	0.201	4.272	...	...	...
Butyric	92.186	4.000	0.206	3.607	...	...	...
Valeric	92.714	4.006	0.203	3.077	...	...	...
Caproic	93.087	4.001	0.203	2.709	...	...	...
Heptanoic	93.329	4.007	0.201	2.464	...	...	...
Octanoic	93.569	4.001	0.200	2.229	...	10.0	26.1
Nonanoic	93.777	4.002	0.200	2.021	...	20.4	25.4
Decanoic	93.896	4.003	0.201	1.901	...	22.5	23.7
Dodecanoic	94.151	4.000	0.200	1.649	...	...	...
		OTHER ALIPHATIC MONOACIDS					
Isoheptanoic	93.275	4.050	0.200	2.475	...	...	...
2-Ethylhexanoic	93.617	4.001	0.200	2.183	...	6.4	23.3
Cyclohexane propanoic	93.667	4.000	0.200	2.133	...	7.8	24.5
Oleic (40% K paste)	89.793	10.003	0.204	...	0.000	...	...
		AROMATIC AND SUBSTITUTED AROMATIC MONOACIDS					
Benzoic	93.099	4.001	0.200	2.700	...	3.4	17.6
m-Cl Benzoic	93.691	4.002	0.200	2.107	...	...	...
p-Cl Benzoic	93.695	4.000	0.200	2.105	...	16.0	25.9
m-NO_2 Benzoic	93.826	4.003	0.200	1.971	...	...	...
p-NO_2 Benzoic	93.738	4.000	0.200	2.062	...	...	...
Cinnamic	93.635	4.000	0.200	2.165	...	3.0	23.9
Hydrocinnamic	93.728	4.000	0.200	2.072	...	...	...
p-Cl Cinnamic	94.033	4.007	0.200	1.760	...	24.5	24.9
p-NO_2 Cinnamic	93.360	4.000	0.200	...	2.440	21.4	22.3
p-OH Cinnamic	93.818	4.000	0.201	1.981	...	...	...
		LINEAR ALIPHATIC DIACIDS					
Glutaric	91.078	4.007	0.200	4.715	...	17.8	47.1
Itaconic	90.903	4.000	0.201	4.896	...	...	...
Adipic	91.484	4.005	0.200	4.311	...	...	...
Pimelic	91.964	4.000	0.200	3.836	...	17.4	43.3
Suberic	92.230	4.000	0.200	3.570	...	...	...
Azelaic	90.639	4.000	0.201	...	5.161	15.4	36.9
Sebacic	92.324	3.500	0.200	...	3.976	12.8	34.4
Tetradecadioic	92.114	4.000	0.200	...	3.686	...	...

Results

The results are discussed by inhibitor type. Reference and conventional coolants are discussed to understand the advantages and disadvantages of the organic acids.

Reference and Conventional Coolants

RA for conventional coolants is typically in the 10 to 14 range. This is due to the inorganic acid based buffer system with pKa's in the 7 to 9 range. Sodium tetraborate, for example, buffers about pH 7.5 and only about 0.5 weight% is required to provide a sufficient RA. Also, the inorganic acids remain soluble to pH's below 3.

Five reference fluids, deionized water, uninhibited EG, uninhibited PG, D 3585 in EG, and D 3585 in PG are used for benchmarking glassware weight losses (Table 2).

There are many interesting features comparing corrosion in water, EG, and PG. First, the expected higher weight loss of Modine versus Sn30A is observed in each fluid. Further, Modine and Sn30A losses are higher when coupled to copper and brass than when uncoupled. This is consistent with solder being poorly protected by the fluids and acting as a sacrificial metal to copper and brass. This galvanic corrosion effect is most noticeable in PG where copper and brass have higher weight losses when coupled to Sn30A (low corrosion) than Modine (high corrosion). In contrast, steel and aluminum losses are lower when coupled with cast iron than when uncoupled. This is consistent with cast iron acting as a cathodic protection electrode, raising the potential of steel and aluminum to a more passive range. Unfortunately, steel and aluminum are not protective of the cast iron and corrosion is high. A different kind of coupling is displayed for aluminum corrosion in PG. This effect is such that aluminum corrosion is higher when copper corrosion is higher. The aluminum and copper specimens are never coupled

TABLE 2—*Weight losses for reference coolants in modified D 1384 test.*

	Factors		Weight Losses, mg					
Acid	Coupling	Solder	Cu	Solder	Brass	Steel	Cast Fe	Al
Water	coupled	Sn30A	3.3	18.5	3.4	118.5	640.6	132.7
	coupled	Modine	3.0	58.9	2.5	178.6	551.1	123.9
	uncoupled	Sn30A	3.3	5.9	2.2	479.2	553.5	155.1
	uncoupled	Modine	4.8	55.3	4.3	433.6	706.0	196.1
EG	coupled	Sn30A	2.4	54.6	2.4	158.6	440.3	34.6
	coupled	Modine	2.3	635.5	4.1	299.3	863.5	36.9
	uncoupled	Sn30A	3.0	12.6	3.2	428.0	601.7	68.5
	uncoupled	Modine	4.6	133.1	6.1	335.2	485.4	84.1
PG	coupled	Sn30A	23.5	122.6	97.8	635.4	1036.1	118.3
	coupled	Modine	2.3	1000.0	4.7	566.1	716.0	60.3
	uncoupled	Sn30A	10.2	19.9	28.7	651.8	898.2	116.3
	uncoupled	Modine	3.3	115.6	4.5	390.9	483.1	95.8
D 3585 in EG	coupled	Sn30A	−0.1	1.6	1.5	0.6	1.0	5.0
	coupled	Modine	−0.2	3.0	1.9	0.2	−0.7	6.1
	uncoupled	Sn30A	−0.7	0.2	1.2	0.1	0.3	1.7
	uncoupled	Modine	1.8	1.0	0.8	0.9	1.1	4.6
D 3585 in PG	coupled	Sn30A	2.3	3.9	1.8	−0.3	−0.3	10.6
	coupled	Modine	1.8	6.4	1.8	0.1	−0.7	13.2
	uncoupled	Sn30A	1.8	2.9	0.9	1.1	−0.1	−12.7
	uncoupled	Modine	1.9	6.2	1.4	0.0	0.4	−2.8

so that an electrical contact effect does not take place. Rather, the effect results from ion diffusion in solution. For this case, copper ions plate out on the aluminum (copper being more noble). This establishes a couple on the aluminum surface between copper (as the cathode) and surrounding aluminum (as the anode). The copper/aluminum couple is well known to corrode aluminum. A general assessment of corrosion depends on what metals are considered the most important. Corrosion is less in water than in EG which are less than in PG based on solder and steel weight losses. However, water is the most corrosive based on aluminum weight losses.

D 3585 specifies a simple corrosion inhibition system for coolants. The inhibitors are expected to provide only basic inhibition and would not be suitable in vehicle use. This simple inhibitor combination, however, shuts down virtually all corrosion in EG and PG, in particular for cast iron. The higher weight losses of Modine versus Sn30A can be seen, though the "high" weight loss is only 3 to 6 mg. There is a coupling effect on aluminum, particularly in PG, where coupled aluminum corrodes slightly more than uncoupled aluminum. The difference from the neat fluids (where coupling reduced losses) is likely due to pH differences between the neat fluids and the buffered D 3585 coolant. In short, uninhibited water, EG, and PG have solder, steel, cast iron, and aluminum weight losses in the hundreds of mg. However it takes essentially only a good buffer system to shut down corrosion.

Conventional coolants (defined here as one where aluminum is protected by silicate and nitrate) have E_{min} of just less than 0 V, E_b of 1 V, and J_{max} of 1.3 mA/cm^2 and higher (Table 3). Two conventional coolants stand out, C-2 and C-5, with E_{min} of 0.2 to 0.3 V and E_b of greater than 1.5 V. J_{max} is typical, ranging from 1.5 to 3.0 mA/cm^2. This is a strong point of these coolants and indicates that special attention has been given to aluminum localized corrosion protection during coolant development.

Aliphatic Monoacids

The five reported RA values for the aliphatic monoacids (Table 1) demonstrate the poor buffer properties of organic acids. Recall these coolants have 4 weight% of the acid present and yet have RAs in the 6 to 8 range (2-ethylhexanoic and cyclohexane propanoic acids) at a pH of 5.5. The other three acids all show some precipitation, a little for octanoic acid and increasing up to decanoic acid. The RAs at a pH of 4.5 are complete precipitation of the acids. This is why the value drops in going from octanoic acid (lowest molecular weight) to decanoic acid (highest molecular weight). The pKa's of these acids are less than 5 which means that very little of the acid has actually been titrated by a pH of 5.5. However, by a pH of 4.5 most of the acid is titrated and precipitated.

The linear aliphatic monoacids are reasonably good at protecting copper, Sn30A, brass, steel, cast iron, and aluminum (Table 4). Except for propionic acid, weight losses for these metals are less than 10 mg. Modine corrosion varies greatly, from a high of 2600 mg in propionic acid to a low of 100 mg in octanoic acid in the coupled bundles (Fig. 1).

Interestingly, Modine loss increases in nonanoic (C_9) through dodecanoic (C_{12}). Also, there is a strong coupling effect on Modine, where weight losses are higher in the coupled bundles than in the uncoupled bundles. This effect is most dramatic in propionic acid, with a weight loss of 2600 mg when coupled and 150 mg when uncoupled. Lastly, the corrosion of aluminum in nonanoic acid in the presence of Modine had very high weight gains of 26 to 54 mg. Small weight gains, <10 mg, are explainable in terms of porosity and insufficient drying. The reasons for the large weight gains are unknown.

Results for the other aliphatic monoacids ranged from very poor, isoheptanoic and oleic (solder) to excellent, cyclohexane propanoic. 2-Ethyl hexanoic acid was better than the linear aliphatic monoacids on solder (50 to 80 mg) but tended to have slightly elevated steel losses (5 to 22 mg).

TABLE 3—*Electrochemical results for individual acid coolants.*

	Galvanostatic		Cyclic Polarization			
Coolant or Acid Tested	E_{max} (V)	E_{min} (V)	E_c (V)	E_b (V)	E_r (V)	J_{max} (mA/cm^2)
			Conventional Coolants			
C-1	1.89	−0.05	−0.69	1.05	−0.60	1.92
C-2	1.99	0.32	−0.80	1.87	−0.65	1.57
C-3	1.31	−0.08	−0.69	1.08	−0.63	4.43
C-4	1.82	−0.08	−0.58	1.36	−0.53	6.31
C-5	1.85	0.19	−0.44	1.62	−0.41	3.02
C-6	1.62	−0.05	−0.70	1.34	−0.63	1.32
			Linear Aliphatic Monoacids			
Propionic	1.10	−0.44	−0.70	0.77	−0.81	15.85
Butyric	1.14	−0.37	−0.68	0.67	−0.68	5.38
Valeric	1.26	−0.29	−0.59	0.83	−0.66	2.04
Caproic	1.80	1.13	−0.79	1.63	−0.60	0.14
Heptanoic	1.79	1.71	−0.55	1.96	−0.55	0.18
Octanoic	3.07	2.76	−0.73	2.10	−0.13	0.04
Nonanoic	3.06	2.37	−0.57	1.70	−0.57	0.04
Decanoic	2.85	1.92	−0.54	2.50	−0.62	0.11
Dodecanoic	4.78	3.72	−0.64	3.00	−0.16	0.01
			Other Aliphatic Monoacids			
Isoheptanoic	2.53	2.44	−0.64	2.30	−0.46	0.02
2-Ethyl hexanoic	2.15	1.76	−0.88	1.97	−0.60	0.06
Cyclohexane propanoic	2.29	1.65	−0.76	2.20	0.01	0.02
Oleic	2.48	1.61	−0.74	2.33	−0.67	0.18
			Aromatic and Substituted Aromatic Monoacids			
Benzoic	1.25	−0.17	−0.94	0.86	−0.69	3.43
m-Cl Benzoic	1.80	−0.07	−0.96	1.80	−0.69	0.39
p-Cl Benzoic	1.85	1.09	−0.76	1.64	−0.67	0.34
m-NO$_2$ Benzoic	1.40	−0.40	−0.79	1.20	−0.60	2.75
p-NO$_2$ Benzoic	1.26	−0.41	−0.67	0.90	−0.63	1.30
Cinnamic	2.24	1.25	−0.53	2.02	−0.63	0.36
Hydrocinnamic	1.54	0.60	−0.98	1.57	−0.63	0.13
p-Cl Cinnamic	2.99	2.17	−0.79	2.34	−0.60	0.06
p-NO$_2$ Cinnamic	2.41	1.70	−0.50	2.00	−0.59	0.07
p-OH Cinnamic	0.85	−0.45	−0.89	0.91	−0.69	3.85
			Linear Aliphatic Diacids			
Glutaric	1.10	−0.25	−0.51	1.10	−0.71	4.86
Itaconic	0.85	−0.49	−0.97	0.45	−0.94	9.46
Adipic	1.01	−0.22	−0.61	0.82	−0.71	5.78
Pimelic	0.63	−0.16	−0.85	0.75	−0.75	2.06
Suberic	1.44	−0.02	−0.55	0.67	−0.66	2.54
Azelaic	2.00	1.93	−0.63	1.87	−0.65	0.11
Sebacic	1.44	0.60	−0.66	1.40	−0.71	0.41
Tetradecadioc	2.00	0.83	−0.77	2.40	−0.67	0.12

The repassivation potential, E_{min}, from BL5-1 test and the maximum current density, J_{max}, from the cyclic polarization test are plotted against increasing chain length of linear aliphatic monoacid in (Fig. 2). Obvious from these plots is the trend to better aluminum protection as chain length is increased. Little protection is provided until caproic acid, C_6, after which E_{min} increases and J_{max} decreases. At the lowest value J_{max}, 0.01 mA/cm^2 for dodecanoic acid, pitting

TABLE 4—*Weight losses for aliphatic monoacids in modified D 1384 test.*

	Factors		Weight Losses, mg					
Acid	Coupling	Solder	Cu	Solder	Brass	Steel	Cast Fe	Al
Propionic	coupled	Sn30A	3.4	57.2	4.1	9.6	27.0	7.2
	coupled	Modine	5.2	2593.2	5.9	44.1	44.1	39.1
	uncoupled	Sn30A	3.0	3.3	3.1	2.1	26.1	12.5
	uncoupled	Modine	3.4	148.6	4.0	0.0	55.2	4.6
Butyric	coupled	Sn30A	2.5	43.8	3.2	0.6	8.4	8.0
	coupled	Modine	6.4	510.1	3.5	1.6	−3.6	4.0
	uncoupled	Sn30A	3.2	6.3	3.1	−0.7	1.0	4.7
	uncoupled	Modine	4.2	88.0	3.2	0.3	0.7	4.1
Valeric	coupled	Sn30A	3.1	35.6	4.5	−0.3	0.7	0.6
	coupled	Modine	5.1	436.8	3.9	0.5	1.4	3.4
	uncoupled	Sn30A	3.8	4.3	2.6	−0.2	1.9	3.8
	uncoupled	Modine	3.6	193.3	4.1	0.8	3.9	3.3
Caproic	coupled	Sn30A	3.5	6.5	4.6	0.7	1.1	4.4
	coupled	Modine	5.2	360.8	5.3	0.1	1.3	3.3
	uncoupled	Sn30A	3.7	2.9	3.1	0.1	0.5	4.4
	uncoupled	Modine	3.2	107.2	2.2	0.7	0.7	1.4
Heptanoic	coupled	Sn30A	1.6	4.6	1.1	−0.4	−0.3	4.2
	coupled	Modine	2.5	170.0	1.1	0.0	−0.2	4.7
	uncoupled	Sn30A	1.2	3.8	0.9	0.1	−0.5	0.8
	uncoupled	Modine	2.1	94.4	0.7	0.6	−0.9	0.4
Octanoic	coupled	Sn30A	2.2	3.8	1.6	−0.2	0.6	0.6
	coupled	Modine	3.0	102.1	4.9	0.1	−0.1	−2.0
	uncoupled	Sn30A	2.3	1.5	1.4	0.6	−0.4	5.7
	uncoupled	Modine	3.0	75.0	1.7	0.5	−1.0	2.1
Nonanoic	coupled	Sn30A	3.7	3.8	2.6	0.5	−0.5	0.8
	coupled	Modine	2.3	107.3	3.2	−0.2	−0.5	−53.5
	uncoupled	Sn30A	2.1	3.0	2.5	−0.2	0.0	2.8
	uncoupled	Modine	3.5	163.8	2.9	0.8	−0.9	−26.1
Decanoic	coupled	Sn30A	2.8	7.8	2.4	1.4	−0.2	6.8
	coupled	Modine	2.1	−9.8	4.1	−0.2	−0.5	2.1
	uncoupled	Sn30A	4.6	6.8	2.8	−0.7	−0.1	6.3
	uncoupled	Modine	3.5	65.6	3.1	0.1	0.0	2.5
Dodecanoic	coupled	Sn30A	5.5	12.5	4.3	0.0	−0.3	−2.8
	coupled	Modine	3.8	411.5	3.7	0.2	0.1	4.4
	uncoupled	Sn30A	4.0	8.4	3.5	0.9	3.5	6.3
	uncoupled	Modine	4.8	214.3	4.4	1.2	4.3	2.7
Isoheptanoic	coupled	Sn30A	2.5	8.6	1.1	0.2	−0.3	3.0
	coupled	Modine	1.3	516.6	0.9	−0.8	−0.9	2.2
	uncoupled	Sn30A	1.2	7.0	1.2	−0.1	−0.1	3.2
	uncoupled	Modine	2.1	390.3	0.5	0.1	−0.9	3.9
2-Ethylhexanoic	coupled	Sn30A	1.6	−0.3	1.0	5.0	8.0	0.0
	coupled	Modine	1.9	51.1	0.9	8.7	0.4	−0.6
	uncoupled	Sn30A	2.3	0.4	0.9	21.5	0.1	0.2
	uncoupled	Modine	2.0	81.9	0.6	9.8	2.7	−3.1
Cyclohexane propanoic	coupled	Sn30A	1.4	−1.1	0.4	−0.4	−0.8	0.3
	coupled	Modine	1.5	15.3	1.1	0.1	−0.4	−4.3
	uncoupled	Sn30A	2.5	−0.1	0.8	0.7	0.2	−0.6
	uncoupled	Modine	2.2	22.1	0.9	0.2	−0.5	−6.9
Oleic	coupled	Sn30A	1.5	31.6	3.1	−1.9	−71.1	−9.3
	coupled	Modine	3.0	560.6	4.2	−5.5	−0.5	−3.1
	uncoupled	Sn30A	0.7	25.3	5.0	−1.3	−0.2	−6.5
	uncoupled	Modine	0.7	298.9	4.2	−3.5	2.2	−19.5

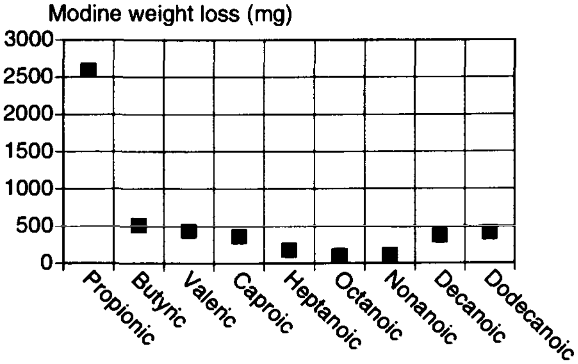

FIG. 1—*Corrosion in aliphatic monoacids.*

is only intermittent and this value is expected to be an experimentally determined minimum limit. Nonanoic and decanoic acid do not fit this pattern. A possibility is that some contaminant aggressive to aluminum is present.

The other aliphatic monoacids show some degree of aluminum protection (Table 4). In particular, isoheptanoic and cyclohexane propanoic acids are distinguished in having high E_{max} and E_{min}, very low J_{max}, and E_r greater than E_c. The last criterium is very important, defining particularly good protection. 2-ethyl hexanoic acid is unique in that J_{max} is low but neither E_{max} nor E_{min} are particularly high.

Aromatic Monoacids

The RA results for aromatic acids show a sharp contrast upon ring substitution (Table 1). Both benzoic and cinnamic acids have a low RA to pH 5.5 and much higher to pH 4.5, similar to what would be predicted for titration through the pKa. However, no precipitate was seen, in contrast to the linear aliphatics. Ring substitution (Cl at the para position) results in precipitation of the acid even at pH greater than 5.5. Precipitation is essentially complete by pH 4.5.

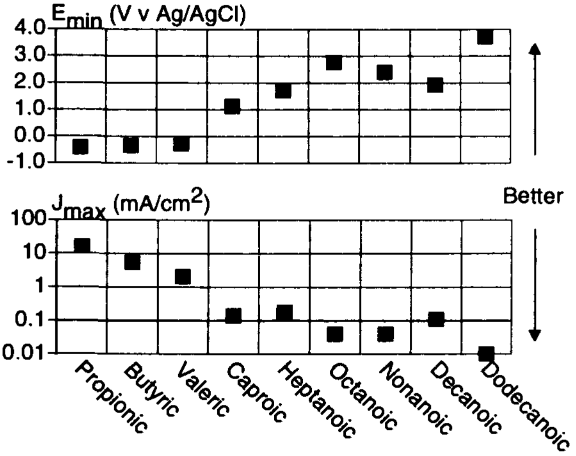

FIG. 2—*Electrochemistry for aliphatic monoacids.*

The aromatic monoacids display a variety of inhibition, (Table 5). p-Cl benzoic, p-NO_2 benzoic, cinnamic, p-Cl cinnamic, and p-NO_2 cinnamic acids protect all the metals. Among these acids, some slight differences in protection of solders, ranging from 3 to 12 mg, can be seen. p-Cl benzoic acid has the lowest losses. m-NO_2 benzoic and hydrocinnamic acid protect all but Modine solder very well. Even then, Modine losses are in the 50 mg range which is good. Benzoic and m-Cl benzoic acids have Modine losses in the 50 mg range also. However, these acids do not protect cast iron, 120 to 250 mg losses, and aluminum, 2 to 19 mg losses,

TABLE 5—*Weight losses for aromatic monoacids in modified D 1384 test.*

	Factors		Weight Losses, mg					
Acid	Coupling	Solder	Cu	Solder	Brass	Steel	Cast Fe	Al
Benzoic	coupled	Sn30A	4.8	3.0	2.8	0.3	252.5	19.3
	coupled	Modine	3.9	89.7	3.2	6.3	252.9	16.5
	uncoupled	Sn30A	2.4	0.2	2.0	0.2	0.3	−12.3
	uncoupled	Modine	2.4	16.8	1.8	0.8	0.3	3.3
m-Cl Benzoic	coupled	Sn30A	2.8	3.4	2.7	−0.2	110.1	15.6
	coupled	Modine	2.7	25.3	2.4	0.3	127.6	11.1
	uncoupled	Sn30A	2.7	1.1	2.2	0.2	−1.5	11.0
	uncoupled	Modine	2.5	8.6	2.8	0.6	186.9	10.5
p-Cl Benzoic	coupled	Sn30A	1.3	0.3	0.8	0.1	−0.3	−8.2
	coupled	Modine	1.5	3.1	0.9	−0.4	−0.2	−2.0
	uncoupled	Sn30A	1.1	0.5	0.6	0.0	−1.1	−5.0
	uncoupled	Modine	1.6	2.5	0.8	−0.4	−0.4	1.8
m-NO_2 Benzoic	coupled	Sn30A	3.1	0.3	2.0	0.5	0.3	2.8
	coupled	Modine	3.3	27.4	2.1	0.1	0.0	−0.5
	uncoupled	Sn30A	2.2	0.5	2.7	0.0	1.0	−4.1
	uncoupled	Modine	2.7	20.1	3.4	0.3	3.8	3.3
p-NO_2 Benzoic	coupled	Sn30A	1.8	1.4	1.5	0.6	1.4	3.2
	coupled	Modine	2.0	11.6	2.0	1.1	5.9	2.6
	uncoupled	Sn30A	1.7	0.8	1.7	0.5	0.9	6.1
	uncoupled	Modine	2.3	9.2	1.7	−0.1	7.3	4.4
Cinnamic	coupled	Sn30A	0.8	1.0	0.3	−0.7	−0.4	3.3
	coupled	Modine	1.2	7.1	1.1	−0.6	−0.8	4.3
	uncoupled	Sn30A	0.6	0.3	0.2	0.0	−0.3	3.5
	uncoupled	Modine	1.4	4.0	0.5	−0.7	−0.1	0.6
Hydrocinnamic	coupled	Sn30A	1.8	2.1	1.4	0.1	0.1	−4.8
	coupled	Modine	1.7	41.0	3.0	−0.3	−1.3	2.0
	uncoupled	Sn30A	2.3	2.1	1.2	−0.8	0.0	−1.4
	uncoupled	Modine	1.6	23.6	1.1	0.1	−0.2	1.2
p-Cl Cinnamic	coupled	Sn30A	2.8	0.7	2.4	−1.2	−0.6	−6.9
	coupled	Modine	2.3	11.9	1.5	−0.5	−0.4	0.2
	uncoupled	Sn30A	2.1	0.4	1.0	−1.1	0.3	1.3
	uncoupled	Modine	2.6	6.7	1.8	−1.4	−0.6	0.6
p-NO_2 Cinnamic	coupled	Sn30A	0.7	1.0	2.3	0.6	−0.3	4.1
	coupled	Modine	2.5	5.9	2.7	0.2	0.0	0.1
	uncoupled	Sn30A	2.0	1.9	2.4	−0.1	−0.8	3.4
	uncoupled	Modine	2.1	4.9	2.2	−0.4	1.0	−4.0
p-OH Cinnamic	coupled	Sn30A	2.4	16.1	6.3	−0.2	90.8	38.0
	coupled	Modine	2.0	85.2	5.2	−1.0	69.2	37.1
	uncoupled	Sn30A	7.7	220.7	13.0	−0.7	35.7	−1.3
	uncoupled	Modine	5.0	39.2	9.4	−0.7	75.1	31.5

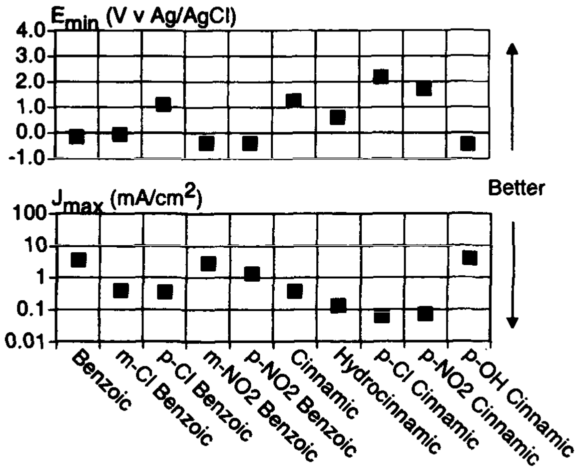

FIG. 3—*Electrochemistry for aromatic monoacids.*

very well. The poor protection of cast iron by benzoic acid is surprising given its common usage in coolants. Also surprising is the very poor protection of p-OH cinnamic acid given the generally excellent results of the other cinnamic acids.

There are three trends in E_{min} and J_{max} for the aromatic monoacids, plotted in (Fig. 3). Benzoic acid and its derivatives are, in general, not effective in providing aluminum pitting protection. This is seen in the typically low (less than 0.0 V) values for E_{min} and high (greater than 1 mA/cm^2) values for J_{max}. The exception is p-Cl benzoic acid. Cinnamic acid and its derivatives are notably better with E_{min} values greater than 1.0 V and J_{max} less than 0.5 mA/cm^2. The substituted cinnamates are the best aromatic monoacids, with values comparable to 2-ethylhexanoic acid. p-Cl is the most effective of the substitutions.

Aliphatic Diacids

The diacids provide better buffering than either the aliphatic or aromatic monoacids (Table 1). RAs of 13 to 18 are obtained by a pH of 5.5 without any precipitation. This is the advantage of having two acid sites, one to buffer and the other to remain soluble. The RAs by 4.5 are essentially complete titration of both acid sites, giving values about twice that of the monoacids. However, only sebacic acid showed any precipitation. The other acids all remained dissolved.

The linear aliphatic diacids can be split into two groups (Table 6). Glutaric, itaconic, and adipic acid belong to the first group characterized by high solder losses and significant cast iron losses. The used coolants had greater than 5 ppm soluble lead. The other acids, pimelic, suberic, azelaic, sebacic, and tetradecadioic acid, belong to the second group. Cast iron and soluble lead are well controlled in this group, but some acids have high Modine losses still. The Modine losses in this group follow an odd/even chain length pattern. Pimelic and azelaic, C_7 and C_9, respectively, have high Modine losses. Suberic, sebacic, and tetradecadioic, C_3, C_{10}, and $C_1$4, respectively, have low losses.

The linear aliphatic diacids provide some protection against aluminum pitting (Fig. 4). Starting with glutaric acid (C_5) protection improves slightly as measured by E_{min} and J_{max} up to suberic acid (C_8). Azelaic acid (C_9) provides very good protection comparable to some of the best monoacids. Longer chain acids, sebacic (C_{10}) and tetradecadioic ($C_1$4), provide good protection, but not as good as azelaic. This may be due in part to use lower acid concentrations

TABLE 6—*Weight losses for aliphatic diacids in modified D 1384 test.*

	Factors		Weight Losses, mg					
Acid	Coupling	Solder	Cu	Solder	Brass	Steel	Cast Fe	Al
Glutaric	coupled	Sn30A	3.6	0.0	2.7	0.9	3.4	4.2
	coupled	Modine	5.6	490.7	5.5	−1.5	3.2	2.3
	uncoupled	Sn30A	2.0	10.6	2.1	−0.2	−1.0	−0.5
	uncoupled	Modine	3.1	124.3	1.6	1.2	1.2	−7.9
Itaconic	coupled	Sn30A	2.1	27.2	1.6	2.6	368.4	11.6
	coupled	Modine	1.7	477.6	5.7	22.5	466.0	19.7
	uncoupled	Sn30A	2.6	20.8	1.5	4.8	93.3	9.9
	uncoupled	Modine	1.8	354.3	1.2	3.2	306.8	11.7
Adipic	coupled	Sn30A	4.3	32.0	3.7	30.3	28.4	6.3
	coupled	Modine	2.4	291.4	5.9	4.1	24.2	8.6
	uncoupled	Sn30A	2.5	22.9	3.3	−0.5	0.6	7.0
	uncoupled	Modine	3.2	223.4	1.8	0.1	2.9	1.8
Pimelic	coupled	Sn30A	1.8	6.1	3.3	0.7	0.2	0.3
	coupled	Modine	2.2	535.3	2.5	0.0	0.0	0.4
	uncoupled	Sn30A	1.4	1.7	1.2	0.1	−0.6	−7.3
	uncoupled	Modine	1.5	511.2	2.3	0.5	1.7	0.0
Suberic	coupled	Sn30A	4.9	2.0	3.3	0.2	−0.7	−0.3
	coupled	Modine	3.9	33.1	3.1	0.4	−0.1	−2.3
	uncoupled	Sn30A	4.0	4.5	1.8	1.1	0.1	−1.9
	uncoupled	Modine	3.2	9.9	3.4	0.2	0.8	−5.4
Azelaic	coupled	Sn30A	3.2	8.2	2.7	0.6	−0.8	2.9
	coupled	Modine	4.1	542.8	4.3	−0.2	0.3	1.1
	uncoupled	Sn30A	3.3	8.3	4.1	0.5	2.7	4.4
	uncoupled	Modine	3.3	531.5	2.9	1.4	0.6	2.3
Sebacic	coupled	Sn30A	2.8	0.9	3.4	−0.3	−0.4	2.7
	coupled	Modine	2.6	20.4	3.5	−0.6	−0.6	−3.3
	uncoupled	Sn30A	3.2	0.4	4.7	0.5	−0.8	8.1
	uncoupled	Modine	3.3	6.0	4.1	0.2	−0.7	9.0
Tetradecadioic	coupled	Sn30A	4.7	0.2	4.2	0.2	−0.2	1.5
	coupled	Modine	4.5	2.5	3.3	−0.2	0.1	−0.9
	uncoupled	Sn30A	6.0	0.4	2.8	−0.1	0.0	3.7
	uncoupled	Modine	6.2	7.8	2.4	−0.1	−0.2	6.0

because of solubility issues. Still, azelaic acid stands out in terms of aluminum pitting protection.

Discussions

Observations from Electrochemistry

The differences in electrochemistry between organic acids and coolants using silicate and nitrate as aluminum corrosion inhibitors will be discussed in terms of what protection mechanisms might be operating and what this means for long term protection.

Typical galvanostatic (BL5-1) and cyclic polarization curves for C-2, the best of the silicate/nitrate coolants, are shown in Figs. 5 and 6, respectively. There are three key features about these curves. The galvanostatic curve always approaches some minimum value asymptotically. The cyclic polarization curve will have a sharp "break" potential, E_b, and a large loop to higher current, assuming that pitting occurs.

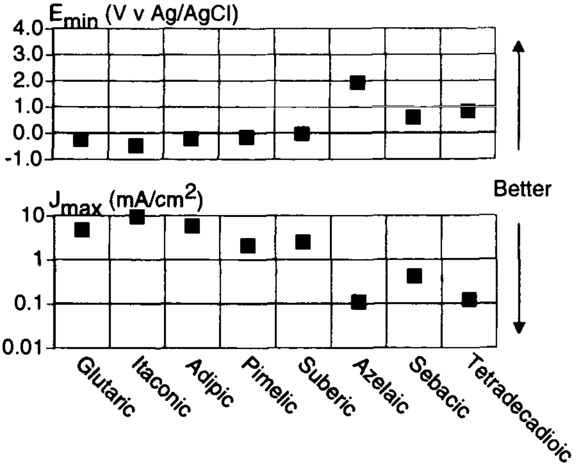

FIG. 4—*Electrochemistry of aliphatic diacids.*

These curves are self consistent in terms of how the two experiments are considered to function. The cyclic polarization is expected to be a snapshot of the potential versus current behavior of the system under test in quasi-steady state conditions. The galvanostatic test is a relaxation type of experiment, effectively determination of the cyclic polarization curve at one particular current. This is represented by the vertical line at 100 $\mu A/cm^2$ in Fig. 6. Upon application of current the potential increases to approximate the point on the cyclic polarization curve before film breakdown, labelled E_{max}. Nearing this potential, film breakdown will occur and the potential will now relax to the point of the cyclic polarization curve after film breakdown, labelled E_{min}. This second point will be approached asymptotically. Thus the shape, if not the exact potentials, of the galvanostatic curve is defined.

In contrast, similar curves for sebacic acid, a good organic acid at providing aluminum protection, are shown in Figs. 7 and 8, respectively. The potential rises, with random oscillations, after achieving a minimum potential. The "break" potential may not be very sharp and

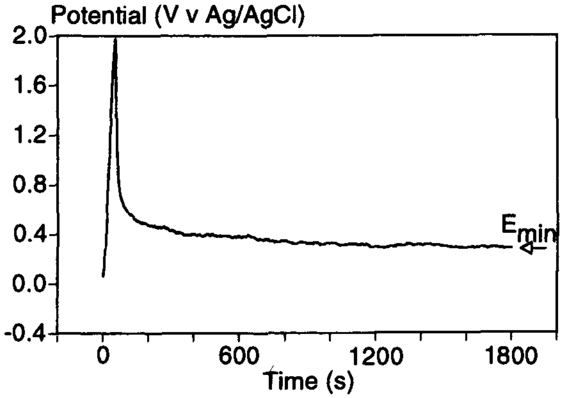

FIG. 5—*Galvanostatic (BL5-1) curve for C-2.*

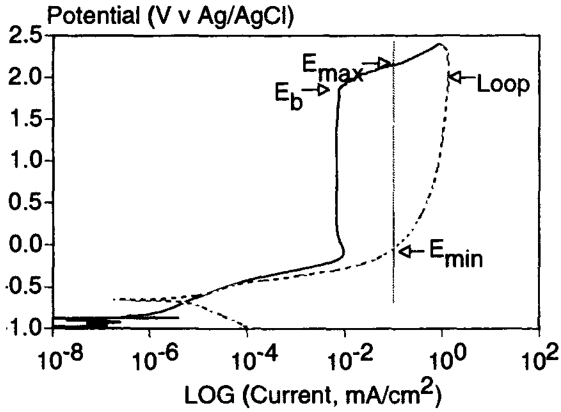

FIG. 6—*Cyclic polarization curve for C-2.*

the loop to higher current displays oscillations and may be quite small. The degree of looping to higher current is captured in J_{max}.

These two curves are not self consistent. There is no mechanism in the cyclic polarization experiment to account for the rise after achieving the minimum in the galvanostatic experiment. Also, the lack of a sharp break potential, oscillations in the galvanostatic and cyclic polarization curves, and small loops after film breakdown are all symptomatic of the mechanism by which organic acids protect aluminum.

The mechanism operative in silicate and nitrate inhibited coolants is one of film repair. This is, localized corrosion is prevented from initiating by the action of nitrate to repair damaged aluminum oxide before penetration to the native metal. A similar mechanism is responsible for film repair after penetration, though slower and not as effective. Overall, then, there is one reversible reaction; aluminum oxide breakdown and formation, where the equilibrium between the reactant (oxide) and product (dissolved aluminum) is influenced by the concentration of nitrate.

The proposed mechanism for organic acid inhibited coolants is reactive adsorption of acid

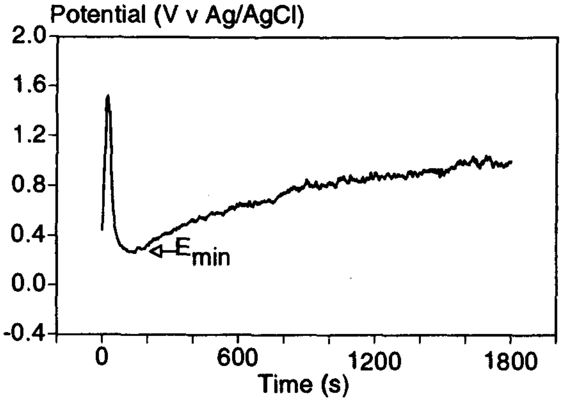

FIG. 7—*Galvanostatic (BL5-1) curve for sebacic acid.*

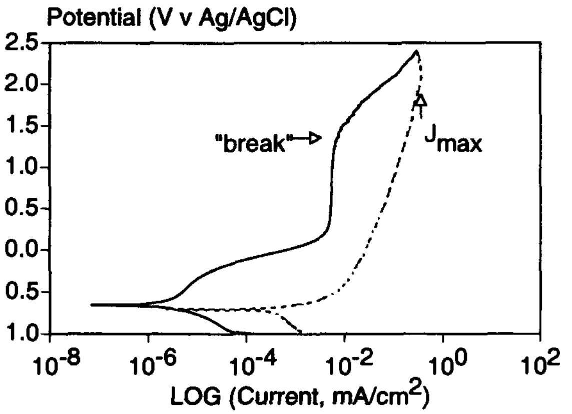

FIG. 8—*Cyclic polarization curve for sebacic acid.*

onto the surface. Corroding sites are acidic, whether the oxide layer is just starting to dissolve or corrosion has exposed native metal. The organic acids precipitate in low pH environments as shown in the RA measurements. The precipitated acid creates a hydrophobic layer. Prior to oxide breakdown, this layer at the reaction site reduces the tendency to initiate pitting, that is, higher E_{max} and E_b. After pit initiation, this layer effectively stops further pitting at that site. This process would continue at the progressively next most active sites. The potential in the galvanostatic experiment rises as pits initiated and falls as they are suppressed. The activation and deactivation of sites results in the oscillations observed in both the galvanostatic and cyclic polarization experiments. There is no inhibitive agent to influence the aluminum oxide breakdown and formation reaction, as with nitrate. Rather, the acids precipitate to form a hydrophobic layer at corroding sites.

Observations About Acid Groups

The linear aliphatic monoacids are reasonable as corrosion protection agents. Weight losses on most metals are low (<5 mg) over the range studied. The exception is lead solder, particularly high lead solder. Losses are lowest for the C_7–C_9 acids, at about 3 mg for Sn30A solder and 100 to 200 mg for Modine (high lead) solder. Octanoic acid is the lowest. Acids of either shorter or longer chain length have progressively greater losses. The greatest benefit of these acids, however, is in providing aluminum localized corrosion protection. In general, longer chain length resulted in lower localized corrosion. In particular, protection by octanoic acid was very good and by dodecanoic acid was essentially complete.

Several branched aliphatic monoacids were studied to see if branching would reduce solder corrosion while not affecting protection provided to other metals. Isoheptanoic acid (branching at 6th carbon) retained protection of most metals but had the high solder corrosion profile of caproic acid (C_6). 2-Ethyl hexanoic acid (branching at 2nd carbon) had reduced solder corrosion (50 mg range), was not quite as good as octanoic acid on aluminum, but was significantly worse on steel (losses from 5 to 20 mg). Cyclohexane propanoic acid (branching at the 4th carbon) was excellent, with very low solder losses (20 mg range) and protection of all other metals.

The aromatic monoacids did not provide the level of expected protection. In particular, the results for benzoic acid on cast iron and aluminum localized corrosion protection are very disappointing. Ring substitution, notably Cl in the para position, can deactivate the ring structure providing significantly better results. Lengthening the molecule, going to cinnamic and hydrocinnamic acid, is highly effective in increasing protection. Again, deactivating the ring structure, substitution of Cl or NO_2, increases effectiveness. Activating the ring structure with OH substitution decreases protection, comparing cinnamic and p-OH cinnamic acids. The cinnamates provided the best combination of corrosion protection.

Aliphatic diacids can be compared with the corresponding monoacid. For a similar chain length, the diacid is more effective at providing general corrosion protection, particularly for solder, and less effective at providing aluminum localized corrosion protection. An exception is azelaic acid (C_9) which had very high solder losses and very good aluminum localized corrosion protection. Sebacic acid and tetradecadioic acid were the best and provided good protection to all metals.

One hint as to the possible protection mechanism of the acids is an apparent relationship between the solubility of the diacids and protection provided. Sebacic acid is soluble up to 2 wt% using sodium salts and up to 3.7 wt% using potassium salts. Sebacic acid provides good protection. Tetradecadioic acid is soluble at 4 wt% using potassium salts and careful addition of the acid. Protection is very good, slightly better than sebacic. In contrast, the aliphatic and aromatic monoacids are readily soluble at up to 4 wt%. The diacids, then, may function by forming precipitate films on the metal surfaces.

Conclusions

The testing of individual organic acids for general corrosion effects and aluminum localized corrosion effects is sufficiently developed to report on the effects of acid structure and individual acids.

In general, aliphatic monoacids provide good aluminum localized corrosion protection while being antagonistic to lead solders. There are definitive trends for the linear acids in terms of protecting against general corrosion and aluminum localized corrosion. Acids of at least 7 carbons are necessary to see good inhibition. Branched aliphatic monoacids exhibit similar behavior. The location of the branching has a major impact on the trade off between general corrosion and aluminum localized corrosion protection.

Aromatic monoacids can be good on cast iron and steel and provide sufficient buffering to prevent corrosion of other metals. Results are quite mixed for the various acids studied due to the activation or deactivation of the ring structure by substituents. In general, activating substituents provide better protection. p-Cl substitution yields excellent inhibitors.

The aliphatic diacids provide better protection against general corrosion than do the corresponding monoacids. However, the diacids are not as good as aluminum localized corrosion. Again there is a trend to better protection being provided by the longer chain acids. Solubility issues partially offset the performance advantage in having to use less acid.

Several acids stand out in providing protection to all metals. These acids are: heptanoic, octanoic, nonanoic, 2-ethyl hexanoic, cyclohexane propanoic, p-Cl benzoic, cinnamic, hydrocinnamic, p-Cl cinnamic, p-NO_2 cinnamic, suberic, sebacic, and tetradecadioic. In addition, dodecanoic acid is particularly effective against aluminum localized corrosion.

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Composition of Incipient Passivating Layers on Heat-Rejecting Aluminum in Carboxylate- and Silicate-Inhibited Coolants: Correlation with ASTM D 4340 Weight Losses

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ABSTRACT: X-ray photoelectron spectroscopy identified compositional differences between passivating layers initially formed in carboxylated coolants, in silicated coolants, and in a mixture thereof on well-controlled 319 aluminum surfaces under heat-rejecting conditions. The layer formed in silicated coolant was primarily silica, while that in carboxylated coolant was primarily hydrated alumina. Competition between inhibitor packages when carboxylated coolant was contaminated from the start with low levels of silicated coolant produced films which were not simply patchwise mixtures of the pure-coolant film types.

The surface analytical results aid the interpretation of subtle differences in weight losses under the ASTM Standard Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions (D 4340) in carboxylated versus silicated coolants that became more pronounced when testing was carried out at a vehicle-like 50% coolant concentration. Results from time-resolved D 4340 measurements and from a two-step cleaning procedure further contribute towards proper evaluation of D 4340 weight losses in the different coolant types.

KEYWORDS: aluminum corrosion, carboxylate, cleaning procedure, D 4340, heat-rejecting aluminum, organic acid, passive layer, silicate, X-ray photoelectron spectroscopy

Extended life-engine coolants relying on carboxylates as the primary corrosion inhibitors can protect cooling system metals for long periods of vehicular service. They maintain more constant major inhibitor concentrations than did the inorganic-inhibited coolants typical of North American vehicle production prior to model year 1996. The complete lack of silicate in such carboxylated coolants avoids the formation of siliceous cooling system. Carboxylate-inhibited engine coolants have shown good protection of aluminum heads in vehicle fleet tests and engine dynamometer tests, and some such coolants have been reported to give exceptionally good performance in forced-flow (dynamic) hot aluminum corrosion tests carried out with heat fluxes corresponding to continuous high-output operation of a light-duty internal combustion engine [*1*]. However, some aspects of the performance of most carboxylate-inhibited coolants, particularly when mixed from the start with silicated coolants, in the ASTM Standard Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting

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Conditions (D 4340-96) (designed to test the protection afforded to aluminum cylinder heads), raised initial questions about these coolants and pointed out the need for a more detailed understanding of the mechanisms of protection of aluminum (for example, see Ref *2*). This work briefly discusses coolant type-related differences in D 4340 results under a range of conditions. Detailed surface analyses by X-ray photoelectron spectroscopy (XPS) of heat-rejecting aluminum exposed to coolant under more idealized circumstances then identify fundamental differences in the types of incipient passivating films formed on heat-rejecting aluminum surfaces in the two coolant types and a mixture thereof. The surface analytical results and time-resolved D 4340-like experiments then shed light on what portion of D 4340 weight losses in carboxylate coolants correspond to actual dissolution of aluminum from the hot surface.

D 4340 Results for Carboxylated and Silicated Coolants and Mixtures

D 4340 Experimental Methods

All numerical D 4340 data reported in this work were generated at GMR&D in apparatus which to the best of our knowledge conforms to D 4340 requirements. Additional details are given in the Appendix on factors not specified in D 4340 which nevertheless may influence the results.

Modifications to Standard D 4340 Procedures—The D 4340 standard calls for a test solution consisting of 25% coolant concentrate diluted with 75% deionized water containing 133 ppm chloride added as sodium chloride. The standard test solution therefore contains 100 μg/mL chloride. Some of the results reported below were run under these standard conditions which were presumably chosen during the development of North American silicated coolants in part to simulate aging through simple dilution. However, we have found three problems associated with doing all hot aluminum corrosion testing only at such high dilution: (1) its application to used coolant samples taken from vehicles routinely gives failing results for North American silicated coolants, whether or not any hot aluminum corrosion problems were seen in the vehicles; (2) such dilution can (perhaps unexpectedly) represent a less severe test for some carboxylate coolants than the actual (near 50%) dilution used in North American factory fill; and (3) competition effects between types of inhibitor packages maximize at different volumetric mixing ratios between the inhibitor packages, depending upon the total glycol concentration. For these reasons, D 4340-like testing was also carried out in 1 : 1 mixtures of coolant concentrate and water, designated "50% glycol," that is, at the concentration recommended in the owner's manuals of North American-built vehicles (and slightly below typical factory fill). The chloride content of the water used to dilute the coolant for such tests was increased to 200 ppm to maintain 100 μg/mL chloride in the test solution. The same 135°C temperature setpoint specified in D 4340 was used for the 50% glycol tests. This temperature, maintained within the bulk of the aluminum sample (the surface will be cooler), lies below the boiling points at the specified 193 kPa (gage) pressure (2210 mm Hg absolute) of both 25% and 50% (by volume) solutions of ethylene glycol (136.5°C and 142°C, respectively [*3*]). The change from 25 to 50% glycol therefore does not cause a change in heat transfer mode from nucleate boiling to convective in a properly run D 4340 test; D 4340 is a predominantly convective test in both concentrations of glycol. To check for possible variations in hot test behavior with water quality, tests were also run using pure deionized water or ASTM corrosive water[2] for dilution of the coolant concentrate.

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[2] ASTM corrosive water is defined in the ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384-96).

Prior to 1995, D 4340 called for post-test cleaning of the aluminum samples with a chromic/phosphoric acid bath, (since superseded by a nitric acid bath). The chromic/phosphoric acid treatment was known to be effective at removing all oxidized aluminum compounds (corrosion products and oxide coatings) while having practically no action on metallic aluminum itself [*4*]. While such a procedure works well for the inorganic-inhibited coolants for which it was developed, it has the possibility of giving misleadingly high apparent weights of aluminum dissolved into the coolant when applied to inhibitor packages which protect the surface with oxidized aluminum compounds. Therefore, the results below were in part obtained with a two-step cleaning/weighing procedure. In the first step the sample was rinsed in a flow of deionized water, rinsed with acetone, dried, and weighed. The sample was then run through the D 4340 cleaning procedure (at the time of this work, the chromic/phosphoric acid bath) and reweighed. The weight change after each step (always referred to the original pre-test weight of the sample) was corrected by the weight change experienced by a blank under the same cleaning procedure. We observed no systematic differences between the acid-cleaned weights obtained by the two-step procedure and those obtained by the normal single-step acid cleaning procedure.

D 4340 Heat-Rejecting Aluminum Corrosion Test Results

Table 1 shows results for standard and modified D 4340 tests in several coolants and mixtures thereof. D 4340 weight losses are reported in mg/cm^2-week as "average ± population standard deviation (number of individual measurements made under these conditions)." The "Low-Si" coolant is a published-formulation North American low-silicate, inorganic-inhibited coolant not intended for use with aluminum cylinder heads or blocks. Results for Low-Si are shown here as a means of judging the calibration of the D 4340 test rigs. "Hi-Si" means a high-silicate North American inorganic-inhibited coolant, either an OEM fill or an aftermarket formulation with similar buffer chemistry. "Carb" means any of several minor variants (e.g., dye changes) of a commercially available, silicate-free, carboxylate-inhibited coolant. While many aspects

TABLE 1—*ASTM D 4340 and modified D 4340 weight losses (mg/cm^2-week).*

Line	Coolant	% Glycol	Dilution Water	Wt. Loss Water-Rinsed	Wt. Loss (Acid-Cleaned)
1	Low-Si	25	133 ppm Cl	11.1 (1)	18.9 ± 0.5 (3)
2	Low-Si	50	200 ppm Cl	0.0_5 ± 0.1 (2)	0.1 ± 0.1 (2)
3	Hi-Si	25	133 ppm Cl	. . .	0.05 ± 0.05 (2)
4	Hi-Si	50	ASTM corr.	0.1 (1)	0.03 (1) but lots of ppt
5	Hi-Si, exhausted in dyno test	50	tap	6.0 (1)	11.5 (1)
6	Carb	25	133 ppm Cl	−0.06 (1)	0.2 ± 0.1 (3)
7	Carb	50	200 ppm Cl	0.1 ± 0.1 (4)	0.9 ± 0.3 (5)
8	Carb	50	deionized	0.1 ± 0.2 (2)	0.9 ± 0.05 (3)
9	Carb	50	ASTM corr.	0.03 (1)	1.1 ± 0.4 (3)
10	75% Carb + 25% Hi-Si	25	133 ppm Cl	. . .	7.1 ± 0.3 (4)
11	90% Carb + 10% Hi-Si	25	133 ppm Cl	. . .	3.8 ± 0.2 (5)
12	99% Carb + 1% Hi-Si	25	133 ppm Cl	0.4 (1)	1.2 (1)
13	99% Carb + 1% Hi-Si	50	200 ppm Cl	. . .	2.0 (1)
14	99% Carb + 1% Hi-Si	50	deionized	1.1 ± 0.01 (2)	1.9 ± 0.05 (2)

of the chemistry of "Carb" discussed here also appear with at least some other carboxylated coolants, magnitudes of effects and other details can vary between formulations.

D 4340-Type Results in Silicated Coolants—The nonmandatory information Appendix XI in D 4340 on interpretation of results suggests that "Generally, . . . coolants that produce aluminum corrosion rates less than 1.0 mg/cm^2-week should be considered as candidates for further evaluation." Fresh silicated coolant with proper levels of inorganic inhibitors and proper balance between them (Table 1, lines 3 and 4) yielded D 4340 weight losses below 0.2 mg/cm^2-week in either water-rinsed or acid-cleaned condition in our apparatus. The tested surface typically maintained some metallic luster. In contrast, the nonoptimized (for hot aluminum) Low-Si coolant tested at 25% glycol (line 1) and Hi-Si coolant previously run to failure by corrosive aluminum head perforation in a dynamometer engine, tested at the 50% glycol level (line 5), yielded (1) acid-cleaned weight losses above 10 mg/cm^2-week, (2) water-rinsed weight losses a bit above half the acid-cleaned value, and (3) severe roughening of the puck surface. D 4340 testing of silicated coolants at 25% glycol has some predictive power for the durability of hot aluminum corrosion protection because the initial dilution of the coolant beyond its nominal working strength reduces a critical factor in silicated coolant performance, the absolute concentration of silicate, as does vehicular service (we have observed very little change in Si content of the coolant during the D 4340 test itself). The Low-Si coolant gives good results when tested at 50% glycol concentration (line 2) because its full-strength Si concentration, which would not remain stable during service in a vehicle, is sufficient to cover up elements of imbalance in the rest of this particular formulation which dominate during testing at 25%. However, absolute silicate concentration alone is not an adequate predictor of D 4340 behavior. Other coolants with the same silicate content as fresh Low-Si gave acceptably low D 4340 weight losses even when tested at 25%. Also, vehicle-aged samples of Hi-Si (near 50% glycol) in which Si levels had fallen below the Si level in 25% fresh Low-Si sometimes yielded weight losses below 0.2 mg/cm^2-week when tested as removed from the vehicle (not further diluted). Initial coolant dilution as a simulation of vehicular aging has worked successfully in the past for a limited number of formulas, but it is not in general a correct means of testing the durability of corrosion protection in all types of coolants.

Line 4 of Table 1 shows that Hi-Si also yielded low D 4340 weight losses when tested at 50% glycol level in ASTM corrosive water. However, a large volume of precipitate formed during testing under these conditions.

D 4340-Type Results in Carboxylated Coolants—The present generation of silicate-free carboxylated coolants can clearly pass the ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light Duty Service (D 3306-94) requirement of 1.0 mg/cm^2-week weight loss maximum under standard D 4340 conditions. Line 6 of Table 1 gives a typical result for Carb of around 0.2 mg/cm^2-week. The Al samples were typically darkened as compared to those run in silicated coolants; and the acid-cleaned weight losses at 25%, though small, seemed reproducibly (albeit not clearly statistically) higher than those for a good silicated coolant in the same apparatus. The contrast with the behavior of high-quality silicated coolant was heightened by increasing the tested coolant concentration to the 50% glycol level (lines 7–9), where acid-cleaned weight losses for Carb in our apparatus averaged near 1 mg/cm^2-week. However, the water-rinsed weight losses have averaged 0.1 mg/cm^2-week and have always remained below 0.4 mg/cm^2-week even when tested at 50% glycol. These results beg the question as to which number, 0.1 mg or 1.0 mg/cm^2-week, better describes the true level of hot aluminum protection provided by this carboxylated coolant. The surface analytical results to follow, coupled with results from time-resolved D 4340 tests, provide an answer to this question.

A small amount of precipitate was always observed during the testing of Carb at the 50% glycol level. No such precipitate was seen at 25% glycol. The precipitate was hard to quantify, as it appeared to adhere to the glass walls of the pressure tube during cooldown. It appeared significantly less in volume than the precipitate formed during the testing of Hi-Si at the 50% glycol level in ASTM corrosive water.

Lines 7–9 of Table 1 compare results for Carb at 50% glycol concentration in pure deionized, chloride-only, and ASTM corrosive water. No significant water quality-related differences were apparent in either the water-rinsed or acid-cleaned weight loss data, nor were there visually striking contrasts in the amount of precipitate formed in the carboxylated coolant in the different waters.

D 4340-Type Results in Mixtures of Carboxylated and Silicated Coolants—The type of D 4340 results which caused the greatest initial concern about the compatibility of carboxylate-inhibited coolants with previous North American formulations are exemplified by lines 10 and 11 of Table 1. Under standard D 4340 conditions (25% total glycol), premixes of silicated coolants and most carboxylate formulations produced acid-cleaned weight losses as high as 7 mg/cm^2-week, substantial amounts of precipitate, and clear roughening of the aluminum sample. The highest weight losses were seen at a premix ratio around 3 Carb/1 Hi-Si. However, the effect was mitigated under circumstances more relevant to vehicular use of carboxylated coolant. First, when the aluminum surface heated uncontaminated 25% Carb long enough to form a protective layer before the addition of Hi-Si contamination, the increases in weight losses were largely suppressed [5]. Second, when tested at 50% total glycol the results were totally acceptable for Carb/Hi-Si mixing ratios of 3:1 and 1:1. Only at mixing ratios below 10% Hi-Si was a (smaller) weight increase induced by contamination with silicated coolant, with the maximum contamination effects (increase in both water-cleaned and acid-washed weight losses of 0.5 to 1.0 mg/cm^2-week shown in lines 13 and 14 of Table 1) appearing around 1% contaminations.

It is perhaps remarkable that concentrations of inorganic inhibitors as low as 0.5% of those in Hi-Si concentrate could have a measurable, if modest, effect on D 4340 weight losses in Carb when tested at 50% total glycol. The surface analytical data to follow confirm the real effects of such low levels of inorganic inhibitors under similar conditions (no forced flow of coolant). The automotive consumer is unlikely to produce the low mixing ratios needed to produce the maximum D 4340 contamination effect at 50% glycol (which would require the consumer to top off a cooling system only 150 mL below the nominal set point). Such low contamination levels might occur in the assembly plant during coolant changeover or during dealer vehicle preparation but can be avoided with proper communication to and diligence on the part of relevant personnel. It should be noted that, in contrast to D 4340 results, hot aluminum testing of mixtures of carboxylated and silicated coolants under conditions of flowing coolant [5] have been reported to produce no surprises; that is, mixtures are reported to behave as simple linear combinations of the behaviors of the pure coolants. Vehicular contamination experiments also have not generated clear effects correlating with the D 4340 contamination phenomena. However, prudence has required that the D 4340 contamination phenomena be better understood and that institutional procedures be adopted to avoid, in service, conditions that D 4340 suggests could modestly degrade the hot aluminum protection of most carboxylate coolants.

Summary of Questions Posed by D 4340 Results—The foregoing sections raise two questions to be investigated in part through surface analysis:

1. Is the proper representative hot aluminum corrosion weight loss of uncontaminated Carb when tested at 50% total glycol the water-rinsed average 0.1 mg/cm^2-week, the acid-rinsed average 1 mg/cm^2-week, or something in between?

2. What are the origin and significance of the modest increase in D 4340 weight loss seen in Carb at 50% glycol when contaminated with very low levels of Hi-Si?

X-ray Photoelectron Spectroscopy of Heat-Rejecting Aluminum Surfaces

X-ray photoelectron spectroscopy (XPS), also called electron spectroscopy for chemical analysis (ESCA), is a vacuum-based, surface sensitive technique which quantifies the elemental composition of a surface and provides some information about the chemical state of each element present [*6*]. X-ray photons with a given energy (here 1486.6 eV) impinge upon a surface and eject photoelectrons out of bound states of the atoms. Each photoelectron has a kinetic energy equal to the photon energy minus the binding energy of the bound state from which the photoelectron was ejected. The spectrometer measures the flux of photoelectrons as a function of kinetic energy. Each element has a characteristic set of bound states; therefore each element gives a characteristic set of photoelectron peaks. Since electrons with relevant kinetic energies can travel only a few nanometers through matter, the technique is surface sensitive, detecting atoms only within about 5 nm of the surface. Different chemical states (for example, oxidation states) of an element give slightly different binding energies. This ''chemical shift'' often amounts to about a 1 eV increase in binding energy for every unit increase in oxidation state of an element. Differential surface charging effects can add artifacts to apparent chemical shift data, requiring careful checks of self-consistency and caution in interpretation, particularly on electrically insulating surfaces as studied here.

Experimental Method

Sample Preparation—The photoemission experiments were performed on cylinders 12 mm in diameter and 14 mm high machined from cast billets of 319 aluminum. Complete D 4340 ''hockey pucks'' would have been too large to fit in the spectrometer, machining of smaller pieces out of the larger samples would have led to unacceptable surface contamination, and the 600-grit surface finish specified in D 4340 is too coarse to allow high-quality surface analysis including depth profiling. One end of each sample was drilled and tapped to fit onto a 25 W soldering iron (rated at 110 V). All sides of the sample were abraded with 400- and 600-grit silicon carbide (SiC) paper. The undrilled end of the sample, on which surface analysis would be performed, was polished with 0.25 μm diamond and 0.05 μm alumina abrasives. The sample was sonicated to remove abrasives, etched 20 s in 1% sodium hydroxide, rinsed with high quality deionized water (from an ion-exchange/carbon/filter recirculation unit fed from a reverse osmosis system) and dried in room air.

Heat-Rejecting Exposure to Coolant—The clean aluminum sample was threaded onto the end of the soldering iron. Forty mL of the test coolant solution was poured into a 50 mL Erlenmeyer flask. The flask was set into a glass crystallizing dish which was filled with room-temperature water (serving as a heat sink) to the 30 mL line on the flask. The sample was then immersed into the coolant to a depth of ~1 cm (even with the external water level) and the soldering iron was clamped in place. The soldering iron was then powered for 2.5 h through a variable transformer set to 80 V (giving a calculated power input around 13 W). This setting was sufficient to initially induce a low but continuous level of boiling on the 600-grit-finish sides of the sample and to generate occasional bubbles on the polished face. The intensity of boiling increased a bit during the 2.5 h of heating as the coolant level dropped by ~8 mm and the (very) approximate applied power/immersed area ratio increased from around 3 to around 7 W/cm^2. At the end of 2.5 h, the soldering iron was switched off for 10 min, the sample was rinsed in flowing deionized water from a house deionized supply plus ultrapure cartridge, and the sample was allowed to dry in air. XPS analyses were done one week after exposure to coolant. These procedures produce a surface that does not necessarily represent conditions at the end of a D 4340 test but should approximate the incipient passivating layers formed in the first few hours of D 4340. The relationships between these films and those formed during vehicular service or after completion of D 4340 will be considered later in this paper.

X-ray Photoelectron Spectroscopy—Samples were introduced into the ultrahigh vacuum chamber of the SSX-101 photoelectron spectrometer through a load lock. A monochromator on the aluminum k-α X-ray source improved resolution and decreased the total X-ray flux onto the surface, thereby minimizing beam damage to organic components. A 0.3 mm beam size with low total fluence was used which, in combination with the monochromator, makes the amount of X-ray damage to the sample unusually low. Since some of the sample films were electrically insulating, charging effects were partially compensated with a 3.0 eV electron flood source. Binding energies in survey scans are shown without further correction for charging, but the energy scales of higher-resolution scans are shifted to assign a binding energy of 284.8 eV to the largest component of the carbon 1s signal (corresponding to the chemical state of carbon in graphite or an aliphatic hydrocarbon, as appropriate for adventitious contamination). Alignment via an optical microscope ensured that spectra were taken of representative areas of the aluminum surfaces rather than in casting voids. For each sample, survey spectra were taken over a wide kinetic energy range to determine the elemental composition (except hydrogen, which is not directly detected) of the surface. The energy ranges for selected elements were then scanned at higher resolution to gain information on the chemical state of these elements. The magnitudes of the signals from the major elements present were then monitored as the surface was sputtered away by a beam of argon ions with an etch rate calibrated at 27 nm/min for an anodic tantalum oxide standard. The algorithm used to calculate atomic percents from photoelectron intensities assumes a film with constant composition over the ~5 nm sampling depth. The sensitivity of the technique to atoms below the surface actually drops off exponentially with distance from the surface.

Table 2 shows the XPS-derived atomic percent compositions of the aluminum samples taken at the surface (before any sputtering with argon ions). The letters identifying samples in this table will be carried through in the text and in the figures to follow; not all sample letters will appear in all figures. Note that the presence of thin carbonaceous contaminant layers right at the surface is a near-universal observance with samples passed through normal room atmo-

TABLE 2—*Surface compositions (atomic % prior to sputtering) and film thicknesses (nm) derived from sputter profiles for aluminum samples.*

	C	O	Al	Si	Cu	Zn	N	Na	K	Ca	P	Cr	S	nm
a. blank	72	16	6.4	...	0.6	...	1.2	2.5	1	...	...	...	1	25
b. diacid std	73	27	...	...	...	...	...	...	...	...	...	...	...	∞
c. Hi-Si	24	51	...	24	...	...	...	1.5	...	...	...	...	...	100*
d. 50% Carb dei	15	59	25	...	...	...	...	0.5	...	...	...	...	...	290
e. 50% Carb ASTM	14	59	27	...	...	0.5	...	...	...	...	...	...	...	300
f. 25% Carb dei	14	60	27	...	...	...	...	...	...	...	...	...	...	320
g. 50% Carb acid-cleaned	16	49	22	1.8	0.8	...	...	...	...	0.5	8.4	2.5	...	9
h. 50% (Carb 1% Hi-Si)	17	50	8.3	7.3	0.5	...	4.4	6.5	...	0.4	5.1	...	...	230*
Bulk alloy composition	...	...	91	5.7	3.2	.02	...	...	...	...	...	...	...	...

*Assumption of same sputtering rate as for Al_2O_3 is questionable (see text).

sphere into a vacuum chamber. Thicknesses in nm are given assuming that the films sputter at the same rate as for Al_2O_3 (* marks cases where this assumption is likely to distort the apparent thickness). In this apparatus, Al_2O_3 has been shown to sputter at 0.57 times the rate for the tantalum oxide standard, that is, at 15 nm/min [7]. The bulk atomic percents for Al 319 of the elements observed on the surfaces are given on the last line for comparison. In Table 2, "..." signifies element not detected.

Control Samples

a.: Blank—Sample a. in atomic percent Table 2, in sputter profile Fig. 1, and in figures to follow is a blank aluminum sample, i.e., polished, etched in 1% NaOH, rinsed, dried, and stored in air, but without any contact with coolant. Table 2, line a., shows that the blank surface was dominated by carbon (C) with oxygen (O) and aluminum (Al) following in elemental abundance. The argon-sputter profile of Fig. 1*a* shows that the C was strongly localized at the surface. The high-resolution C 1s spectrum of Fig. 2*a* is dominated (>96%) by a single peak at 284.8 eV, as is typical for adventitious hydrocarbon contamination. Traces of the copper (Cu) but not the silicon (Si) minor components of the alloy were seen, along with small amounts of alkali from the etchant and nitrogen (N) (from reaction of the active etched surface with air?). Sputtering away the carbon within the first 10 seconds (<3 nm*) left the aluminum and oxygen of the aluminum oxide layer formed during the exposure to air and water after the 1% NaOH etch. The statistics of ion impingement lead to a roughening of the surface during sputtering and the knocking of surface atoms into the subsurface region. These effects blur the apparent boundary between an oxide layer and the underlying metal. It is therefore common practice to take the spot in a sputter profile where the oxygen signal reaches half of its initial (or highest) value as representative of the oxide thickness [*8*]. This convention gives the thickness of the aluminum oxide layer on the blank surface as approximately 25 nm.

b.: Carboxylic Acid Reference—Table 2, line b. gives the XPS-determined atomic composition of crystals of decanedioic (sebacic) acid $HOOC(CH_2)_8COOH$. This compound is the acid form of the primary inhibitor in the prototypical published-formula carboxylated coolant AL-39 [*9*]. The crystals were pressed into an indium foil for mechanical support. The observed carbon/oxygen atomic ratio of 2.7 agrees with the stoichiometric C/O ratio of 2.5 within the accuracy of the method. Figure 2*b*, showing details of the C 1s emission spectrum, clearly shows two peaks separated by 4.5 eV due to carbon atoms in two chemical environments. The peak at 284.8 eV, comprising 77% of the total, was due to CH_2 (aliphatic hydrocarbon) carbon. The peak at 289.3 eV, comprising 16% of the total, arose from the COOH (carboxylate) carbons. The stoichiometric fractions for these two peaks would be 80% and 20%, respectively. The curve-fitting software also placed 6% of the total intensity in a peak at 286 eV, as might be expected for carbon in an intermediate oxidation state, for example, the COH of an alcohol or glycol (but no glycol was present in this reference experiment). Such a peak may indicate reduction of a small amount of the bulk carboxylic acid under the action of the X-ray beam in vacuum. Prior attempts to study the adsorption of carboxylates from aqueous solutions onto clean metals using apparatus which avoided atmospheric contamination of samples during transfer from the solution to the vacuum chamber [*10*], but which did not have a monochromator on the X-ray source, yielded only the CH_2 peak and a peak with a binding energy 1.1 eV lower than the carboxylate peak identified here which may have arisen from reduction of most of the adsorbed carboxylate to an aldehyde-like oxidation state. Experience to date suggests that XPS using non-monochromated sources may not be able to detect carboxylate carbon due to rapid decomposition of carboxylates by the higher total X-ray flux with its concomitant secondary electrons.

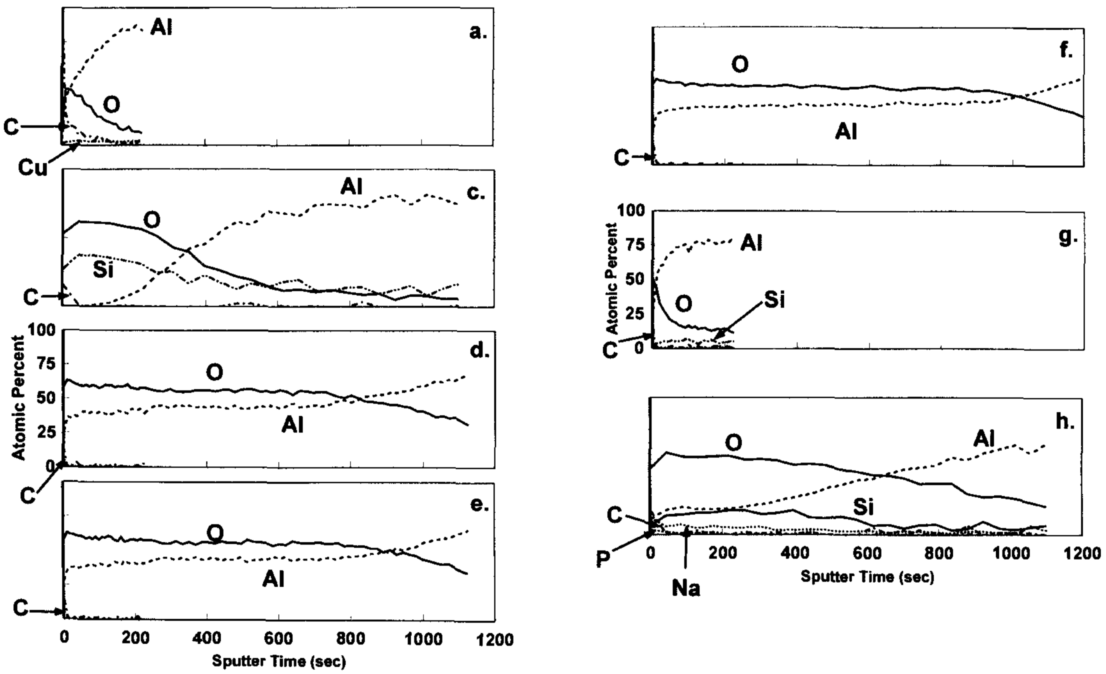


FIG. 1—*Sputter profiles (atomic % as function of time under argon-ion beam) for films formed on aluminum surfaces: a. blank, c. 50% Hi-Si in deionized water, d. 50% Carb in deionized water, e. 50% Carb in ASTM corrosive water, f. 25% Carb in deionized water, g. acid-cleaned 50% Carb in deionized water, and h. 50% (99% Carb + 1% Hi-Si) in deionized water.*

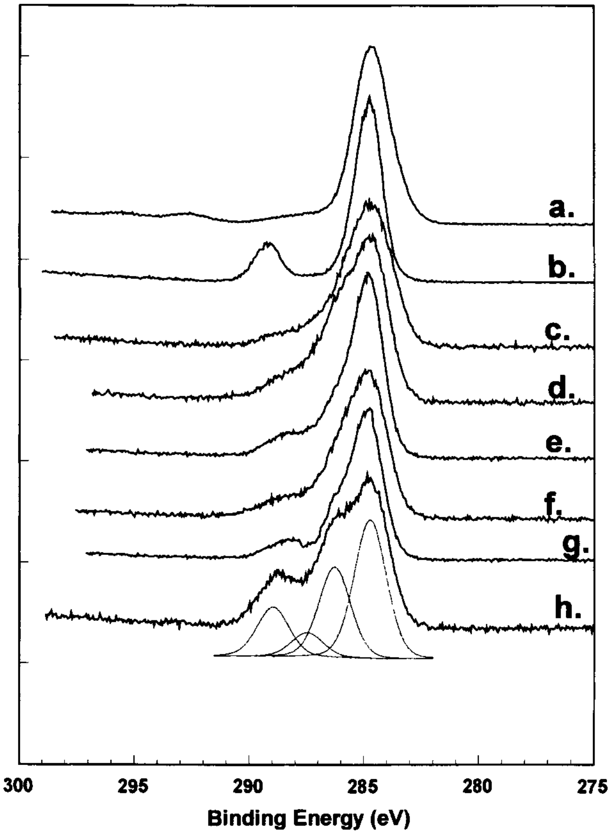


FIG. 2—*High-resolution carbon 1 s photoelectron spectra for: a. blank, b. dodecanedioic acid reference, c. Hi-Si, d. 50% Carb in dei, e. 50% Carb in ASTM, and f. 25% Carb in dei, g. acid-cleaned 50% Carb, h. 50% (99% Carb + 1% Hi-Si). Bottom shows fit of four chemical-shift components to h.*

c.: Incipient Passivating Layer in Silicated Coolant—Table 2, line c. gives the elemental composition of the water-rinsed passivating layer formed on aluminum which heated a 50% solution of Hi-Si coolant for 2.5 h and then was rinsed and dried. The complete XPS survey scan is shown in Fig. 3*c*. The spectrum was dominated by silicon and oxygen whose ratio, 1 to 2, suggests a composition closer to SiO_2 than to a hydrated form such as H_2SiO_3 or its polymers. High-resolution scans of the O 1s and Si 2p emissions showed single chemical-shift components, suggesting that each of these two elements is in a single uniform chemical environment. Note that no aluminum was visible. Only a trace of alkali metal (sodium) was seen. No trace of the phosphate and borate buffers nor of the other inhibitors were visible. The sputter profile of Fig. 1*c* shows that the carbon is concentrated right at the surface. The high-resolution C 1s spectrum of Fig. 2*c* shows that the sum of adventitious hydrocarbon-like carbon at 284.8 eV plus COH-type carbon at 286.0 eV (as would be expected for ethylene glycol), comprise about 90% of the carbon signal. The other 10% of the signal, at higher binding energies, may indicate the presence of small amounts of carbonate, glycol oxidation products, or carbonaceous impurities in higher oxidation states. The sputter profile of Fig. 1*c* shows the atomic percent of oxygen drops to half of its maximum value in 400 s, giving a sputter thickness equivalent

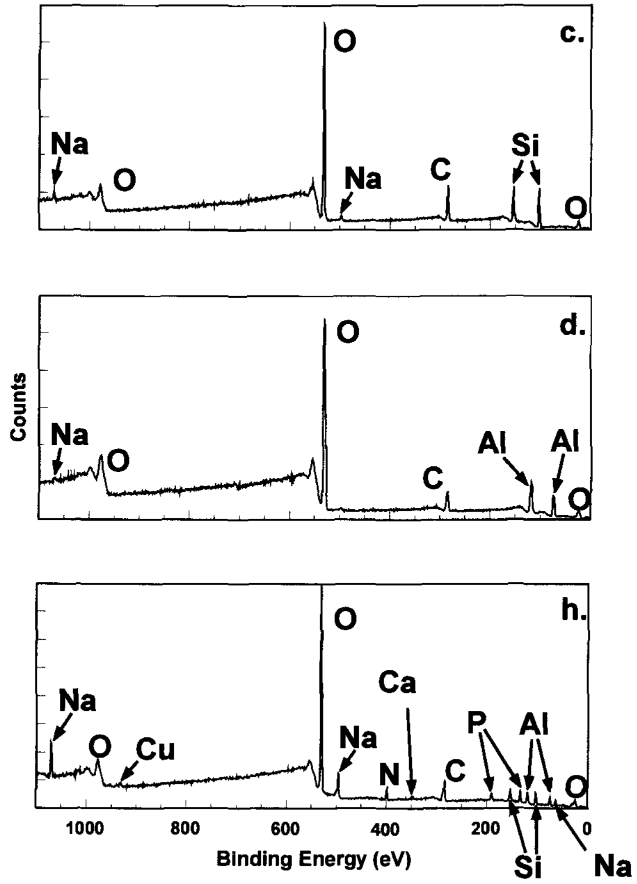


FIG. 3—*XPS surveys for: c. Hi-Si, d. 50% Carb in deionized water, and h. 50% (99% Carb + 1% Hi-Si) in deionized water.*

to ~100 nm of alumina. From a published table of sputter rates [*11*] in which SiO_2 is shown to sputter away three times as quickly as Al_2O_3 one might conclude that the film thickness is actually ~300 nm; however, extreme caution is needed in transferring relative sputter rates from one apparatus to another. Figure 4 gives successive high-resolution scans of the Al 2p emission as the Hi-Si passivating film is sputtered through. No aluminum is seen at the surface (front scan). The emission from the underlying metallic aluminum at 72.5 eV becomes clear at about the 6th scan (the nominal depth of the SiO_2 overlayer) and subsequently grows in. No oxidized aluminum (emission expected from oxidized aluminum around 75 eV) is seen at the surface, and at most a trace, maximizing around the 6th scan, is ever seen. The thin alumina present on the blank prior to exposure to the silicated coolant was not thickened significantly during exposure to coolant. It is clear that the incipient passivating layer in this silicated coolant under the conditions of this experiment is totally exogenous to the metal, that is, it contains no elements derived from the metal itself but consists of SiO_2. This is the reason behind the use in this paper of the term *passivating layer*, as opposed to the more usual *passive layer*, since the latter term through usage has come to imply a protective film (usually oxide) grown from elements of the metal itself.

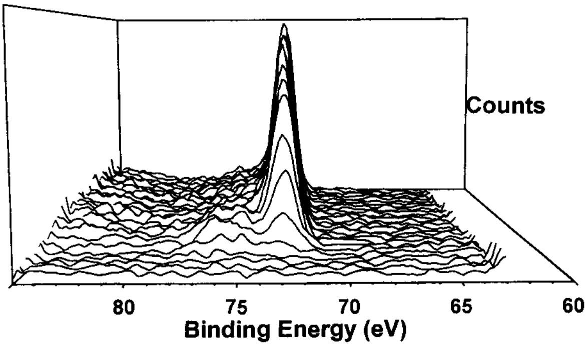


FIG. 4—*Successive high-resolution aluminum 2p spectra as the passivating layer formed in Hi-Si is sputtered through. Surface at front.*

d., e., f.: Incipient Passivating Layer in Carboxylated Coolant—Table 2, lines d.–f. show XPS surface elemental compositions for three different aluminum 319 samples after 2.5 h heating of carboxylate-inhibited coolants (Carb) prepared as follows: d. 50% solution in deionized water; e. 50% solution in ASTM corrosive water; f. 25% solution in deionized water. A complete survey scan for 50% Carb in deionized water is shown in Fig. 3*d*. The surface elemental compositions of these three films were similar, in each case containing 59 to 60% O, 25 to 27% Al, and 14 to 15% carbon. The compositions differed in trace elements: a. shows 0.5% sodium (Na), b. shows 0.5% zinc (Zn), and c. shows neither. It is not clear whether these slight differences were significant, but it is conceivable that the bicarbonate in ASTM water renders insoluble the $<1\%$ Zn initially in the alloy which otherwise dissolves away from the surface.

The sputter profiles of Figs. 1*d–f* show that the carbon was once again localized right at the free surface of the films. These films took longer to sputter off than those discussed above. The 1/2 O point in each case lay at or just beyond the end of the sputter profile, suggesting film thicknesses (actually lower limits) of 290, 300, and 320 nm, respectively, in terms of Al_2O_3. The films formed in Carb under these three conditions therefore appear to be at least as thick as the film formed in Hi-Si. The initial passivating films formed in the carboxylated coolant were predominantly endogenous to the metal surface; i.e., they consisted primarily of a layer of oxidized aluminum which was roughly ten times thicker than the oxide present on the surface prior to contact with the coolant. This data shows that little of the carboxylate inhibitor package was incorporated into the bulk of the film. The O/Al atomic ratios of 2.2–2.4 observed for these films suggest that they are more hydrated than Al_2O_3. The films appear to be at least as hydrated as the stable hydrated oxide Boehmite (formal stoichiometry AlO(OH), with O/Al = 2) that is formed during processes used to seal anodized coatings on aluminum to improve corrosion resistance [*12*]. The details of the chemical shifts of the O 1s emissions for these films are also consistent with a hydrated oxide or oxyhydroxide [*13*], in each case comprising an oxide component with 40% of the total O 1s intensity and a hydroxide-like component (shifted 1.6 eV to higher binding energy) with 60% of the total intensity. The excess "hydroxide" component above 50% can be accounted for by the presence of oxygenated carbon compounds right on the surface.

Figures 2*d*, *e*, *f* show details of the C 1s emissions from the surface of each film. It should be recalled that carbon constitutes only 15% of the surface and is localized within at most 2.5 nm of the surface (10 s sputtering). For all three surfaces the largest carbon component (comprising 50 to 70% of the total C) is that at 284.8 eV corresponding to aliphatic carbon or graphite. The second largest component, comprising 20 to 30% of total carbon or 3 to 5% of the surface atomic composition, lies at 286.2 eV, as would be expected for carbons singly bound to one oxygen, as for both carbons in ethylene glycol. The curve-fitting software suggests two more components at higher binding energies: 289.0 eV as seen for carboxylate carbon in pure sebacic acid and 287.6 eV, as one might expect for a ketone-like carbon and might be produced as a first step during beam-induced reduction of carboxylate. If one groups these last two peaks together to represent an upper bound of carboxylate content, one can generate a possible rough description of the carbon content [localized in the top <2.5 nm of these 300 nm films] as 20 to 30% (poly?)ethylene glycol (less in e.) plus 70 to 80% carboxylate inhibitor. The presence of similar levels of the 289 eV component in Figs. 2*c* (Hi-Si) and 2*g* (acid-etched) bring into question the reliability of the assignment of this component to the carboxylate groups of inhibitor molecules; adventitious carbon impurities in a high oxidation state (for example, bicarbonate) may also be present.

In summary, the films produced by heating the carboxylate-inhibited coolant for 2.5 h are best described as ~300 nm of hydrated alumina AlO(OH) without any significant content of carboxylate inhibitors throughout most of its thickness, topped off with a <2.5 nm layer containing carbon which may be about 70% carboxylate inhibitor and 30% (poly?)ethylene glycol. The only significant difference detected between films formed in Carb at 50% dilution is deionized or ASTM water or at 25% deionized water is a <1% Zn component seen on the surface in ASTM water and some variation is detected glycol-like carbon.

g.: Effects of Chromic/Phosphoric Acid Cleaning on Films Formed in Carboxylated Coolant—Table 2, line g. gives the XPS surface elemental composition for 319 aluminum which had heated 50% Carb in deionized water for 2.5 h, was rinsed in water, and then was cleaned with the chromic/phosphoric acid treatment specified by D 4340 prior to 1995 (including a final thorough rinse in deionized water). The spectrum was still dominated by 49% O, 22% Al, and 16% C; but 8% phosphorus (P) and 2.5% chromium (Cr) are incorporated into the surface from the cleaner, 1.8% Si and 0.8% Cu appear from the alloy, and 0.5% Ca shows up, probably from the tapwater rinse specified immediately after the acid cleaner. The sputter profile of Fig. 1*g* shows that the film on the acid-cleaned sample is much thinner than the films merely rinsed with water after being removed from the carboxylated coolant. The 1/2 O point at 36 s implies an Al_2O_3 thickness of 9 nm, less than half as thick as even the thin oxide layer present on the blank surface prior to exposure to coolant. The Cr, P, and C peaks disappeared very rapidly during the sputtering; all three elements are localized within 2.5 nm of the surface. The Si and Cu levels rose towards the atomic percents present in the bulk alloy as the thin oxide was sputtered off the surface. The similarity of the C 1s detail spectrum of Fig. 2*g* to the C 1s spectra for the other samples heated in carboxylate coolant shows the need for caution in stating that the carbonaceous layers of the latter are derived from the carboxylate inhibitors. It seems unlikely that a carboxylate inhibitor overlayer would survive intact while the hydrated alumina was removed out from beneath it by a strongly oxidizing acid.

The acid treatment clearly removes the oxygen from the film formed in the coolant. Since the acid is an oxidizing (rather than reducing) agent, the removal of this oxygen is almost certainly accompanied by the removal of the aluminum ions of the oxide as well. The implications of this observation on the proper interpretation of acid-cleaned D 4340 weight loss data for carboxylate coolants will be considered later.

h.: Incipient Passive Layer in Carboxylated Plus 1% Silicated Coolant—Table 2, line h. gives the XPS surface elemental composition of an Al 319 surface which had rejected heat for 2.5 h to a 50% solution in deionized water (99% Carb plus 1% Hi-Si). The survey scan is shown in Fig. 3*h*. O (50 atomic %) once again dominated the spectrum, and superficial C (17%) was again present; but now a range of elements provided the cations paired with the oxygen. Of these, Al (8.3%) still dominated, but barely. Si (7.3%), Na (6.5%), P (5.1%), and N (4.4%)

were all likely derived primarily from the coolant(s) (the alkali content of both coolants was predominantly Na). The Cu (0.5%) and perhaps a minority of the Si were derived from the alloy. The N 1s is binding energy of 399.2 eV (charging-corrected to place the predominant C peak at 284.8 eV) suggests an amine-like, as opposed to nitrate-like, chemical state. Since Augustynski has reported XPS evidence for a similarly-reduced N species (assigned as ammonium) on aluminum surfaces exposed to aqueous solutions containing only sodium nitrate [*14*], the N in the contaminated-coolant film probably arises from the nitrate inhibitor in the silicated coolant. The chemical shift of the P is consistent with the presence of (partially protonated) phosphate within the film. No evidence of boron (B) was seen in the film despite the presence of borate in the silicated coolant. This is likely to be due to a higher surface activity for phosphate than borate. However, some caution must be exercised in drawing such a conclusion from this data since the product of the relative elemental sensitivity factors for P vs. B and the ratio of P to B in the silicated coolant would give a ten-fold advantage to the detection of P versus B in these experiments.

The sputter profile of Fig. 1*h* shows that once again the carbon was localized right at the surface, where it made up about 17% of the atoms, similar to what was seen before. The 1/2 O point at 880 s suggests a film thickness of 230 nm on the alumina scale, i.e., perhaps a bit thinner than in the absence of the 1% contamination with silicated coolant. The Na and P were enhanced at the surface but at least the Na, and probably the P, extended much farther into the film than the carbon. O, Al, and Si, being the majority components of the film, showed depressed atomic percentages at the surface due to the superficial carbon content. Si was present in the film at more than twice its atomic percentage in the underlying alloy, and its abundance dropped as the film was sputtered through. This result indicates that the preponderance of Si observed came from the coolant solution even though the Si level in that solution was well under 10 ppm.

This mixed-coolant film appears to be oxygen-poor compared to the films formed in the two pure coolants. If one assumes the presence of SiO_2 and AlO(OH), as inferred for the two pure-coolant films, there is not enough oxygen left in this film to provide charge balance for the Na, P, and oxidized C components. Formation of some aluminum carboxylates and aluminum phosphates (localized near the outer surface) and lesser hydration of the aluminum oxide might explain the observed stoichiometry.

The high-resolution C 1s surface spectrum of Fig. 2*h* for Carb contaminated with 1% Hi-Si shows a higher proportion of carbon with the "carboxylate"-like chemical shift than was seen in any of the other films. This result raises the possibility that there is a significantly larger concentration of carboxylate inhibitor molecules in the outer portion of this film than in the others. If so, however, the carboxylates must also be regularly arranged with their COO^- ends pointed outwards away from the metal, where XPS can preferentially detect them (the photoelectrons from the $—CH_2—$ groups would be attenuated by the overlying COO^-), because the observed ratio of carbon with a carboxylate-like binding energy to aliphatic carbon on this surface significantly exceeds the (COO^-/CH_2) stoichiometric ratio of any intentional component in this coolant. One must also consider the possible presence of a highly-oxidized adventitious contaminant, such as bicarbonate.

Summary of the Composition of the Mixed-Coolant Film—Despite the fact that the coolant used for this experiment contained only 1% of the concentration of inhibitors in working strength silicated coolant and 99% of the inhibitors in working strength carboxylated coolant, the resulting film had roughly equal contributions from the two inhibitor packages: an approximate surface stoichiometry (excluding carbon) of $Al_{0.2}Si_{0.2}Na_{0.1}P_{0.1}N_{0.1}O$. The first conclusion to be drawn is that, at least under the conditions of this experiment, the inorganic inhibitor package has overall much higher surface activity per unit solution concentration than does the carboxylate inhibitor package; even a large preponderance of carboxylate inhibitors is insufficient to completely obscure the activity of the inorganic package. In addition, the film in the mixed coolant was clearly not just a mixture of patches of the films typical of pure carboxylated coolant on one side and pure silicated coolant on the other. The mixed-coolant film contained elements of the silicated coolant inhibitor package (P and N) and of both inhibitor packages (Na) which were not detectably incorporated in the film formed in either pure coolant. The 1% admixture of the silicated coolant into the carboxylated coolant (at 50% total coolant concentration) yielded a mixed layer, in part silica as in pure silicated coolant, in part alumina as in carboxylated coolant (albeit perhaps a less completely hydrated alumina), in part incorporating components more likely to confer some solubility (Na and phosphate), and possibly with enhanced carboxylate, as opposed to alumina, content. This apparent competition between mechanisms of initial passivation appears to correlate with the ca. 0.5–1 mg/cm^2 larger D 4340 weight losses measured in this particular coolant mixture.

Correlation of Surface Analytical, Static D 4340, and Time-Resolved D 4340 Data

Aluminum Lost to Coolant in D 4340

D 4340 measures the weight loss of an aluminum sample after (1) it has rejected heat to coolant and (2) it has been subjected to a standard cleaning procedure designed to remove all oxidized aluminum species. While this is clearly a useful measurement in the case of coolants so bad that physical removal of metallic aluminum through hot transport corrosion would threaten imminent perforation of a cylinder head and/or other loss of vehicular function (acid-cleaned weight losses above about 10 mg/cm^2-week tested as the coolant would be used in a vehicle), it is not clear that the standard cleaned-sample weight loss is the best measure for distinguishing between more subtle differences between coolants, i.e., standard weight losses up to about 2 mg/cm^2-week which do not necessarily directly portend major corrosion of heads. A better measure of coolant performance in this more subtle regime would be the total amount of aluminum lost from the surface into the coolant (i.e., not just into a bound surface layer which may be protective). The direct approach to this measurement, quantitative analysis of dissolved aluminum in the coolant, does not give meaningful results in this case because of the exceedingly low solubility of aluminum ions in carboxylated coolants. One quick measurement attempt found an upper bound near 2 ppm after adding a higher level of aluminum nitrate to Carb. Both the pH (near 8, where aluminum ions have low solubility in glycol solutions) and the presence of carboxylate inhibitors which form insoluble compounds with Al can contribute to this low total Al solubility. Adhesion of solids to tube walls and incorporation of glycol into the solids make it difficult to accurately quantify the amount of loose solids formed in the coolant, even in so simple a test as D 4340. However, the combination of knowledge from surface analytical measurements and time-resolved D 4340 measurements using the two-step cleaning procedure can give a more accurate picture of (1) how much aluminum is actually leaving the sample surface and (2) just when during the contact with the coolant that aluminum is lost.

XPS of the incipient passivating film formed in uncontaminated Carb showed a layer composed predominantly of hydrated aluminum oxide consistent with a stoichiometry of AlO(OH). During the brief (2.5 h) exposure to the coolant the film had grown to a thickness of about 300 nm; only the outermost <2.5 nm of that film showed evidence for significant concentrations of carboxylates. Limited surface analysis and analytical electron microscopy of aluminum surfaces of automotive components exposed to Carb for thousands of hours showed that the thicker, typically (but not always) black film was also predominantly hydrated aluminum oxide with an outer layer enriched in carboxylate, but the total film thickness exceeded 1000 nm (greater than the sampling depth of analytical electron microscopy and too thick to sputter through with argon ions) and the carboxylate-enriched outer zone extended about 20 nm in from the surface. It therefore appears that the films formed in Carb during extended testing or vehicular service can thicken about 10-fold over the incipient layers discussed in detail here, but seem to maintain the same basic chemistry seen in the incipient passivating layers.

Comparison of the XPS data for incipient films formed in 50% Carb before and after the complete chromic/phosphoric acid cleaning procedure showed that the acid almost completely removed the hydrated alumina (Boehmite-like) layer. If the typical 1 mg/cm^2 difference between the water-rinsed and acid-washed D 4340 weight losses were due to removal of a film with the density of Boehmite (3.014 g/cm^3) [*15*], that film would need to be 3000 nm thick, in rough agreement with the approximate thicknesses of films formed on aluminum automotive components in Carb. Such a film would contain 0.55 mg/cm^2 of oxygen and hydrogen. If it had formed without any loss of aluminum to the coolant one would have expected a weight **gain** of 0.55 mg in the water-rinsed weight measurement (perhaps less the small weight of the original air-formed film on the aluminum), rather than the (fortuitously) near-zero value typically observed. However, it is common to leak some metal ions into solution during the formation of protective oxide layers. For example, well-controlled studies of the passivation of the nickel (100) single crystal surface in dilute perchloric acid have shown that roughly one nickel ion is lost to solution for every nickel ion incorporated into the passive layer (the potentiostatic passivation current efficiency of a UHV-cleaned surface is around 0.5) [*10*]. Zero weight change during the formation of a 3000 nm Boehmite layer would require dissolution of 0.55 mg/cm^2 aluminum ($\times$ 19 cm^2) into the 500 mL of test solution as a passivating layer containing 0.45 mg/cm^2 of Al and 0.55 mg/cm^2 of O and H is formed, equivalent to 20 ppm Al going into the coolant. However, since the experimental solubility of Al^{3+} in 50% Carb is only around 2 ppm, most of the dissolved aluminum would show up as a dispersed solid (about 20 mg, if it appeared as Boehmite). We have filtered finely divided solids with demonstrated aluminum content equivalent to as much as 15 mg of Boehmite from the coolant at the end of a D 4340 test in Carb and believe that the rest of the solids adhere to the walls of the glass pressure tube.

Given the water-rinsed weight loss (Δw) and acid-rinsed weight loss (Δa) (both referred to the pre-test sample weight and corrected for blank cleaning losses), what is the correct expression for the weight of aluminum lost to coolant (Al_{diss}) during D 4340 in Carb? Since the water-rinsing procedure removes, if anything, only loose material unlikely to provide good protection to the surface, all of Δw should be added in to Al_{diss}. If ($\Delta a - \Delta w$) is the weight of a protective hydrated oxide film containing 45 weight% aluminum which is removed by the acid, then by the above discussion, $Al_{diss} = \Delta w + (1 - 0.45)(\Delta a — \Delta w)$. Since the w/0 aluminum in the oxide film is not known to better than 10% and is as properly expressed as 50% or 1/2 rather than 45%, a more facile (but less transparent) working approximation would be:

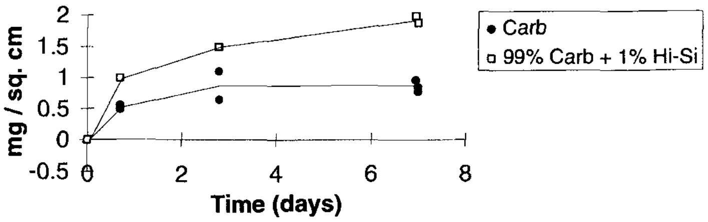
$$Al_{diss} = (\Delta w + \Delta a)/2$$

It therefore appears that the proper answer to the first question posed at the end of the D 4340 results section is (by an accident of the combining weights in aluminum oxides) that the best estimate of aluminum lost to coolant during D 4340 in uncontaminated 50% Carb is *the average of the water-rinsed and acid-cleaned weight losses*, that is, around 0.5 mg/cm^2-week. This number, while within the standard D 4340 1 mg/cm^2-week suggested quality criterion, is still measurably higher than the total weight losses found in good silicated coolants. If this result were both representative of a continuous higher corrosion rate and relevant to vehicular behavior, it could indicate a disadvantage of the carboxylate technology. However, comparison of water-cleaned with acid-cleaned weight losses in light of the surface analytical data has suggested that much of the loss of aluminum to carboxylate coolant occurs during initial formation of the passivating film. Time-resolved D 4340 measurements provide an additional test of this hypothesis.

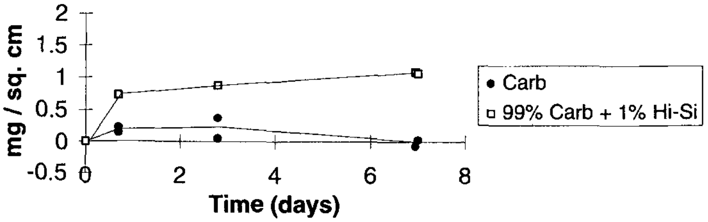
Time-Resolved D 4340 Measurements

Figure 5 shows D 4340-type results at 50% total glycol concentration for tests run for times shorter than the one week specified in D 4340, as well as for tests running the full week. Weight loss data are plotted as a function of total test time and are shown both for pure Carb (in deionized or ASTM corrosive water) or for 99% Carb + 1% Hi-Si (in deionized water). Figure 5*a* shows standard acid-cleaned weight losses. Figure 5*b* shows water-rinsed weight losses, and Fig. 5*c* shows the proposed best approximation of the amount of aluminum lost to carboxylated coolant, that is, the mean of the water-rinsed and acid-cleaned results. In every case the rate of weight decrease fell off after the initial data point at 17 h (or perhaps before, though the significantly thinner passivating layers seen after 2.5 h suggest that several days before falloff

a. acid-cleaned weight losses @ 50% total glycol



b. water-cleaned weight losses @ 50% total glycol



c. estimated aluminum lost to coolant @ 50% total glycol

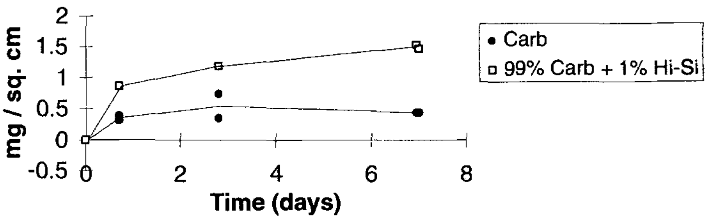


FIG. 5—*Time-resolved D 4340 (modified) weight losses for 319 Al in:* (filled circles) *50% Carb and* (open squares) *50% (99% Carb + 1% Hi-Si).*

is closer to the truth than several hours before falloff). In uncontaminated Carb the integral aluminum loss to coolant appeared to be, within the scatter of the measurement, time-independent after the first day, plateauing around 0.5 mg/cm^2. These results suggest that, at least for uncontaminated Carb, the corrected D 4340 determinations of aluminum lost to coolant do arise from a pulse of aluminum dissolution during the initial formation of the passivating layer on the aluminum surface rather than from a continuous corrosion process. If similar loss/area of aluminum to coolant occurred during the initial passivation of the aluminum heads from a 4-cylinder engine, one would expect that about 1 g of aluminum compounds (weight as Boehmite) would be introduced as a powder into the cooling system before the coolant passages of the head completely passivated.

The results of Fig. 5 for Carb premixed with 1% Hi-Si seem to show both a doubling of the weight loss during the initial day of the test and then an apparent continuation, albeit at a reduced rate, of measurable loss of aluminum to coolant during the entire week of a standard D 4340 test. XPS showed that the composition of the surface layer on aluminum after 2.5 h exposure to such contaminated coolant gave evidence of competition between the inhibitor packages, in particular, the presence of components from the inhibitor packages not seen on the surface at all in the absence of such competition. The D 4340 results at 50% total glycol suggest not only that this initial mixed surface layer allows more aluminum to escape to coolant during the initial buildup of the protective layer but also that low-level initial contamination can also delay the development of the full level of passivation of which the uncontaminated carboxylated coolant is otherwise capable.

Summary and Conclusions

At least under the conditions of the surface analytical part of this work (incipient passivating layers after 2.5 h of heating), the inorganic-inhibited North American coolants protect hot aluminum with silica films which are totally exogenous to the aluminum; i.e., they contain no elements of the metal itself. D 4340 procedures give very low (<0.2 mg/cm^2-week) weight losses in coolants which successfully passivate hot aluminum via this mechanism. In contrast, the passivating layers formed on hot aluminum in carboxylate-inhibited coolants are largely endogenous to the metal; that is, they are composed primarily of aluminum oxide formed locally from the aluminum alloy and water. The roles of the carboxylate inhibitors are likely to be (1) to promote the formation of highly protective hydrated forms of alumina and (2) to aid in the repair of defects in the alumina layer. The XPS observation of carboxylates (or carbon in any form) only at the outer surface of the oxide suggest that the inhibitors work by changing the uptake of water, oxide/hydroxide ions, and/or aggressive species such as chloride, at the outer surface of the film. Associated with the formation of this endogenous passivating layer and in part with its removal by the standard acid cleaning treatment, one-time (as opposed to continuous) weight losses appear in D 4340-type testing with some pure carboxylated coolants tested at 50% glycol concentration. A modified two-step (water rinsing, followed by acid-etching) post-test sample cleaning method can establish the relative magnitude of the real and illusory components of the initial "corrosive weight loss" in such coolants. The mean of the water-rinsed and acid-cleaned surfaces represents the best simple figure of merit for the amount of aluminum lost from the solid surface to the coolant. This figure of merit shows that a small amount of aluminum is lost to coolant (to form solids) during the formation of passivating layers in carboxylated coolants.

D 4340 weight losses measured in mixtures of carboxylated and inorganic North American coolants can vary with sample history, coolant mixing ratio, and total coolant concentration. The seemingly alarming D 4340 weight losses at 10 to 50% Hi-Si in 90 to 50% Carb with 25% total coolant concentration are suppressed either by pretreatment of the hot aluminum surface with uncontaminated carboxylate coolant or by increasing total coolant concentration to the 50% glycol typical of North American OEM factory fill and service recommendations. However, at the 50% glycol level surprisingly small admixtures (1 to 5%) of buffered silicated coolants can produce subtle but reproducible increases in D 4340 weight losses. Under these conditions of contamination, XPS showed formation of a mixed incipient passivating layer incorporating levels of inorganic inhibitors far exceeding their relative preponderance in the mixed coolant. The competition between inhibitor packages appears to both increase the loss of aluminum to coolant during formation of the passivating layer and to delay the development of full passivating power in that layer.

The gross contamination effects seen in standard D 4340 testing at 25% glycol have not shown up in a number of contamination tests using other laboratory procedures or factory-filled vehicles. It is not clear that the subtle effects seen here in the D 4340-like testing at 50% glycol level could be reliably quantified in vehicles, even if they occurred. In the absence of vehicular proof that these more subtle D 4340 results are *not* relevant to vehicular behavior, prudence has required that due care be taken to prevent low-level (for example, 1%) contamination of carboxylated coolants with silicated, inorganic-buffered coolants prior to complete establishment of protective layers on the aluminum surfaces. Measures taken to prevent contamination of carboxylated coolant early in the life of the vehicle have removed a possible path to the formation of unnecessary levels of aluminum-containing solids in the coolant and have delivered to customers the full aluminum-protecting power of the pure carboxylated coolant. Similar precautions should be taken to prevent low-level contamination during laboratory and vehicle test procedures designed to probe the intrinsic properties of carboxylate-inhibited coolant formulations.

Dedication

This paper is dedicated to the late Edward A. Pluskwa of Delphi Harrison Thermal Systems, a true gentleman who served General Motors and the ASTM D15 Committee well for many years.

APPENDIX

Details of D 4340 Testing Apparatus

The 319 alloy aluminum samples used in this work were machined from billets cast at GMR&D and have each been resurfaced and reused at least ten times. Pucks machined from more recent castings at GMR&D, samples bought out of catalogs of standard sources, and samples bought from standard sources under special specifications have all shown a higher level of porosity which we have considered unacceptable. The heat transfer bars and cell top plates were machined from 304 stainless steel. Each glass tube was supported from the top and was surrounded by a concentric cylindrical shield of clear plastic with an inside diameter of 20 cm. The top of the each shield was positioned 1.5 cm below the top of the glass tube, placing the bottom of the shield 7 cm below the top of the heat transfer bar. During steady-state operation, an average of 210 W heating power was applied to each cell; however, it appears that much of this power was dissipated to the air without passing through the ca 19 cm^2 aluminum/coolant interface. The often overly-small (for reliable conclusions to be drawn) data sets reported here are in many cases complemented by additional works carried out by the suppliers of candidate materials which are, however, not included in the numbers given here.

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Fleet Test Evaluation of Fully Formulated Heavy-Duty Coolant Technology Maintained with a Delayed-Release Filter Compared with Coolant Inhibited with a Nitrited Organic Acid Technology: An Interim Report

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REFERENCE: Aroyan, S. S. and Eaton, E. R., "**Fleet Test Evaluation of Fully Formulated Heavy-Duty Coolant Technology Maintained with a Delayed-Release Filter Compared with Coolant Inhibited with a Nitrited Organic Acid Technology: An Interim Report,**" *Engine Coolant Testing, Fourth Volume, ASTM STP 1335,* R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 43–51.

ABSTRACT: This paper is a controlled extended service interval (ESI) study of the comparative behaviors of a nitrite/borate/low-silicate, low total dissolved solids (TDS) coolant maintained with delayed-release filters, and an organic acid inhibited coolant technology in heavy-duty engines. It reports both laboratory and fleet test data from 66 trucks, powered with different makes of heavy-duty diesel engines. The engines were cooled with three different types of inhibitors and two different glycol base (ethylene glycol and propylene glycol) coolants for an initial period exceeding two years and 500 000 km (300 000 miles). The data reported include chemical depletion rates, periodic coolant chemical analyses, and engine/cooling system reliability experience. The ongoing test will continue for approximately five years and a 1.6 million km (1 million miles) duration. Thirteen trucks were retained as controls, operating with ASTM D 4985 specification (GM-6038 type) coolant maintained with standard ASTM D 5752 supplemental coolant additive (SCA). Engines produced by Caterpillar, Detroit Diesel Corp., Cummins Engine Co., and Mack Trucks are included in the test mix.

KEYWORDS: fleet, extended service, delayed-release, organic acid, phosphate, nitrite, fully-formulated, inhibitors, silicate depletion, propylene glycol, radiators, water pumps

This paper supports the practice of extending the life of existing fully formulated, low total dissolved solids, phosphate-free, low-silicate (PG or EG) coolants to at least 500 000 km (310 694 miles) when properly maintained with state-of-art delayed-release filters. Information was derived from both laboratory evaluations and a fleet test of 66 trucks powered by various engines (Detroit Diesel, Caterpillar, Cummins, and Mack). Thirteen trucks were used as control vehicles filled with standard, phosphated, low silicate ASTM D 4985 type conventional coolant [ASTM Specification for Low Silicate Ethylene Glycol Base Engine Coolant for Heavy-Duty Engines Requiring a Pre-Charge of Supplemental Coolant Additive (SCA) (D 4985-94)]. The paper presents data that show both North American "fully formulated" and organic acid inhibited glycols perform acceptably in extended service applications. [Note: Tables 1 and 2 provide explanations of both general and inhibitor terminologies used throughout this paper.]

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TABLE 1—*General terminology.*

Antifreeze	Pure glycol (typically 95% min) with an inhibitor package added.
Conventional coolant	The coolant chemistry, usually based on ethylene glycol, that contains a corrosion inhibition package often consisting of inorganic inhibitors such as silicate, phosphate, nitrate, and azoles.
Coolant	A fluid consisting of water and glycol, typically at 50% each whose function it is to act as a heat exchange fluid for the engine while protecting the metals against corrosion.
EG	Ethylene Glycol, the most common chemical used to prepare anti-freeze products.
Fill-For-Life℠	A coolant strategy employing phosphate-free RP-329 or RP-330 coolant maintained with delayed-release filters, eliminating scheduled coolant changes.
GM-6038	The GM-6038 antifreeze specification provides an actual recipe for phosphated, low silicate heavy-duty fluid that many antifreeze blenders have emulated to prepare ASTM D-4985 compliant antifreeze. This antifreeze requires a pre-charge of SCA before being used. It is commonly used as a control because its formulation is public domain.
OEM	Original Equipment Manufacturer
Organic acid inhibitors	Any of a group of carboxylic acids including sebacic and other mono and/or dibasic acids applicable as corrosion inhibitors in engine coolant.
PG	Propylene Glycol, a less toxic member of the glycol family used by some antifreeze manufacturers as their chemical base. PG coolants are desirable in some environmentally sensitive applications, such as national parks.
PM	Preventative Maintenance Interval, typically defined by the oil change interval.
RP	A Recommended Practice of the TMC, often a purchasing specification.
SAE	Society of Automotive Engineers
SCA	Supplemental Coolant Additive
TMC	The Maintenance Council of The American Trucking Association

TABLE 2—*Inhibitor terminology.*

pH	A measure the alkalinity of the coolant
Nitrite	Primary inhibitor for wet sleeve liner pitting protection
Nitrate	Primary inhibitor for solder and aluminum protection
Silicate	Primary conventional inhibitor for aluminum protection
Phosphate	Primary inhibitor for pH buffer and iron protection
Molybdate	Primary inhibitor for cavitation-erosion and iron protection
Azole	Primary inhibitor for copper and brass protection.

The primary function of coolant is to act as a heat-transfer fluid to remove excess heat from the engine. Coolant prepared with antifreeze and water is used to reduce the freeze point and to prevent corrosion of cooling system metals and cavitation-erosion of diesel wet sleeve cylinder liners. The existing conventional coolant technology has been successfully used for over 30 years. Metals that must be addressed include steel, cast iron, copper, brass, lead solder, extruded and cast aluminum. For years, the OEMs' recommendations have been to change the coolant every two years, 240 000 to 385 000 km (150 000 to 240 000 miles), or 4000 operating h. The data presented here demonstrate that phosphate-free, fully formulated PG or fully formulated EG can provide extended life of up to 500 000 km (300 000 miles).

Coolant Compositions

There were four types of coolant involved in the test:

1. Propylene Glycol base, phosphate-free, low silicate package (TMC RP-330).
2. Ethylene Glycol base, phosphate-free, low silicate (TMC RP-329).
3. Ethylene Glycol inhibited nitrited carboxylic-acid technology (CAT EC-1).
4. GM-6038 type coolant meeting ASTM D 4985 specification maintained with a standard charged-filter SCA program (control).

Experimental Procedures

Laboratory Trials

The test coolants were evaluated in the laboratory for compliance with the TMC RP-329 specification. This specification requires that the coolant meet both the ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light Duty Service (D 3306-94) and ASTM D 4985 performance criteria. The coolants were also independently analyzed before the tests. All three coolants passed the ASTM D 3306 (light-duty) and D 4985 (heavy-duty) performance requirements and most OEM specifications.

Fleet Test Protocol

The test coolants were installed in the 66 trucks. The cooling systems were completely drained, thoroughly flushed with tap water, and filled with antifreeze pre-diluted to 50% with deionized water. Initial samples were taken, and the glycol concentration and physical properties were determined and recorded. Additional samples were obtained at every PM and were sent for a complete analysis.

In preparing for the fleet test, several obstacles had to be addressed:

- Locating a facility that would agree to the test program.
- Providing for the possibility of losing some of the test vehicles due to accidents.
- Accidental contamination with different coolant technology.
- Possibility of reassignment of vehicles to other locations.
- Change in fleet management
- Coolant loss through leakage.

Before the test, the author met with each fleet and explained the importance of preventing any coolant contamination. The objective going into the test regimen was to operate 66 trucks

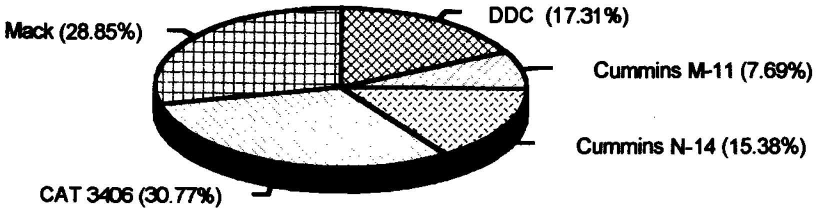

FIG. 1—*Test truck engine distribution by manufacturer.*

for 800 000 to 1 600 000 km (500 000 to 1 million miles). Figure 1 illustrates the distribution of engine manufacturers in the test trucks.

Test Fleet Distribution

Test Fleet A—A private packaging company located in the North-Central United States. The test trucks are Freightliners powered by Cummins N-14 engines. The trucks deliver the company's own products to customers.

Test Fleet B—A manufacturing company located in the Midwest United States specialized in short-haul delivery. The test trucks are Peterbilt, Kenworth and Freightliners powered by Cummins N-14 and Caterpillar 3406 engines.

Test Fleet C—A long-haul freight company located in the Southern United States. The test trucks are Freightliners powered by Detroit Diesel Series 60 engines.

Test Fleet D—An LTL and truckload freight company located in the Eastern United States. The test trucks are powered by Mack engines, operating medium and long-haul routes.

Status of the Fleet

The project is expected to offer the schedule given in Table 3 for engine teardown availability by manufacturer.

TABLE 3—*Engine teardown schedule.*

Engine/Coolant	**Current Accumulated Experience (km)**	**Teardown Availability (500K Km)**
Cat 3406 / Fill-For-Life	580,000	Available
Cat 3406 Propylene Glycol	400,000	2nd quarter, 1998
Cat 3406 NOAT	400,000	2nd quarter, 1998
Cat 3406 Control	400,000	2nd quarter, 1998
Cat 3176 FFL	250,000	2nd quarter, 1999
Cat 3176 OAT (non-nitrite)	200,000	2nd quarter, 1999
Cummins N-14 FFL	450,000	First Quarter, 1998
Cummins N-14 PG	425,000	First Quarter, 1998
Cummins M-11 FFL	275,000	2nd quarter, 1999
Cummins M-11 SPG	350,000	3rd Quarter, 1998
DDC Series 60 FFL	175,000	3rd quarter, 1999
DDC Series 60 NOAT	200,000	2nd quarter, 1999
DDC Series 60 SPG	350,000	2nd quarter, 1998

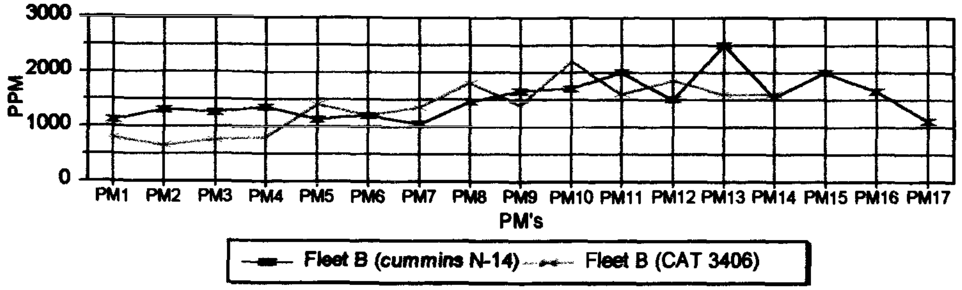

FIG. 2—*Nitrite in EG coolant w/SCA. Conventional: phosphated, low silicate.*

Fleet Test Data

The authors have tracked inhibitor depletion in the four coolants. Previous studies [*1*] have shown that depletion rates of carboxylic acid inhibitors in coolants are so low as to be regarded as insignificant. There were 13 control vehicles in fleet test. All the trucks had experienced acceptable performance from their assigned coolant program. The maintenance personnel have demonstrated exceptional ability to follow the proper procedures and generate extremely useful data. The preventative maintenance interval for control vehicles was approximately 32 000 km (20 000 miles). The following charts summarize the depletion rates of the inhibitors of each individual coolant in the various engines.

Inhibitor Depletion

Nitrite is the primary inhibitor for wet sleeve liner pitting protection. Azole is the primary inhibitor for the copper and brass protection. Silicon protects cast aluminum. The behavior of nitrite, azole, and silicon in each engine is reflected in the following graphs. In each, the abscissa is scaled in preventative maintenance (PM) interval periods (1 PM = 32 000 km). The ordinate is scaled in parts per million (ppm) of inhibitor concentration.

Figure 2 shows the average nitrite behavior in a conventional, phosphated, low silicate control coolant. The inconsistency in the nitrite level observed in both engines is due to the manual maintenance program and the non-nitrited (ASTM D 4985) antifreeze used by the fleet. The maintenance practice requires addition of SCA at every PM.

Figure 3 describes the average silicon (infers silicate) concentration in the control coolant. It remains within an acceptable concentration range.

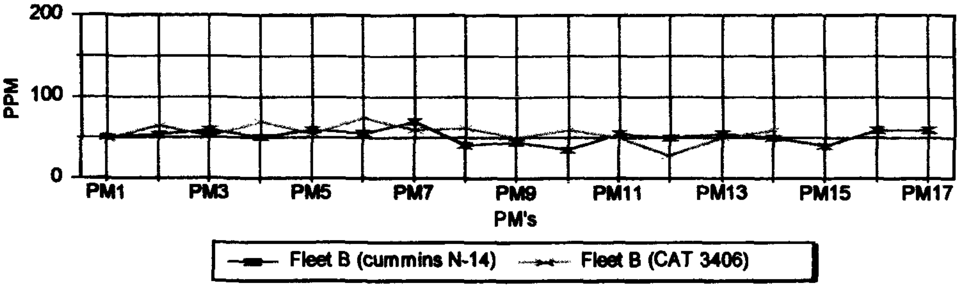

FIG. 3—*Silicon in EG coolant w/SCA. Conventional: phosphated, low silicate.*

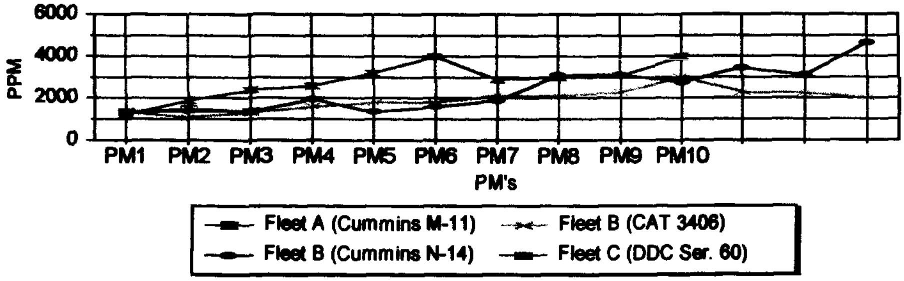

FIG. 4—*Nitrite in PR-329 coolant. Fully formulated, phosphate-free.*

Figure 4 depicts the average nitrite depletion for a fully formulated, phosphate-free coolant maintained with a delayed-release filter instead of adding supplemental coolant additive (SCA) at every PM. The change interval for the delayed-release filter is 240 000 km (150 000 miles). The nitrite behavior differs in each type of engine. The authors hypothesize that nitrite requirements vary by engine make. Nevertheless, all of the engines are adequately protected.

Depletion of the silicate is represented in Fig. 5. The behavior is similar in all the trucks. This coolant is maintained by a delayed-release filter in order to detect and offset the depletion of silicon as the coolant ages. The intent of the filter appears to be achieved.

Figure 6 illustrates the average nitrite depletion in a fully formulated, phosphate-free PG coolant when SCA is not added at every PM. Nitrite concentrations remained within the specifications in all trucks.

The silicon average depletion behavior in fully formulated, phosphate-free coolant, is different in each group (Fig. 7). However, all the trucks remain within specification.

Figure 8 describes the average depletion of nitrite in a nitrated organic acid technology (NOAT) coolant. The low level of depletion verifies that ongoing protection for wet sleeve liners will exist without frequent coolant maintenance.

Tolyltriazole behavior (Fig. 9) in NOAT reflects dramatic reduction of TTZ concentrations with time, presenting a concern that copper and brass protection may be compromised if the coolant fails at a period of 250 000 to 300 000 km (150 000 to 200 000 miles).

The data from these trucks confirm that the concentration of the carboxylic (organic) acids does not seem to change significantly with time (Fig. 10). The authors note that the fluctuation in carboxylates reflected in the graph may be due to experimental variance, and/or the need for significant makeup coolant. The sample preparation requirements, which allow the measurement of carboxylate content, are very sophisticated and may contribute to some variance.

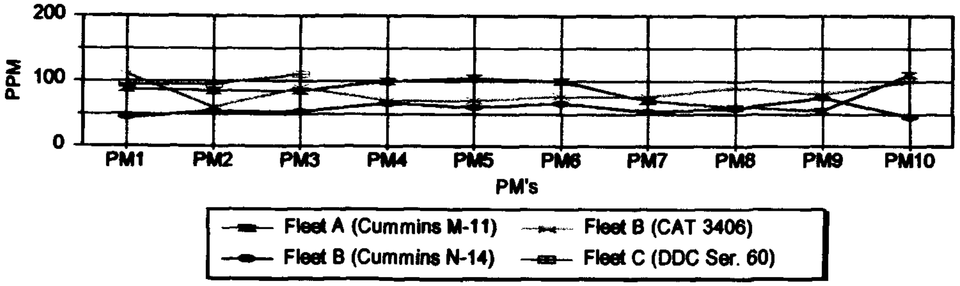

FIG. 5—*Silicon in RP-329 coolant. Fully formulated, phosphate-free.*

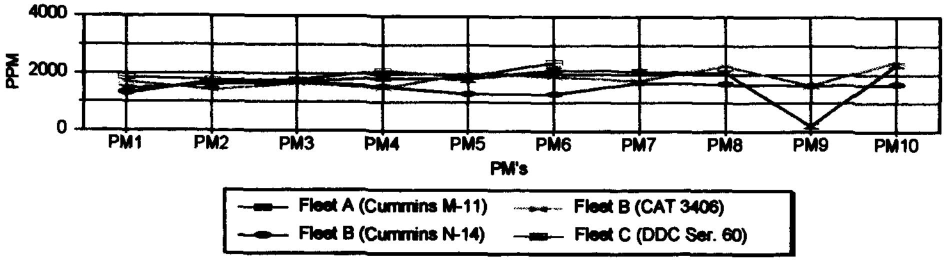

FIG. 6—*Nitrite in RP-330 (PG) coolant. Fully formulated, phosphate-free.*

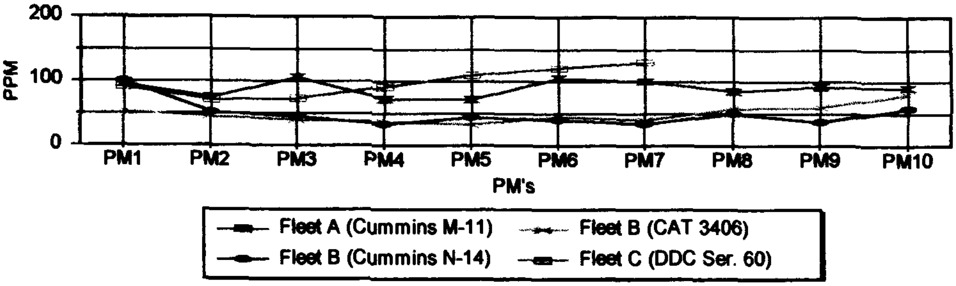

FIG. 7—*Silicon in RP-330 (PG) coolant. Fully formulated, phosphate-free.*

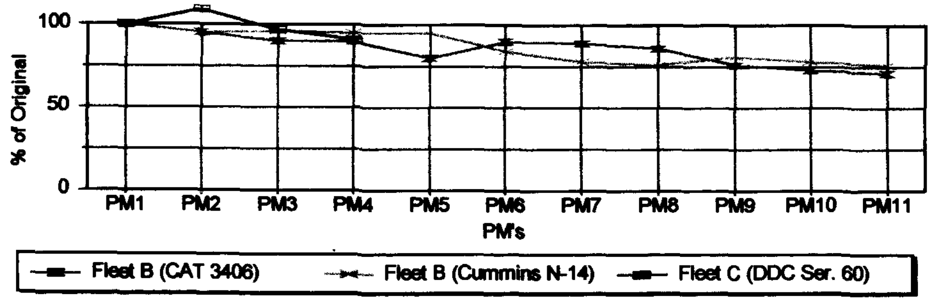

FIG. 8—*Nitrite in NOAT technology. Silicate- and phosphate-free coolant.*

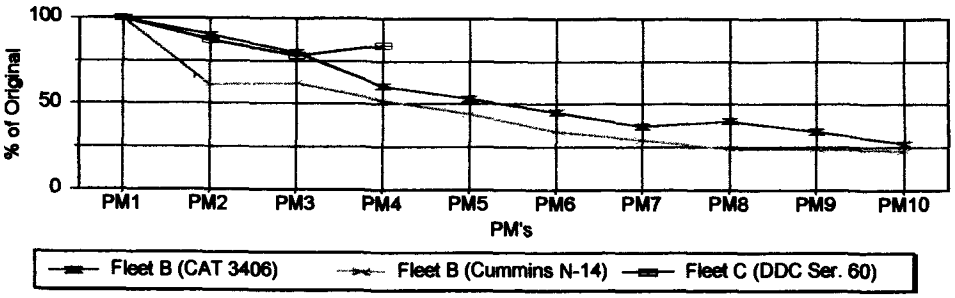

FIG. 9—*Tolyltriazole in NOAT coolant. Silicate- and phosphate-free coolant.*

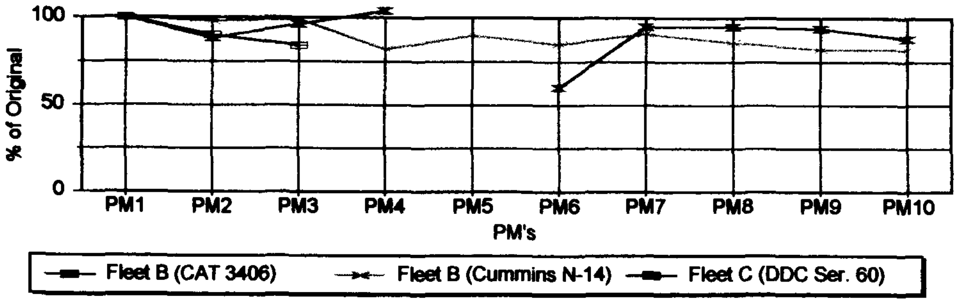

FIG. 10—*Organic acid concentration. Silicate- and phosphate-free coolant.*

The tolyltriazole depletion in the NOAT coolant occurs as a function of copper and brass protection. An interesting phenomenon in the NOAT was the elevation in the silicon content, in spite of the fact that there is no silicate in the coolant or "booster" chemistries. The elevation may possibly be leached from the silicone hoses.

Many of the trucks in the ongoing fleet test will continue to an ultimate duration of five years or 1.6 million km (1 million miles).

In the fleet tests, the performance of each coolant, to date, is acceptable and chemical parameters remain within the manufacturers' specifications. Curiously, the lead content is high in two of the fully formulated, phosphate-free PG coolant vehicles. These vehicles continue in operation, with attention to any differences between them and sister vehicles being researched. No system or component failures have occurred. The source of lead has yet to be determined. Copper, cast iron and cast aluminum are not evident in any of the fleet vehicles. The pH levels remain acceptable in all coolants.

Conclusions

1. The test is being successfully controlled to prevent contamination of the test coolants.
2. All three coolants are performing acceptably, as demonstrated by the absence of any engine or cooling system component failures and general absence of metal ions in the coolants.
3. Nitrated organic acid inhibited coolant is performing equal to phosphate-free "fully formulated" technology. Neither has demonstrated a performance advantage when both were maintained per manufacturers' recommendations. The propylene glycol variant of the "fully-formulated" technology offers similar maintenance intervals to NOAT.

Summary

Interim results of a 66-truck fleet test suggest that nitrited organic acid inhibited (NOAT) coolant is similar in performance to two phosphate-free fully formulated (one PG and one EG) coolants. All the technologies are performing acceptably.

Acknowledgments

The authors wish to acknowledge The Penray Companies, Inc., for their support in preparing and shipping the test coolants test to each location. The authors acknowledge the help of the fleet personnel at each fleet location, and the two independent laboratories for their assistance in maintaining consistent coolant evaluations.

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and J. K. Listebarger[3]

Engine Coolant Technology, Performance, and Life for Light-Duty Applications

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REFERENCE: Turcotte, D. E., Lockwood, F. E., Pfitzner, K. K., Meszaros, L. L., and Listebarger, J. K., "**Engine Coolant Technology, Performance, and Life for Light-Duty Applications,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335,* R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 52–75.

ABSTRACT: Recently there has been interest by motor vehicle manufacturers in developing longer-lived automotive engine coolants with an emphasis on organic acid technology (OAT) [*1*]. Paradoxically, the lifetime of conventional technology remains largely undefined. Concerns arising from the depleting nature of silicate have led to modern conservative change recommendations of 30 000 to 50 000 miles (~48 279 to 80 464 km) [*2*].

In the present work, laboratory bench test, engine dynamometer and vehicle service data from traditional silicate, hybrid and nonsilicate coolants are compared and contrasted. A new electrochemical test is used to examine passivation kinetics on aluminum. It is shown that performance and lifetime are independent of chemistry and cannot be generalized. Examples include an American silicate coolant with excellent performance on high-heat-rejecting aluminum (80 W/cm^2), European and American silicate coolants with performance defined lifetimes in excess of 300 000 miles (482 790 km), and an OAT coolant with laboratory high lead solder protection. It is concluded that the primary benefit of OAT is to meet global specifications that include chemical limitations.

KEYWORDS: corrosion, coolant, silicate, automotive, aluminum, organic acid

North American silicate-based coolants were developed by the early 1980s to protect aluminum engine components [*2*]. Well stabilized silicate-containing coolants have been used successfully in Europe also [*3*]. As an inhibitor, silicate is efficient, inexpensive and protective of many metals. The depleting nature of silicate has been attributed to its ability to function as a film forming inhibitor [*4*]. The technology of formulating well stabilized silicate coolants can be complex. Silicate coolants without adequate stabilization can self-polymerize into gel or deplete rapidly in engine service [*4*]. Silicates likely have been falsely implicated in water pump seal failures. Investigations of water pump seal failures have indicated that the mechanism is far more complex than simply coolant chemistry or the presence of silicate [*5–8*]. Modern silicate coolant change intervals are quite conservative. Adamowicz and Falla [*9*] have shown that today's change intervals can be extended considerably.

Alternative inhibitor technologies have been widely investigated to augment or replace silicate technology. The first engine coolant application of carboxylic acids was probably reported by Butler and Mercer [*10*] in 1977 for silicate-free formulas. The use of organic acids (OA) as corrosion inhibitors has recently been reviewed [*11*]. Since carboxylic acids tend not to deplete

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[3] Ashland Chemical, Dublin, OH.

in vehicle service, it has been postulated that they may offer extended service life advantages over current technology. The literature is mixed on the subject. In addition to increased costs for OA coolants [*9*], azole yellow metal inhibitors tend to deplete [*12,13*], high lead solder corrosion may be significant [*8,13,14*] and cavitation erosion-corrosion performance is reduced [*8*] or improved [*15*]. However, these concerns may not be relevant since yellow metals are well protected [*14*], solder is no longer commonly used and if the cavitation protection is acceptable. OA coolants are reported to have benefits over silicate coolants on high heat-rejecting aluminum (@ 75 W/cm^2 max.) [*16,17*] under dynamic conditions. It has been reported that only silicate-free coolants based on synergistic combinations of aliphatic organic acids can provide adequate protection under these conditions [*17*]. This is inconsistent with many years of successful coolant application experience worldwide. In the current work, dynamic heat transfer tests show that both silicate and acid coolants can protect aluminum as expected.

Recent light duty coolant specifications with chemical limitations including the reduction or elimination of silicate [*1*] have been published by manufacturers. The minimal chemistries of these specifications favor OA technology, may simplify global automobile coolant sourcing and extend coolant service life. This paper will examine the ability of an OA coolant to offer extended life through comparisons with conventional coolants in extended engine dynamometer and 100 000 mile (160 930 km) vehicle service testing. The results show that modern service intervals can be extended with either technology. Overall data suggest the silicate technology is superior in performance and potential lifetime. OA coolants are shown to passivate slowly by an electrochemical thermal scratch test; this is consistent with observations of diminished performance when the corrosion mechanism is fast, as in cavitation erosion-corrosion, erosion or liner pitting. Scanning electron microscopy (SEM) was used to evaluate field components. Results from field service testing were not entirely consistent with ASTM laboratory test results for the OA coolant.

Experimental Results and Discussion

Heat-Rejecting Aluminum Scratch Test

An electrochemical cell based on the standard ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions (D 4340-96) has been developed. The cell can be used with a variety of standard electrochemical techniques. An important feature is that it is based on a well accepted test known to discriminate coolants and correlate with field experience. It is unique in that it captures the heat-rejecting aspect of a cylinder head in a short-term electrochemical test. Recording the open circuit potential versus time while heating the specimen has been found to give kinetic information on a coolant's ability to passivate as in a scratch test. Qualitative electrochemical noise in the voltage time trace can give mechanistic information [*18*]. Pitting and film formation can be discerned. A freely corroding electrode responding to a thermal depassivation event in the presence of an engine coolant captures the dynamic nature of the corrosion process in a way that traditional driven cell experiments cannot.

During the test, the native oxides are thermally fractured resulting in abrupt depassivation. The corrosion potential is monitored to measure the extent of depassivation and to evaluate repassivation. Aluminum repassivation typically involves capacitive protective oxide growth [*19,20*]. Well inhibited conventional coolants show less depassivation and repassivate quickly. Less inhibited coolants give larger depassivation and may or may not repassivate. The aluminum surface may also darken at potentials approaching −1000 mV versus silver polysulfide (SPS). Simple monitoring of the corrosion potential versus time can give insight into differences in passivation kinetics between types of coolants.

The ASTM D 4340 test cell is modified to allow for electrochemical measurements as shown in Fig. 1. The standard cast aluminum alloy, UNS A03190 (SAE 329), is tapped for electrical connection and serves as the working electrode. The specimen is wet polished on a Buehler metallurgical polisher using 120, 240, 400, and 600 grit paper sequentially. The specimen is air dried and used directly. Silicone O-ring seals join a 12-in.-long (30.48 cm) Pyrex tube of 2 in. (5.08 cm) inside diameter to the specimen and top plate assembly. The specimen is positioned on a stainless steel T-shaped heat transfer block bottom wrapped by a 950 W band heater as shown in Fig. 1. This provides approximately 11.7 W/cm^2 thermal loading. The heater is housed in a box with variac control, although not shown. A type J thermocouple monitors specimen temperature through a 2¼-in. (5.7 cm) hole.

The cell is held together by threaded rods through the top and bottom plates. The top plate is modified to allow a graphite counter electrode and silver polysufide coated platinum reference

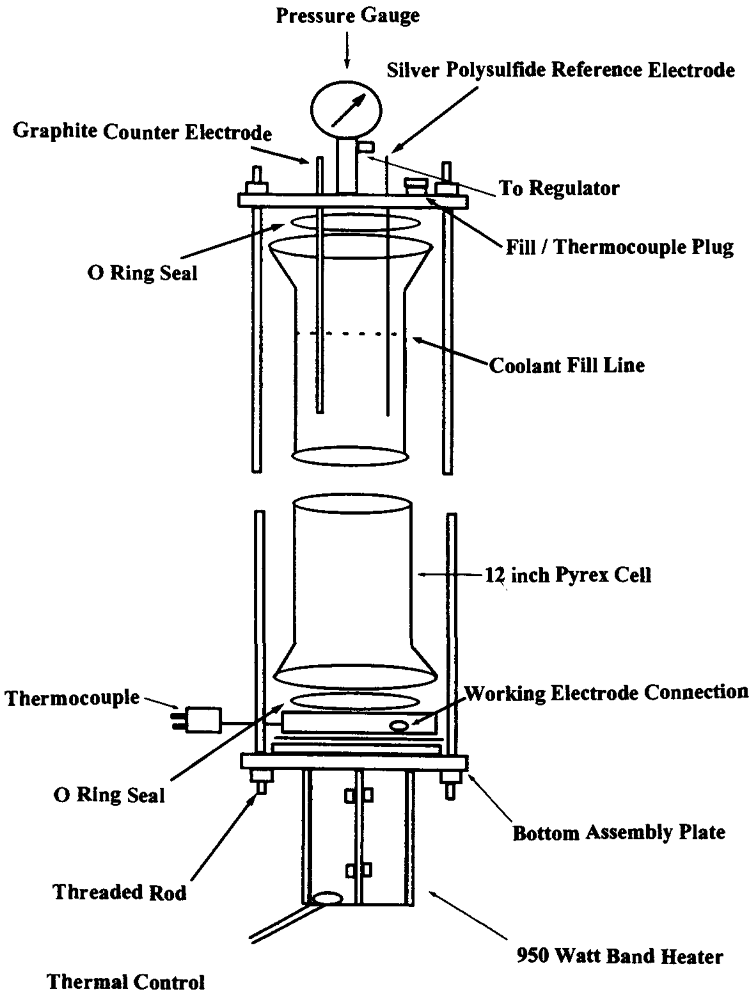

FIG. 1—*Modified ASTM D 4340 test cell.*

electrode. A pressure gage and fill/thermocouple hole complete the top plate openings. A Kiethly model 179 digital voltmeter monitors cell potential through a Thurston Bell Associates EB 1005 electrobuffer. Open circuit potential, E_{oc}, is measured between the reference and the working electrode. It is recorded on a Linseis L6514B four-channel recorder.

Five hundred milliliters of 25% coolant distilled water mixture with 100 ppm chloride fills the cell. The electrodes are inserted and it is pressurized to 28 psi (193 kPa). The open circuit potential, E_{oc}, is recorded for approximately 30 min and then the heat is turned fully on. At 250°F (121°C), the heat is turned back to 70% on the variac and the temperature rises and maintains at 275°F (135°C). Incipient nucleate boiling is observed. The test has shown a high degree of repeatability and reproducibility. Different test cells have produced results on the same coolant that are virtually superimposable. Data on three commercial coolants meeting the ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light Duty Service (D 3306-94) and Specification for Low Silicate Ethylene Glycol Base Engine Coolant for Heavy Duty Engines Requiring a Pre-Charge of Supplemental Coolant Additive (SCA) (D 4985-94) are presented.

The resultant potential versus time transients are shown in Fig. 2 for (A) an American high silicate formulation, (B) a molybdenum based Japanese nonsilicate type, and (C) an organic acid coolant. In each case the corrosion potential increases or becomes more noble with time until rapid depassivation from heating occurs. The variac is set to 70% prior to the minimum in potential. The voltage time plots from A and B repassivate and return to open circuit potentials slightly more negative than at room temperature prior to heating. C does not repassivate on the time frame of the experiment. The metal sample darkens visibly but no deposits form. Similar darkening of metals in contact with organic acid coolants has been reported [9]. Voltage noise is present on B and C after 35 min. Coolant B was reported to have field head pitting problems, and the qualitative voltage fluctuations are consistent with this. The noise on curve C may be due to incomplete film formation. Unstable protective films are a source of potential noise [*21*,*22*]. This suggests a reaction between the acid and the aluminum corrosion products as opposed to an initial protective film. Neither specimen B nor C showed any visual evidence

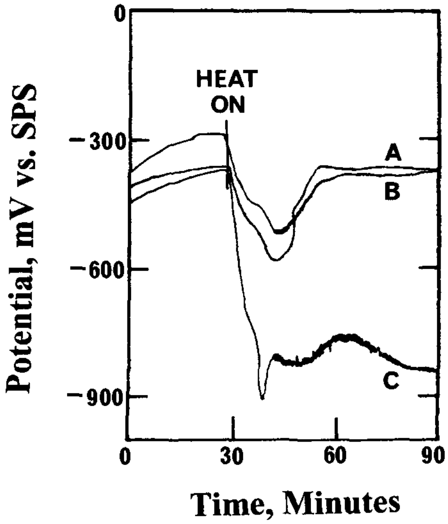

FIG. 2—*Potential vs. time transients.*

of pitting. It can be concluded from Fig. 2 that the organic acid coolant passivates aluminum much more slowly than the other coolant types. Several different OAT coolant formulations have been found to give similar behavior.

The Ford pitting test by Wiggle and Hospadaruk [*23–26*] is probably the best known galvanostatic pitting test for coolants on aluminum. A 100 $\mu A/cm^2$ current is passed, and the minimum of the resultant potential decay curve reported as E_{pit}, the pitting potential. This is considered indicative of the most reactive pit sites. The test was developed for silicate type coolants and has been correlated with simulated service circulation tests. Typically, pits are visible on the specimen surface following testing for silicate coolants, but several organic acid coolants show uniform surface darkening and an absence of discrete pits. The test is proven for the heterogeneous current distribution expected from a silicate coolant giving a generally passive surface with discrete pit sites. Its application to the homogeneous current distribution response is uncorrelated. If the slower passivating OAT coolant does not form a passive layer quickly enough to allow defects in the layer to support the current applied, then the applied current may simply thicken the overall surface oxide giving the darkened post test specimen. Oddly, aluminum seems to corrode generally in the presence of organic acids despite large negative open circuit potentials or large applied currents.

Dynamic Heat Transfer Test

This test was used to evaluate aluminum corrosion protection under high heat-rejecting conditions, 80 W/cm^2 maximum, and dynamic flow conditions. A diagram of the test apparatus is shown in Fig. 3. A gear-driven pump circulates the test mixture over a metal test specimen.

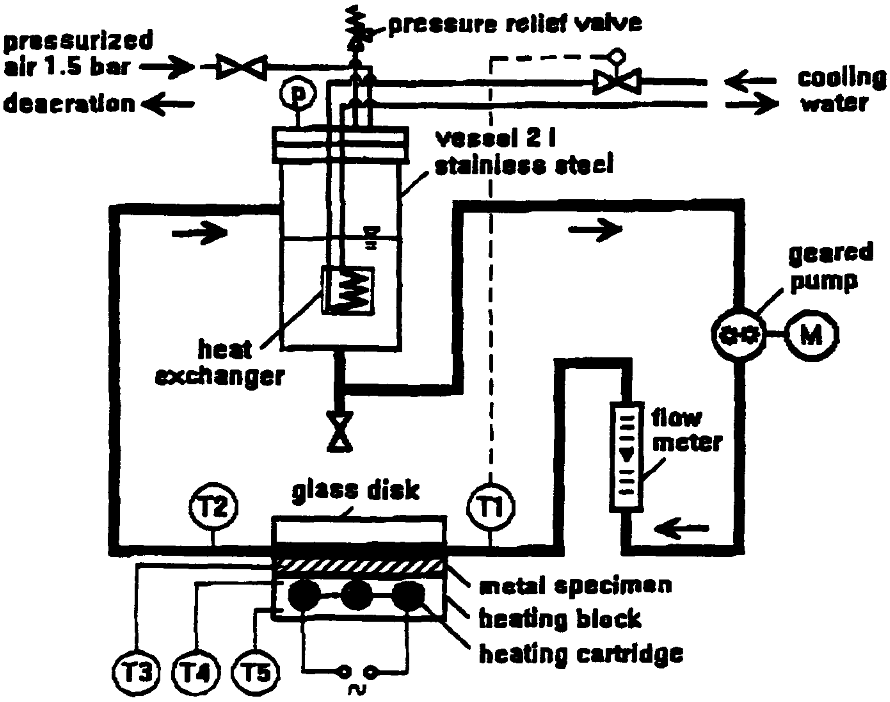

FIG. 3—*Dynamic heat transfer test apparatus.*

TABLE 1—*Test conditions.*

Test duration	48 h
Coolant volume	1 L
Pressure	1.5 bar (21.8 psi)
Flow rate	3.5 L/min (210 L/h)
Heating block output	1890 W max. (3 × 630 W)
Free specimen diameter	55 mm
Specified heated surface loading	80 W/cm^2 max.
Coolant temperature inlet, T1	95°C ± 1°C (203°F)
Concentration of test fluid	20 or 40%

The test specimen is supported by a thermal transfer block which houses a heating cartridge. A pressurized 2 L stainless steel vessel houses a water cooled heat exchanger. Five temperatures are measured, T1 is the inlet temperature of the test mixture; T2 is the outlet temperature of the test mixture, T3 is the specimen temperature, and T4 and T5 are the upper and lower portions of the heating block, respectively. The test conditions are outlined in Table 1.

The metal specimen is cast aluminum G-Al Si 10 Mg. The surface is polished on both sides to a roughness of 0.8 to 1.0 μm. The samples are rinsed with distilled water and treated for 5 min with acetone before drying for 15 min at 60°C. After cooling to room temperature the specimen is weighed to an accuracy of 0.1 mg. Special care must be taken to assure the thermocouple hole is perfectly clean and dry prior to the weighing.

The five temperatures are continuously recorded during the test. Following the test, the apparatus, test fluid and specimen are visually inspected. The location and nature of deposits, and fluid changes, such as turbidity and particulates are noted. The specimen is cleaned by pretreating under running water with a soft brush to remove lightly adherent deposits. Wire brushes and scouring powder are not allowed. Aluminum samples are chemically cleaned for 5 min at 80°C in a 5% by volume phosphoric acid and 2 weight% chromium oxide solution. The specimen is again rinsed under running water and scrubbed with a soft brush. Next the specimen is immersed in an ultrasonic acetone bath for 5 min. Finally, the specimen is again oven dried and weighed. The weight change, surface condition and corrosion morphology are reported. Also, the pH, hardness, and conductivity of the tested solution are determined. The test apparatus is disassembled and cleaned following each test. Dilute acetic acid is used to remove deposits. The system is rinsed with tap water and finally with distilled water. Seals and tubes are replaced after each test.

The specimen temperature is plotted versus test duration in Fig. 4 for the three coolants tested. A is a poorly stabilized, low silicate based coolant purposely prepared for this test; B

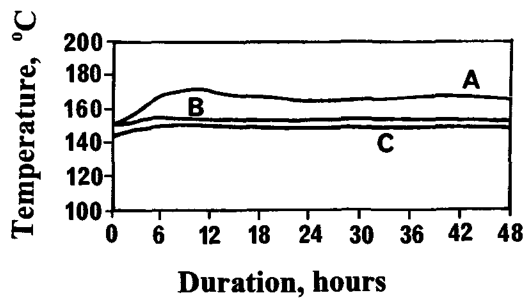

FIG. 4—*Specimen temperature versus test duration.*

TABLE 2—*Results.*

Coolant Type	Weight Change, mg/specimen
Dicarboxylic acid blend OAT	−21.2
Monocarboxylic acid blend OAT	−23.5
Mono/dicarboxylic acid blend OAT	−32.7
U.S. silicate based traditional formula	−4.1

is an organic acid coolant containing no silicate or common inorganic inhibitors; and C is a high silicate, phosphate buffered traditional American coolant. The shape of the specimen temperature versus time curves can indicate the buildup of a surface film. If the films limit thermal transfer the surface temperature is expected to rise as in A. In the absence of thermal transfer limitations, straight line behavior indicates adequate corrosion protection as shown for B and C. Several OAT coolants were investigated and gave good results similar to B. The results also show that a well stabilized silicate coolant can give performance that is equivalent to an organic acid coolant. Similar positive results have typically been found for many European silicate and hybrid formulations. The poor results for silicate technology reported by Van de Ven and Maas [*16,17*] could not be duplicated for a well stabilized silicate coolant but were readily duplicated for a poorly stabilized formula. Weight loss data are reported in Table 2 for four coolants meeting ASTM D 3306.

The weight changes reported in Table 2 are recorded following the described chemical cleaning. The silicate coolant appears superior, however, the chemical cleaning induces weight loss on the OAT samples. If the OAT tested specimens are weighed without chemical cleaning, minimal weight losses are typically found, similar to the silicate coolant result reported. No advantage to blends of mono and dicarboxylic acids was found. For all OAT coolants tested, darkened aluminum was obtained following testing and cleaning.

In summary, no advantage to OAT technology could be found following dynamic heat rejection testing on aluminum. Well stabilized silicate technology provided equivalent aluminum protection.

Extended Engine Dynamometer Tests

The Ford engine dynamometer test [*27*] was used to estimate the useful life of three different coolant technologies by extending the duration. The standard test has been used successfully to distinguish coolant performance [*4*]. Key stresses include maintaining a 35°F (1.6°C) difference across the radiator, thermal cycling and corrosive water. The radiator is immersed in a water bath to maintain the temperature differential. The speed of 2400 rpm at 28 bhp (20.8 kW) is equivalent to driving at highway speeds up a 10% grade. An American high silicate coolant, a European silicate based benzoate-nitrite formulation and an organic acid coolant meeting the chemical requirements of GM 6277M with no inorganic inhibitors were tested. The parameters of the tests are presented in Table 3. ASTM weight loss coupons were removed and replaced at standard 96 h intervals. A 2 to 4 oz (56.7 to 113.4 g) coolant sample was taken at each 96 h interval and makeup coolant additions were recorded. Coolant samples were chemically analyzed by common industry methods. One radiator was wind tunnel, heat-rejection tested before and after the engine test to evaluate effects from radiator deposits. Comparisons of post test aluminum from the cylinder head and radiator tubes were made using surface techniques. The dynamometer tests were continued until coupon losses became large or the

TABLE 3—*Ford dynamometer test conditions.*

Engine	1.9 L Escort
Radiator	Contour/Mystique
Speed	2400 ± 25 rpm
Torque	83 Nm (28 bhp)
Cycle	16 h on/8 h off
Coolant concentration	45%
Radiator input	225°F (107.2°C)
Radiator output	195°F (90.5°C)

test was compromised due to unrelated component failure. The test-ending failures experienced included an externally corroded radiator draincock and a radiator coolant hose.

The 96 h interval coupon weight loss data for the organic acid coolant tested is plotted in Fig. 5. The test was terminated at 1728 h. This is equivalent to 129 600 miles (208 565 km) assuming a speed of 75 mph (~120 km/h). Cooling system metals are well protected with the exception of cast iron and steel. A spike in corrosion losses occurred between 500 and 1000 h, and the protection diminished after 1248 h. Aluminum showed losses of 3 to 28 mg per coupon over the test. Yellow metals and solder were well protected for the entire interval. Following the engine test, the radiator had a 4.5 to 12.2% decrease in heat rejection capability. The liquid side pressure loss was not noticeably changed, the air side pressure loss accounted for the decrease and is typical for extended water bath exposure. The radiator was sectioned

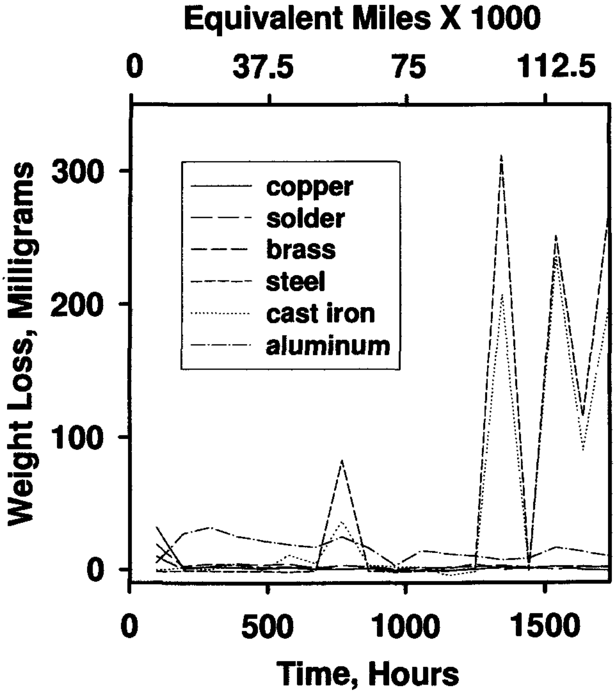

FIG. 5—*Ninety-six-hour interval coupon weight loss data.*

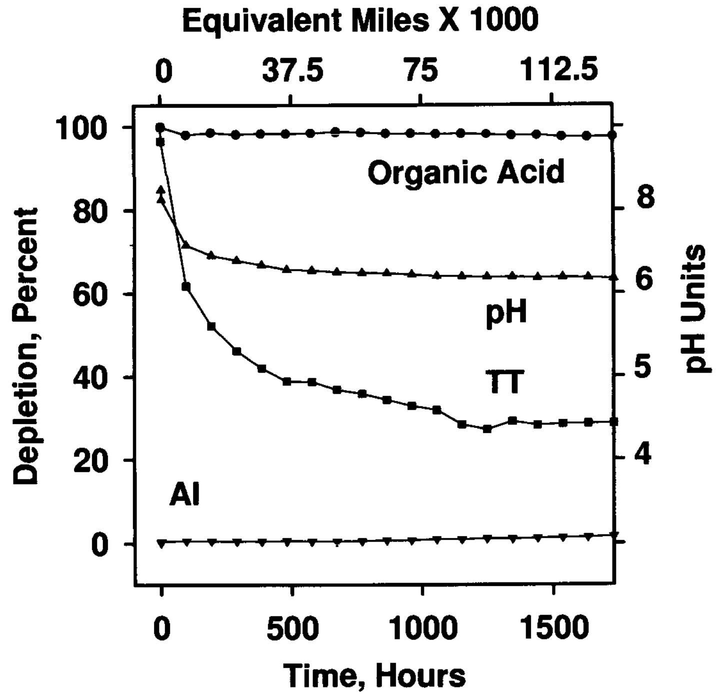

FIG. 6—*Coolant chemistry plot.*

following the wind tunnel testing. The header was well protected and free of deposits. The aluminum metal was coated light tan and free of deposits. The tubes were sectioned and judged free of deposits or pits. The metal was also colored tan.

The head was sectioned longitudinally to expose the cooling passages. The aluminum was well protected and free of deposits or pits. The surface color varied from near metallic to brown and black. The bottom portion was darker, particularly near the exhaust valves. The heater core was sectioned and the aluminum was metallic and well protected. The cast iron block was well protected and free of deposits. The water pump had a cast iron body and steel impeller. It was well protected and not expected to show distress. White deposits were observed at the weep hole. The plastic pressurized overflow bottle yellowed in the area of hot coolant contact but was otherwise unchanged.

Coolant chemistry is plotted in Fig. 6. The organic acid concentration is virtually unchanged over the test as has been well reported earlier [*12,15*]. The tolytriazole depletes substantially, and the pH drops nearly two units. Aluminum cannot be found in solution to a resolution of 2 ppm. Although the engine was well protected for the duration of the test, it is clear that the nondepleting organic acid was of little use in protecting new ferrous metal coupons once the pH dropped. Conversely the depletion of tolytriazole had no impact on the ability to protect new yellow metal coupons.

Corrosion coupon weight losses for the American coolant are shown in Fig. 7. Yellow metals passivate slowly initially but all metals are well protected over the duration of the test. Cast aluminum had only weight gains. Cast iron losses begin to grow over the test, approaching 30 mg after 3000 h or approximately 250 000 equivalent miles (402 325 km). The test was terminated when a cooling system hose failed. The aluminum head was sectioned and evaluated.

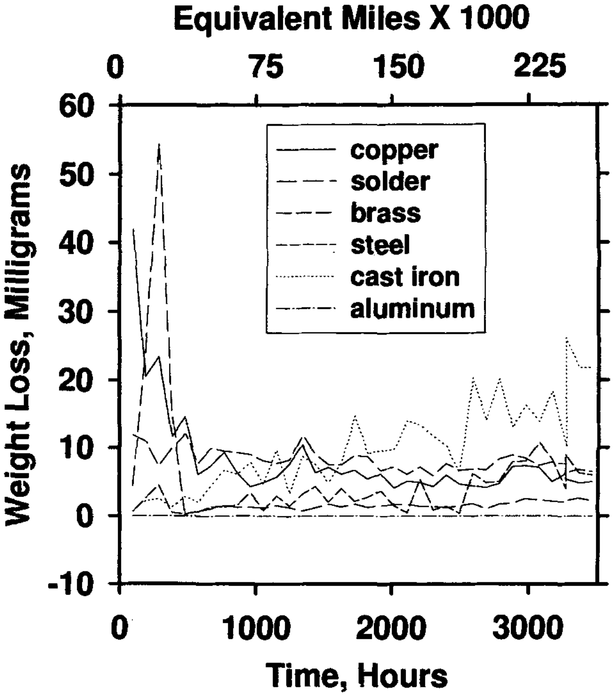

FIG. 7—*Corrosion coupon weight losses—U.S. coolant.*

It was metallic, well protected and had a small number of dark pits or casting voids distributed over the surface. The cast iron block was well protected and free of deposits. The aluminum radiator and heater core were metallic and free of deposits.

The coolant chémistry is plotted in Fig. 8 for this test. The silicate drops quickly to 40% and then decreases slowly for the remainder of the test. It is reported [*4*,*9*] that the silicate makes a thin, protective layer initially on aluminum and that a lesser amount remains in solution to repair the film. Poorly stabilized silicate coolants deplete rapidly and completely in this test and fail by aluminum transport deposition [*4*]. Barring a corrosion event or mechanical failure, such deposition could have been the endpoint for even this test on a well stabilized coolant, but by extrapolation of silicate depletion alone perhaps after 900 to 1200 additional hours.

Figure 9 shows the coupon weight loss results for the extended dynamometer test on the European silicate hybrid coolant. As in the last example, yellow metals are observed to passivate slowly. All cooling system metals are well protected for the duration of the test. Cast iron coupons showed increased weight losses after 4000 h. Unfortunately, the test was lost due to an externally failed radiator draincock. The coolant was able to passivate new coupons for 4896 h or 367 200 equivalent miles (590 935 km). The radiator and heater core were well protected. The cast iron block was free of corrosion or deposits. The aluminum head was sectioned. The top was light tan in color and free of pits. The bottom half was similar to the top but had a distribution of shallow pits over the surface. The aluminum had darkened in regions near the exhaust valves.

The pH remained relatively constant over the duration of the test as shown in Fig. 10. The silicate depleted and leveled off similar to the previous example. No aluminum was found in solution despite the presence of pits in the head. Figure 11 shows the behavior of nitrate and

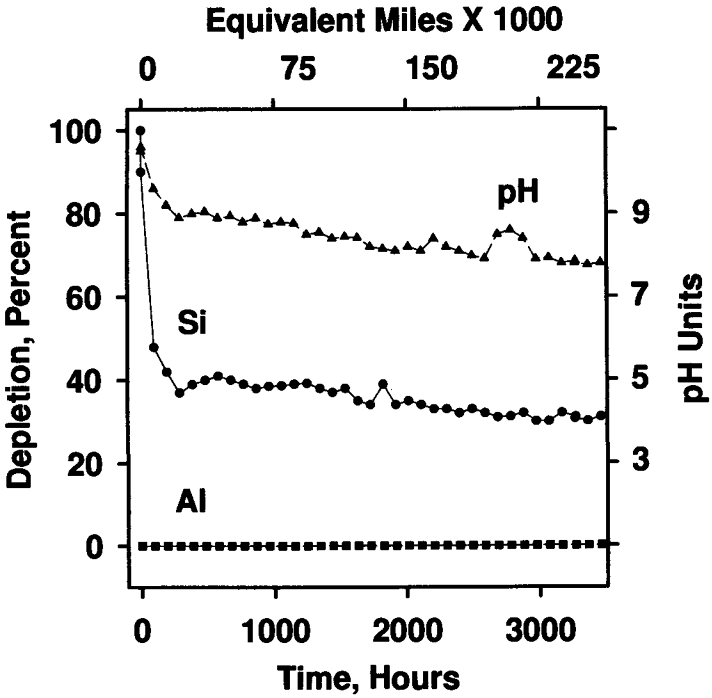

FIG. 8—*Coolant chemistry plot.*

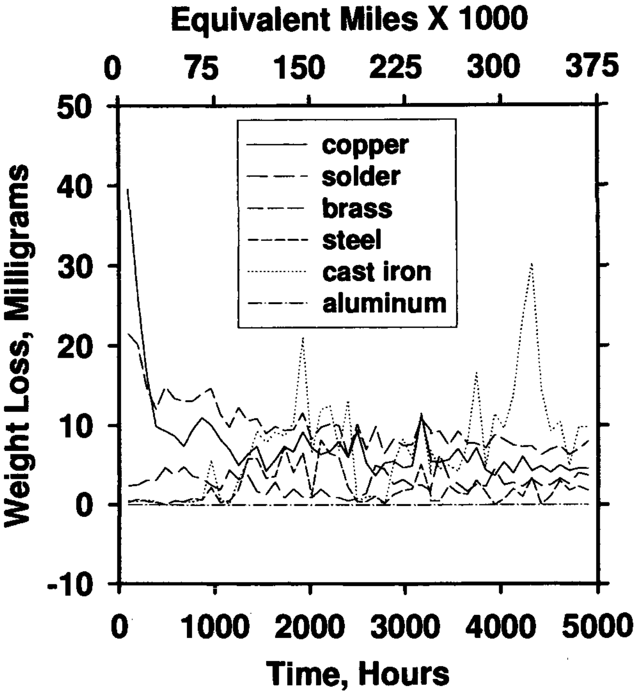

FIG. 9—*Coupon weight loss results—European coolant.*

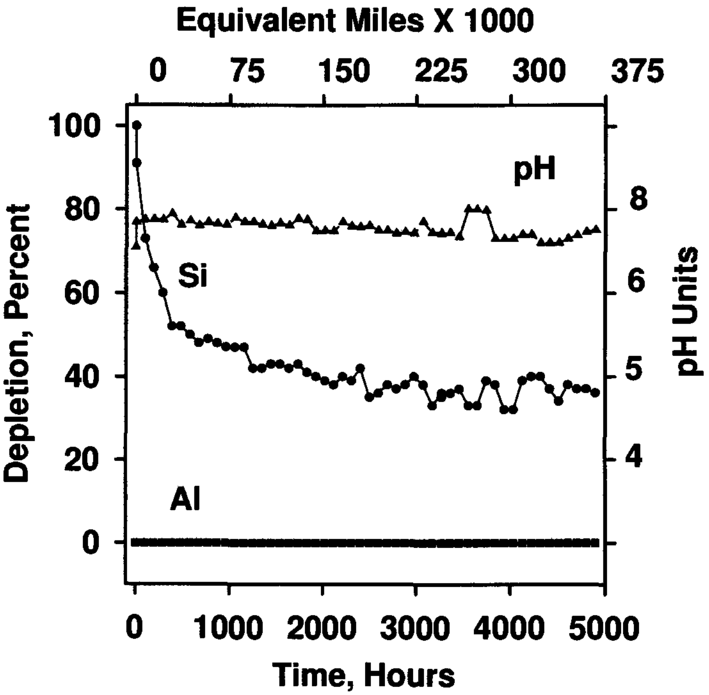

FIG. 10—*pH duration.*

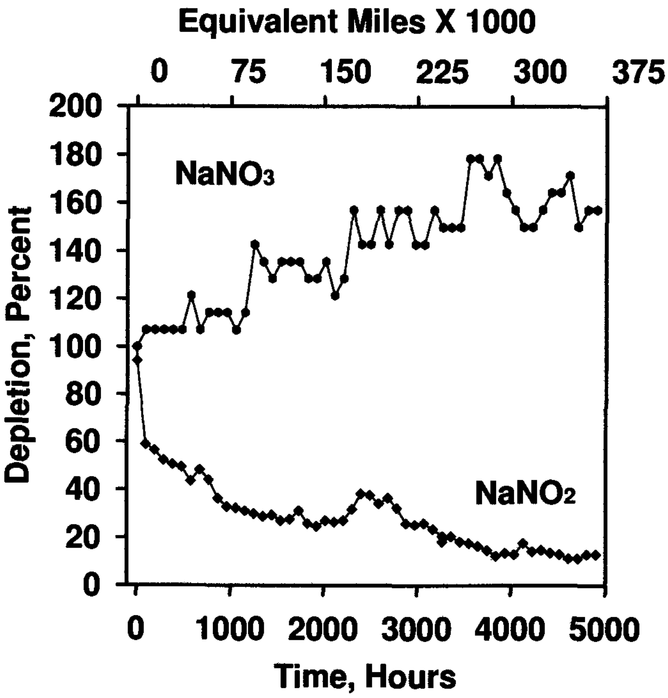

FIG. 11—*Nitrate and nitrite behavior.*

nitrite over the duration of the test. Nitrite is oxidized to nitrate and thereby depleted. The nitrate concentration increases correspondingly.

It was not possible to determine how an engine fails with a well stabilized silicate engine coolant in these tests. At high mileage, it was shown that localized corrosion can occur despite the ability to passivate new coupons. It is not clear that changing the coolant would stop such a localized attack once it commences. It is likely that such an attack could lead to perforation or aluminum transport deposition at much higher mileage. As a practical matter, the mileage at which this may occur is well beyond the useful life of the host vehicle. All the coolants tested are capable of far exceeding conventional coolant change recommendations of 30 000 to 50 000 miles (48 279 to 80 465 km). The nondepleting acid coolant was the shortest lived in terms of the ability to passivate fresh metal coupons. Even so, in an all aluminum system, the acid coolant lifetime might be extended dramatically.

Vehicle Service Tests

Twenty-four Chrysler vans with the 5.9 L (360 in.^{3}) engine were tested in the Colorado Rocky Mountains. Half the vans had a traditional low silicate coolant while the other half were filled with an organic acid coolant containing no inorganic components. Both coolants meet ASTM D 3306, D 4985 and pass the standard Ford dynamometer test. The vehicles are used to transfer skiers between Denver International Airport and Vale, Colorado. The trip is 110 miles (177 km) each way. The driving is mixed with highway and city inputs, however, idling in traffic is common. The vans operate 18 h per day on and 6 h off, seven days a week. In three weeks, it is possible to accumulate 8000 miles (12 874 km). Vans completing the test accumulated 100 000 miles (160 930 km) in one year. Of the OAT vans, seven completed the test uncontaminated, two finished prematurely in an uncontaminated state. For the silicate containing vans, six completed the test uncontaminated while two finished prematurely uncontaminated.

Engines used in the test were either new or rebuilt. Cooling systems were flushed and cleaned with a chelator type cleaner prior to test fluid introduction. The radiators and heater cores had approximately 25 000 miles (40 232 km) at test inception. Water pumps and timing covers were replaced. The test coolant was mixed 50% with tap water. Corrosion coupons were placed in the heater circuit per the ASTM Test Method for Engine Coolants by Engine Dynamometer (D 2758-94). Solid coupons were used for solder. A gallon of prediluted top off coolant was placed in each vehicle and care was taken to keep each vehicle properly topped off. Maintenance logs were kept for all vehicle repairs and concerns. Coolant samples of 2 to 4 oz (56.7 to 113.4 g) were taken at 8000 miles (12 874 km) intervals. Engines were removed, destructively evaluated and photographed at test end. One-gallon (3.78 L) retainer samples were taken from each test vehicle and evaluated by the ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384-96) and D 4340.

The corrosion coupon results for uncontaminated vehicles are shown in Tables 4A and B. Weight losses are shown in mg per coupon, a negative weight loss is a weight gain. The silicate coolant protected all cooling system metals to within the ASTM Test Method for Simulated Service Corrosion Testing of Engine Coolants (D 2570-96) limits for D 3306. There was little difference between high lead and standard solder.

The organic acid coolant did not protect ferrous metals and solder as well as the silicate coolant; however, yellow metals and aluminum were well protected. The large losses on Modine solder are unexpected as the coolant gave minimal losses in ASTM D 1384 and D 2570 laboratory testing. Noticeably larger losses on steel and cast iron were also not suggested by earlier testing. It follows that effects of flow and thermal cycling impact the acid coolant more. This is consistent with the slower passivation conclusion for organic acids from the heat-rejecting

TABLE 4—*Corrosion coupon results from vehicle service.*
(A) Silicated Coolant.

	Aluminum	Cast Iron	Mild Steel	Brass	Solder 70/30	Modine	Copper
Mean	−7.13	1.25	−0.13	13.5	25.80	26.67	10.38
Std. Dev.	11.37	10.51	1.73	5.42	23.93	38.90	3.58
Min.	−34	−8	−3	9	3	−18	7
Max.	2	22	3	26	60	52	18
Size	8	8	8	8	3	5	8

(B) OAT Coolant.

	Aluminum	Cast Iron	Mild Steel	Brass	Modine	Copper
Mean	−1.60	12.40	17.80	10.20	1071.60	0.80
Std. Dev.	33.35	14.20	38.13	3.70	774.53	4.09
Min.	−60	−1	0	6	155	−6
Max.	23	30	86	16	1720	4
Size	5	5	5	5	5	5

aluminum electrochemical test. Results for ASTM D 1384 testing of fluid drained from representative vehicles is shown in Table 5. Results are in weight loss of mg per coupon. Samples were adjusted to standard 33% dilution with ASTM corrosive water.

The aluminum protection suggested by these results was confirmed with ASTM D 4340 tests. Both coolants passed the test at 50% and standard 25% dilution following 100 000 miles (160 930 km) of service. The overall results for the OAT coolant are similar to new fluid yet not representative of actual vehicle service coupon results. The silicate coolant results are within the range of variation for vehicle service data except for the cast iron result which may be explained by the additional dilution. Therefore, the glassware test may better discriminate silicate technology. OAT coolant results do not correlate well with the field data in a false positive manner for solder and ferrous metals.

Chemistry from an uncontaminated OAT coolant test van is shown in Fig. 12. The results closely parallel the engine dynamometer chemistry of Fig. 6. The acid is essentially nondepleting, and the pH changes slowly over the test. The tolytriazole depletes to 40%, and no aluminum is found in solution. Similar information for a silicate coolant test van is given in Fig. 13. The behavior is similar to the engine dynamometer results of Fig. 8 for a silicate

TABLE 5—*Post fleet test laboratory testing.*

Specimen	Silicate Coolant	OAT Coolant
Copper	2	4
70/30 solder	3	3
Modine solder	43	4
Brass	1	2
Steel	1	2
Cast iron	35	3
Cast aluminum	0	0

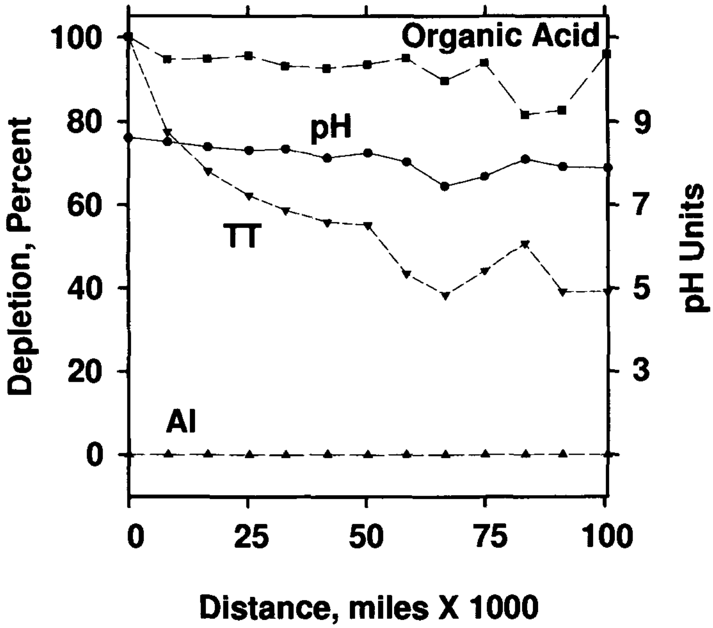

FIG. 12—*Chemistry from uncontaminated OAT coolant test van.*

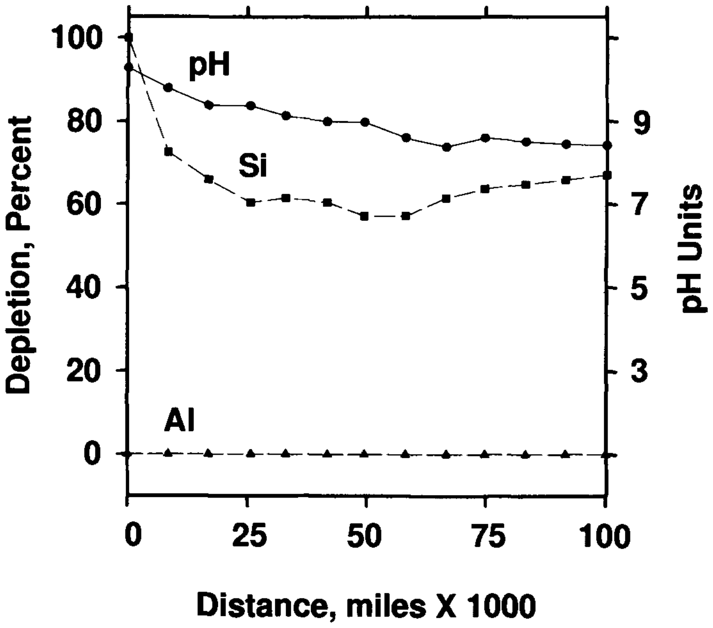

FIG. 13—*Chemistry from silicate coolant test van.*

FIG. 14—*Aluminum water pump protected by silicate coolant.*

coolant. The silicate drops rapidly initially and levels off at approximately 60%. The pH decreases slowly over the test, and no aluminum is found in solution.

Destructive evaluation of the engines and cooling system components following the test revealed that cast iron cylinder heads and blocks were well protected with each coolant. The acid coolant left a gray film on components as has been reported earlier [9]. The silicate engines were more metallic in appearance. The brass radiators and heater cores were also well protected with each coolant, and a dark film was noted on the headers in many cases. Thermostats, radiator caps and coolant overflow bottles were recovered in good condition. Aluminum water pumps were protected by the silicate coolant as shown by a representative example in Fig. 14. The steel impeller shows some cavitation damage in Fig. 15 but the aluminum alloy UNS A05140 body is well protected and retains the original casting marks. The timing cover was similarly well protected, and the weep hole was typically clear.

A water pump from an uncontaminated organic acid test van is shown in Fig. 16. The impellers resembled Fig. 15 but the aluminum body was distressed by cavitation erosion-corrosion. All acid coolant pumps examined looked similar with lesser corrosion on the timing

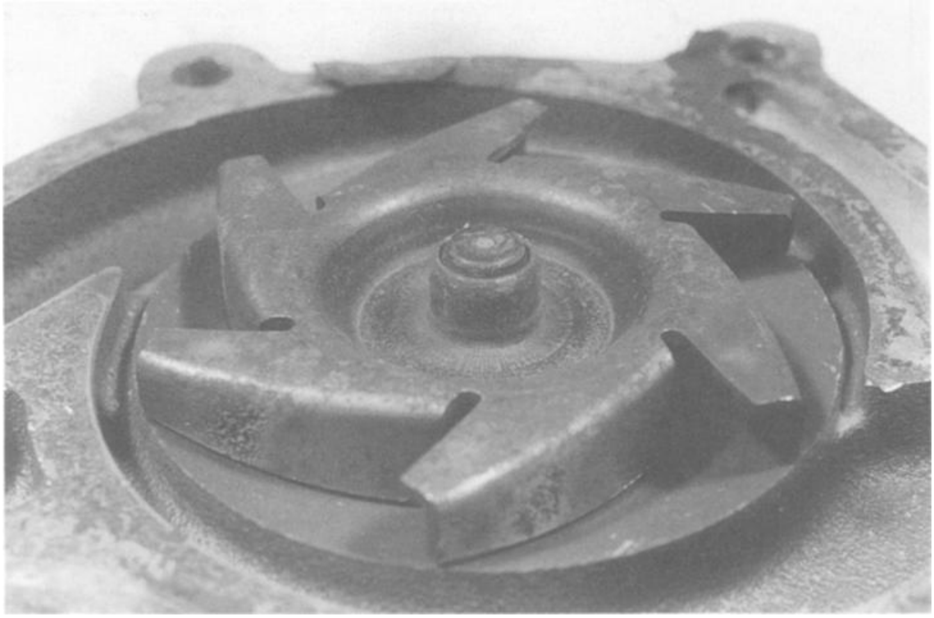

FIG. 15—*Cavitation damage to steel impeller.*

cover. Vehicles examined at 50 000 miles (80 465 km) had roughly half the damage of pumps from vehicles completing the test. This suggests that changing the coolant will have no beneficial effect. A high mileage silicate-contaminated vehicle showed relatively limited damage consistent with protection after silicate coolant introduction. No pump perforations were obtained. Parts were sectioned and pit depth was measured. It varied considerably but was less than one-third total wall thickness at maximum. No water pumps were lost due to seal leakage with either coolant. All vehicles operated normally throughout the fleet test with no overheating.

Overall, both test coolants gave a long and uneventful service life. It is concluded that the acid coolant has less ability to passivate aluminum under cavitation conditions than the silicate coolant. This is consistent with the electrochemical heat-rejecting aluminum test. If acid coolants passivate slowly, as suggested by the test, then corrosion phenomena acting on a faster time scale than the passivation mechanism will preclude passivation. Such fast corrosion mechanisms also could include abrasion from core sand, debris or rapid flow. That this may have occurred is suggested by the high lead corrosion coupon data.

ASTM test data showing diminished cavitation protection with acid coolants have been reported [*8*]. No previous field confirmation of this has been reported. It has also been reported that OAT coolants have superior performance to silicate coolants in the ASTM Test Method for Cavitation Corrosion and Erosion-Corrosion Characteristics of Aluminum Pumps with Engine Coolants (D 2809-94) [*15*]. Both coolants in this investigation pass the D 2809 test and show minimal damage after 1000 h. In discussions at ASTM Committee D15 it has been suggested that this test is too severe because acid coolants that fail the test give good field results. In this vehicle service test, the opposite was found. Good results in the D 2809 test do not guarantee acceptable field performance.

Scanning electron microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDS) and a thin window detector was used to characterize the corrosion morphology. Several water pumps were sectioned and the aluminum body in the region near the impeller examined at

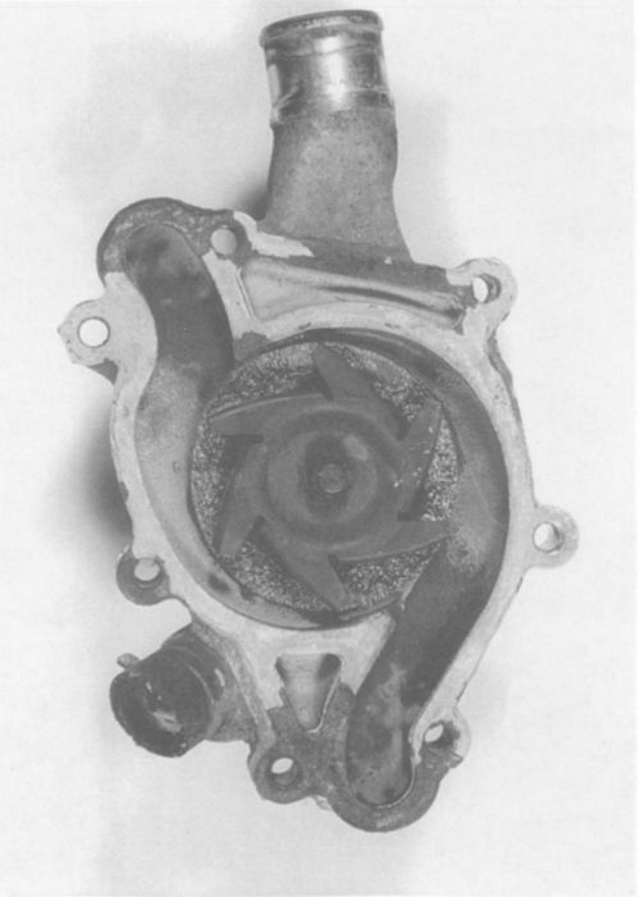

FIG. 16—*Water pump from uncontaminated organic acid test van.*

various magnifications ranging from ×18 to ×760. Figure 17 shows an aluminum section from a completed silicate coolant vehicle at ×18 (reduced by 15% to fit). The metal is well protected, and casting ridges are visible. Dark regions are surface contamination.

Figure 18 shows an aluminum section from an OAT coolant test van at ×7 by optical microscopy (reduced by 15% to fit). The round damaged areas from energetic bubble implosion are clearly visible. A white deposit is also visible on the surface. Pits were observed to lead to secondary and tertiary pits underneath. Figure 19 shows the same sample at ×740 by SEM (reduced by 15% to fit). Three surface phases were identified by EDS. The aluminum surface appeared as if etched, with grain boundaries readily visible. Long iron rich spicules were found, a silicon rich phase at the grain boundary and a silicon depleted phase within the grain boundary. The silicon depleted phase often was observed to be cracked as shown in Fig. 19. Corrosion seems to proceed through material removal within the grain boundary by cracking. The silicon rich boundary areas and the iron rich areas seem resistant to removal. This leads to the ragged skeletal appearance of the macro-corroded part. Specimens from three OAT test vehicles were examined and found to be very similar. The cracks suggest that physical force is applied, and evidence of subsequent smoothing or wear exists. Both are consistent with cavitation erosion-

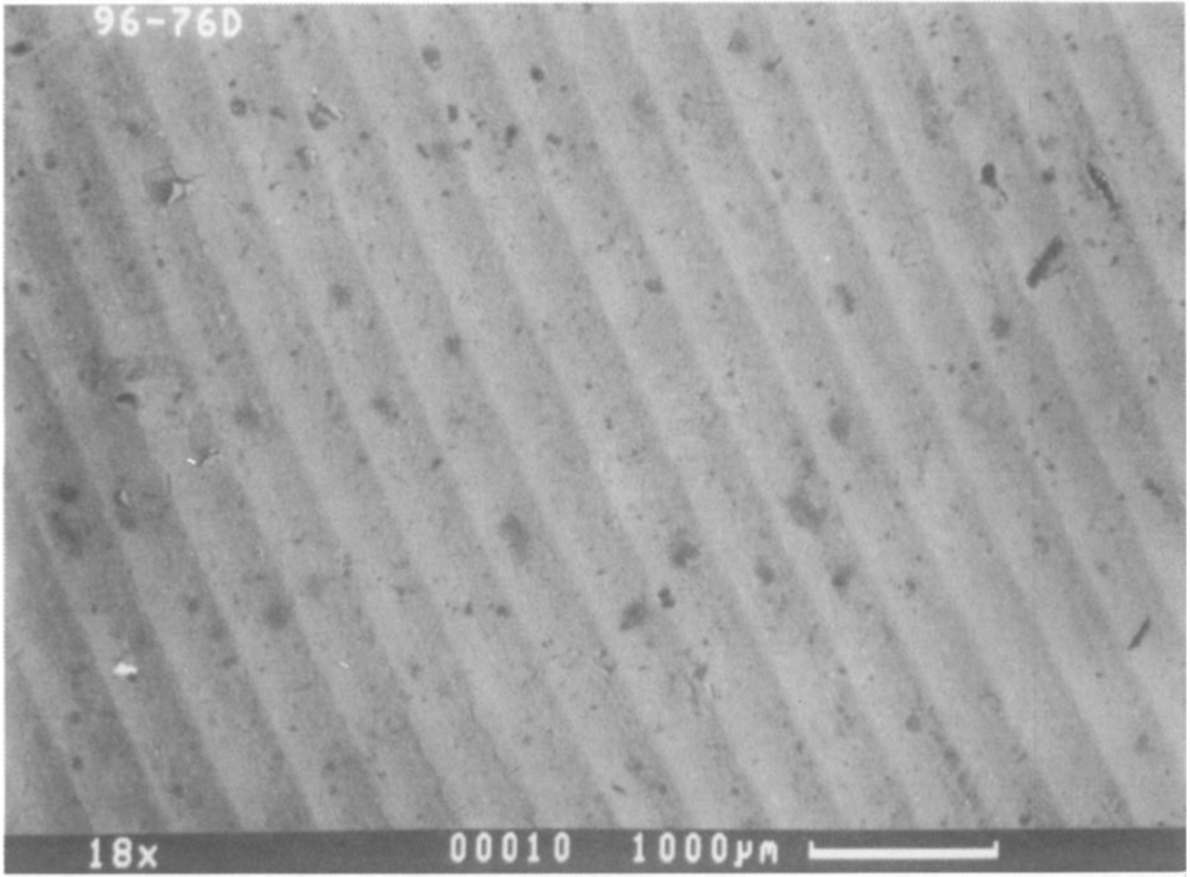

FIG. 17—*Aluminum section from silicate coolant vehicle (reduced by 15% to fit).*

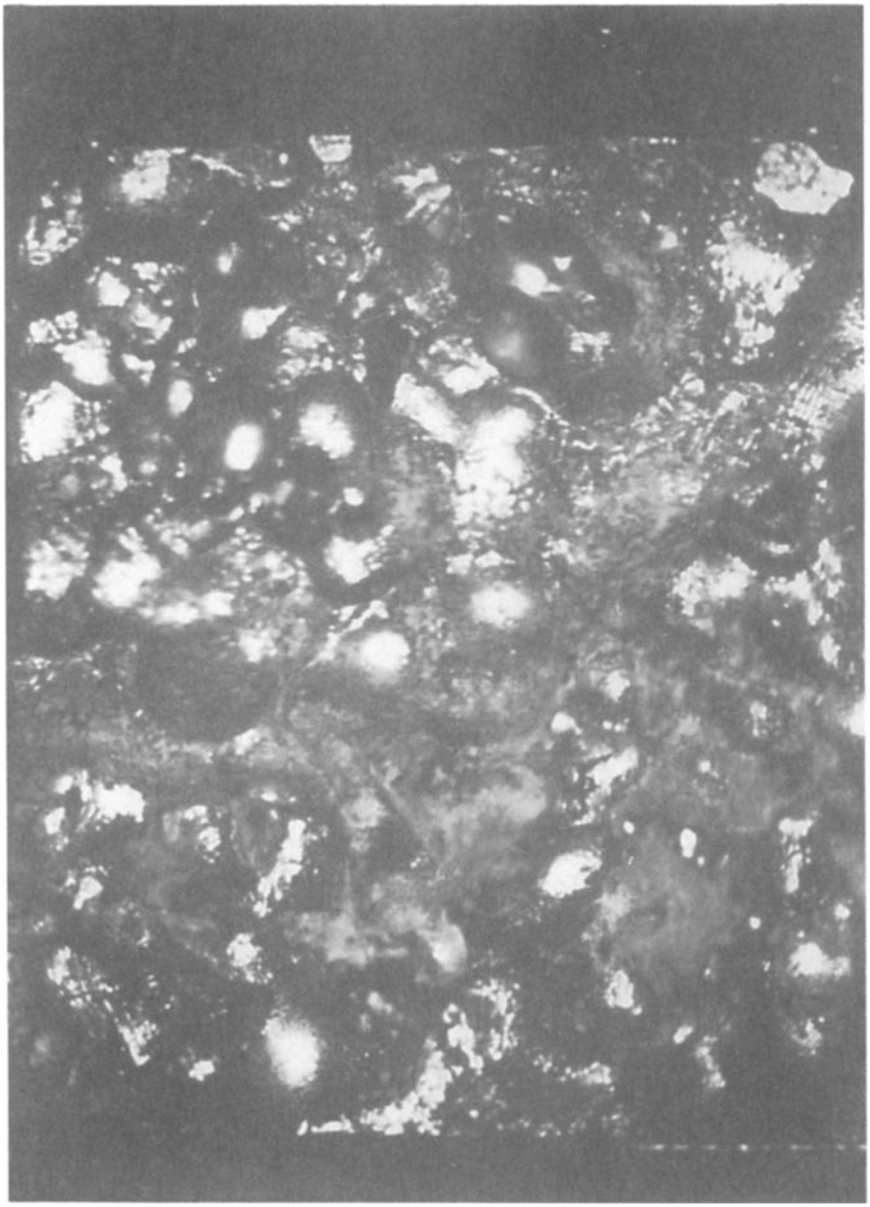

FIG. 18—*Aluminum section from OAT coolant test van (reduced by 15% to fit).*

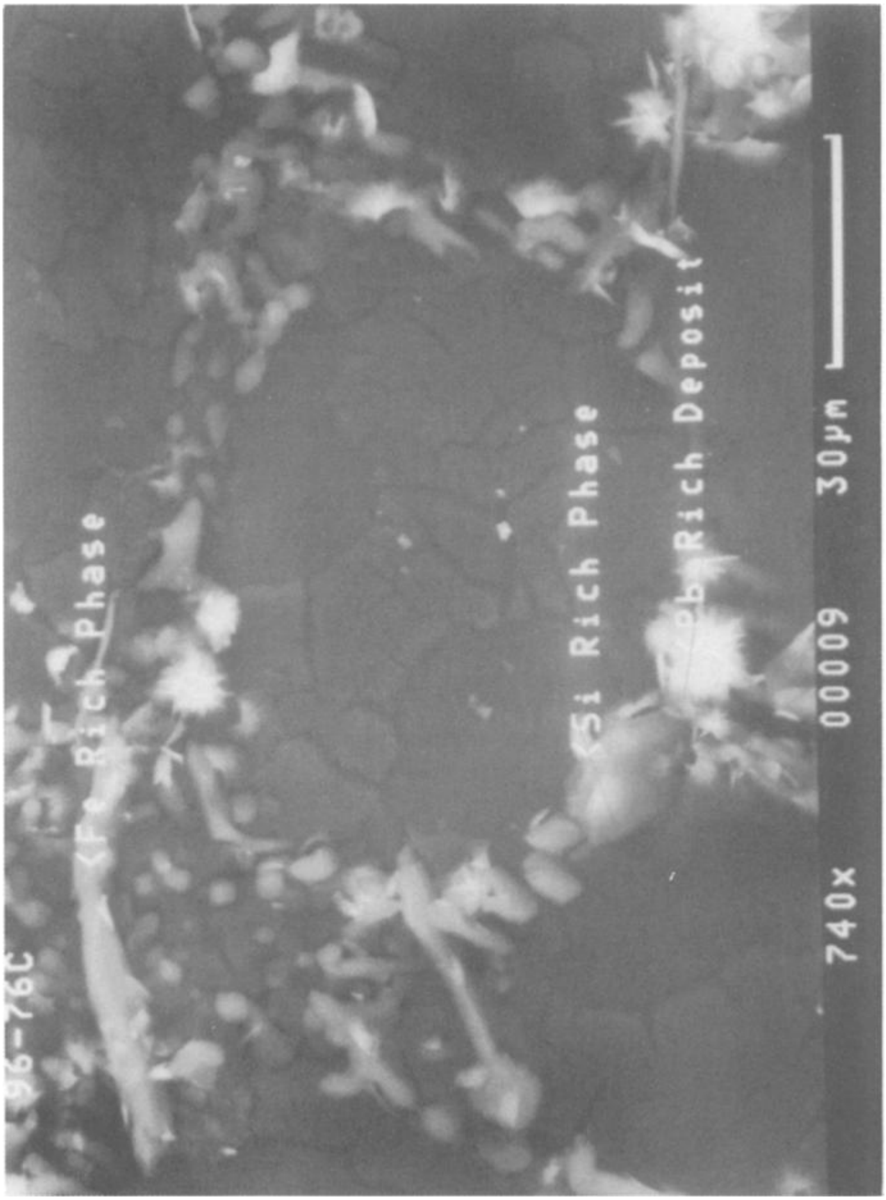

FIG. 19—*Same section as Fig. 18 at ×740 (reduced by 15% to fit).*

corrosion and not galvanic or deposition related phenomena. The fact that silicon- and iron-rich areas are not removed easily is probably due to physical differences like hardness and not due to inhibition by the coolant.

The possibility of silicon depletion from inner grain boundary regions leading to the fracture and material removal cannot be dismissed. It suggests a mechanism for silicate coolant protection. An "as-tested" water pump metal sample from a silicate test van was too rough for high resolution microscopic grain boundary investigation. Work continues in this area.

Conclusions

It has been shown that a silicate coolant passivated aluminum more quickly than an organic acid coolant. This likely accounts for differences in performance under fast conditions such as cavitation erosion-corrosion. Both well-stabilized silicate and nonsilicate coolants give passing results under dynamic high heat flow aluminum corrosion testing. A poorly stabilized silicate coolant was shown to give the poor results previously reported for all silicate coolants. Confirmation of these results has been recently reported [*28*]. Engine dynamometer testing demonstrated that both silicate, hybrid and OAT coolants can give extended change intervals. However, the silicate technology probably is the longest lived in terms of formulation stability as given by the ability to passivate new corrosion coupons. Coolant chemistry was observed to deplete for all coolants studied. The nondepleting nature of organic acids showed no real performance benefit in dynamometer and fleet tests. The partial depletion of other components in several formulations caused no measurable detriment in the same tests.

Vehicle service testing resulted in silicate and OAT coolants that operationally performed equivalently over 100 000 miles (160 930 km). The cavitation protection was less with the OAT coolant. Scanning electron microscopy was used to explore the cavitation corrosion-erosion morphology and mechanism. ASTM bench tests did not correlate well with the OAT coolant field performance. This indicates the importance of adequate fleet testing and destructive post-test component evaluation to coolant development work.

In conclusion, long-lived, quality engine coolants can be formulated with silicate, hybrid and nonsilicate technology. The minimal chemistry of OAT coolant is useful in meeting the chemical limitations of global specifications. Coolant technology applications should be consistent with known performance parameters. Work continues on alternative technologies for aluminum corrosion protection [*29,30*].

Acknowledgments

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Copper-Triazole Interaction and Coolant Inhibitor Depletion

REFERENCE: Bartley, L. S., Fritz, P. O., Pellet, R. J., Taylor, S. A., and Van de Ven, P., "**Copper-Triazole Interaction and Coolant Inhibitor Depletion,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335,* R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 76–85.

ABSTRACT: To a large extent, the depletion of tolyltriazole (TTZ) observed in several field tests may be attributed to the formation of a protective copper-triazole layer. Laboratory aging studies, shown to correlate with field experience, reveal that copper-TTZ layer formation depletes coolant TTZ levels in a fashion analogous to changes observed in the field. XPS and TPD-MS characterization of the complex formed indicates a strong chemical bond between copper and the adsorbed TTZ which can be desorbed thermally only at elevated temperatures. Electrochemical polarization experiments indicate that the layer provides good copper protection even when TTZ is absent from the coolant phase. Examination of copper cooling system components obtained after extensive field use reveals the presence of a similar protective layer.

KEYWORDS: automotive coolants, corrosion inhibitors, inhibitor depletion, aging simulation

A major factor affecting the routine maintenance and useful life of coolants in automotive applications is corrosion inhibitor depletion. Inhibitors, added to prevent corrosion of cooling system components, must be present at or above minimal levels in order to provide protection. While initial levels in commercially available coolant products are designed to meet these requirements, inhibitors will typically deplete in use. Inhibitor depletion can be caused by decomposition. Alternatively, an inhibitor may be consumed in the process of creating a protective layer on cooling system components thus blocking attack of corrosive agents [*1*,*2*].

Triazole containing compounds such as tolyltriazole and benzotriazole are widely used corrosion inhibitors [*3*]. When added to coolants in sufficient quantity, they prevent or retard the corrosion of copper and brass. Several papers describe the protective effect of triazoles on copper for corrosion protection. Cotton [*4*] proposed the formation of a polymeric material on copper surface exposed to benzotriazole. Electrochemical studies indicated repression of anodic reactions after benzotriazole treatment. Subsequent studies [*5*] showed that the layer thickness increased with increasing pretreatment temperature and that protection increased with increasing film thickness as these films became more compact and less permeable. More recently, studies [*6*] of tolyltriazole protection of copper systems have revealed the formation of a stable monolayer of tolyltriazole on copper attributed with a strong corrosion protection effect. This monolayer formation involved the direct reaction of TTZ with metallic copper.

While highly effective at levels initially present in fresh coolants, triazoles, like many other inhibitors deplete in actual automotive use. Their depletion in automotive applications has been noted [*7*,*8*]. In these fleet tests, tolyltriazole levels were observed to drop to as low as 40% of

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their initial levels after only 80 000 miles (128 744 km) of vehicle use. Tolyltriazole has also been observed to deplete in heavy duty application [9]. Here, on average TTZ levels dropped to 40% of initial levels after 125 000 miles (201 162 km) use. The depletion rate depended on engine platform. The mechanism by which triazoles deplete from the cooling system has not been established.

In the present study, coolant aging was simulated in bench experiments to determine factors affecting tolyltriazole depletion. Aging was simulated by exposing coolants to high surface area metal powders. Aged coolants were analyzed for inhibitor depletion. Metal powders and corresponding metal electrodes, treated with coolant in the simulations were characterized by X-ray photoelectron spectroscopy, by temperature programmed desorption/mass spectrometry and by cyclic polarization. Based on results, a mechanism for depletion is proposed.

Experimental

Coolant Aging Simulations

Aging tests were conducted in appropriately sized glassware equipped with condenser, thermocouple, motor driven stirring paddle and nitrogen purge line. In a typical experiment, a glass flask was filled with 500 cm^3 of Havoline Extended Life Coolant, 1000 cm^3 of corrosive water (as per ASTM Standard Test Method for Corrosion Test for Engine Coolants in Glassware, D 1384) and 28 g of finely powdered metal particles (200+ mesh). Havoline Extended Life Coolant is a carboxylic acid-based coolant available commercially from Texaco Lubricants Company. Before beginning, the reaction system was stirred and purged with nitrogen then heated to reflux (about 105°C under atmospheric pressure). Coolant samples were withdrawn periodically and analyzed for tolyltriazole and for their carboxylate content.

Cyclic Polarization Experiments

Copper electrodes (1 cm^2 area) were either aged in coolant under conditions described previously or were freshly polished prior to cyclic polarization experiments. Those electrodes aged in coolant were washed with deionized water but given no additional treatment prior to electrochemical studies. Untreated electrodes were freshly polished prior to use. All electrodes are allowed to equilibrate in the appropriate test solution prior to the polarization scan. For the aged copper electrodes the test solutions consisted of corrosive water (as per ASTM D 1384) diluted to 33% concentration. For fresh copper electrodes, the test solution consisted of 2000 ppm tolyltriazole dissolved in ASTM corrosive water, diluted to 33% with deionized water. Once equilibrated, the electrode was polarized to increasingly anodic potentials at a scan rate of 1 mV/s until rupture potential was attained. At the rupture potential, a rapid increase in the polarization current was observed to occur as the protective layer on the electrode broke down. After rupture, and when the current reached a predetermined maximum value, the scanning direction was reversed toward more cathodic potentials. A repassivation potential was often observed on the reverse scan at the point where the polarization loop closed. Typical parameters obtained from the polarization scan included the open circuit potential, the rupture potential, the repassivation potential, and the passivation current (that is, the current that permeates an electrodes coating at potentials below the rupture potential). Polarization analysis has been shown to correlate with corrosion phenomena in the field [*10*].

X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed on a VG Instruments ESCALAB 5, Mkl system. XPS data were collected with Mg k-a X-rays at 300 W. Samples were prepared for XPS analysis by mounting on powder sample stubs as a parallel array with silver paint. The samples were oriented parallel to the X-ray beam in order to eliminate beam shadowing. Photoelectron binding energies were referenced to adventitious carbon at 284.7 eV.

Gas Chromatography/Mass Spectrometry (GCMS)

A direct insertion probe was loaded with metal powders obtained following aging simulation tests. Powders were washed extensively and dried prior to analysis to remove coolant from the aging study. The probe was inserted into the high vacuum (10^{-10} atmospheres) ionization region of the mass spectrometer and heated slowly to identify any evolved semi-volatiles.

Fleet Data

Fleet test data used in this report have been previously described elsewhere [*8*]. In general data were obtained from over 100 General Motor's cars and light-duty trucks with varying engine sizes, block and head materials, and radiator types.

Results and Discussion

In order to simulate and accelerate the effects of typical cooling system components on the depletion of a coolant's corrosion inhibitors, Havoline Extended Life Coolant/Antifreeze (HELAC), an organic acid technology containing tolyltriazole, was refluxed in the presence of finely powdered cooling system elements such as copper, aluminum or iron. Samples of coolant were routinely withdrawn from the refluxing mixture and analyzed for inhibitor contents and for the presence of corrosion products. Results obtained from this simulated aging study are exemplified by data presented in Fig. 1. Here the relative concentration of the coolant's organic

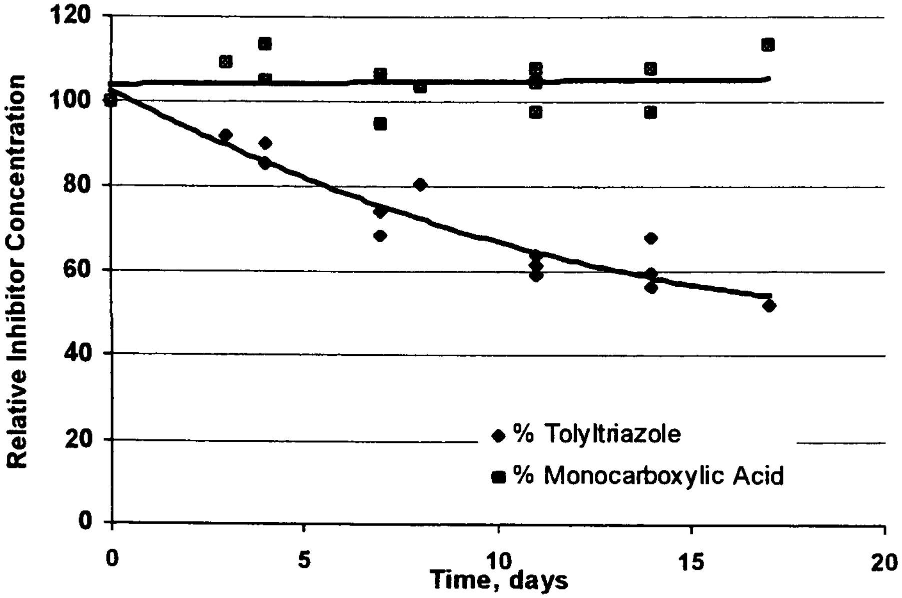


FIG. 1—*Coolant aging simulation with HELAC.*

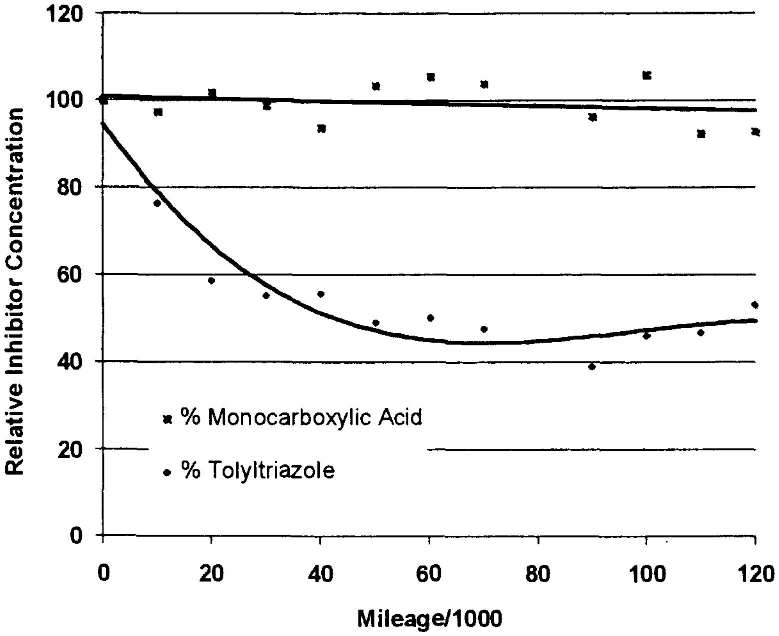


FIG. 2—*Fleet testing with HELAC.*

acid and tolyltriazole (TTZ) are plotted as a function of treatment time. The data were collected over a 2 week test period during which time the TTZ content was observed to decrease by 50% while little change was noted in the coolant's carboxylate content. For comparison purposes, average inhibitor concentrations obtained from a fleet test using HELAC are presented in Fig. 2. The fleet test from which these data were obtained has been previously described [*8*]. From the figure we see that TTZ depletes to about 40% of its initial value after 80 000 miles (128 744 km) of service while the carboxylate content remains relatively unchanged.

Another example of the aging simulation is presented in Fig. 3. The figure explores the effect of mercaptobenzothiazole (MBT) addition to HELAC on its tolyltriazole depletion. Data obtained with MBT-free Havoline are also plotted for comparison purposes. As seen from the figure, the addition of MBT very significantly retards TTZ depletion relative to the MBT free coolant. TTZ depletion from a commercial MBT containing coolant (GM6043) has been monitored in the same fleet evaluation described previously. Results of that evaluation are provided in Fig. 4. Over the course of the 70 000 mile (112 651 km) evaluation, TTZ levels remain within 80% of their initial values. MBT analyses of fleet and simulation samples (not shown) indicate that in both cases MBT depletion is quite rapid. The good correlation observed between the simulation and the actual fleet experience strongly suggests that factors causing tolyltriazole depletion are similar in both evaluations.

As mentioned previously, the depletion of tolyltriazole could conceivably be due to decomposition or to its consumption in the formation of a protective layer on copper containing components in the fleet or on the copper powder in the simulation. Tests were conducted using the simulation to provide insight into factors affecting tolyltriazole depletion observed in the field. Simulation experiments were repeated using HELAC refluxed in mixture with powdered aluminum and with powdered iron. The results of these experiments are summarized in Fig. 5. Here again, tolyltriazole coolant levels are plotted against days of treatment time. From the

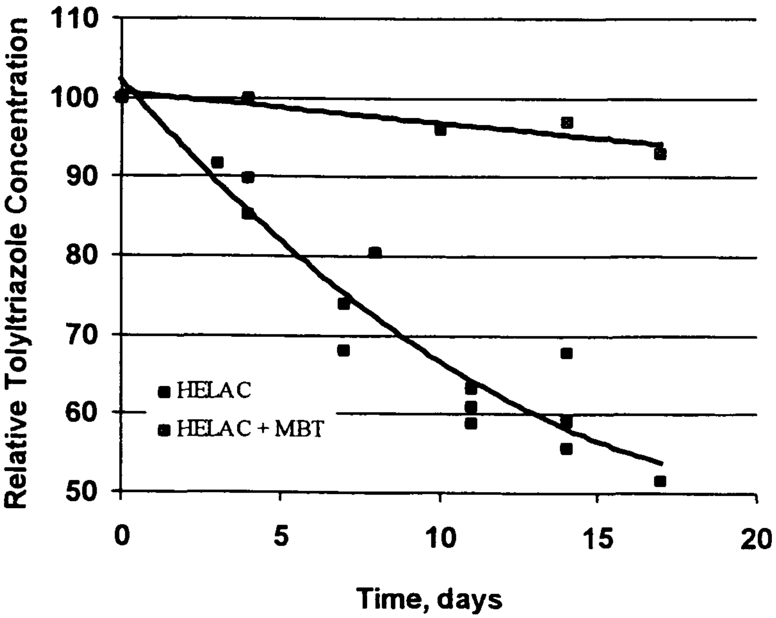
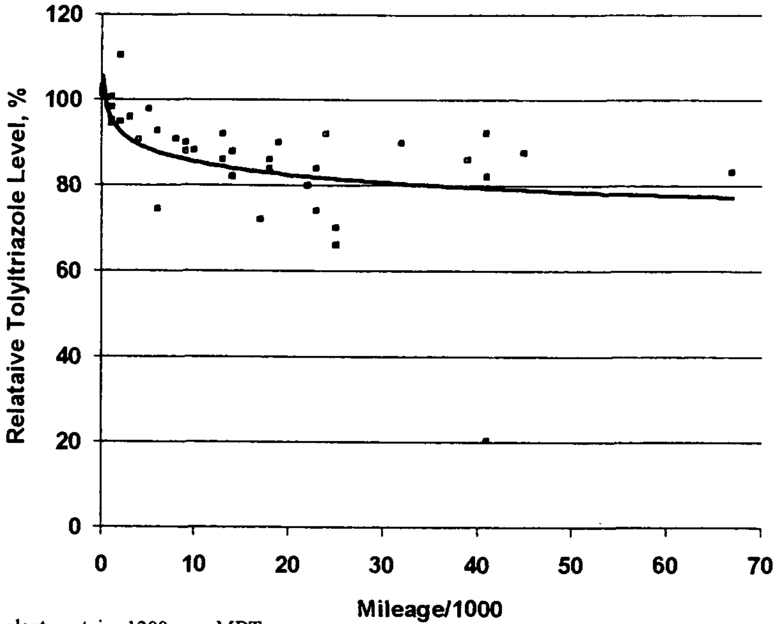


FIG. 3—*Effect of MBT on TTZ depletion: simulation.*



* Coolant contains 1200 ppm MBT

FIG. 4—*Effect of MBT on TTZ depletion: fleet data.*

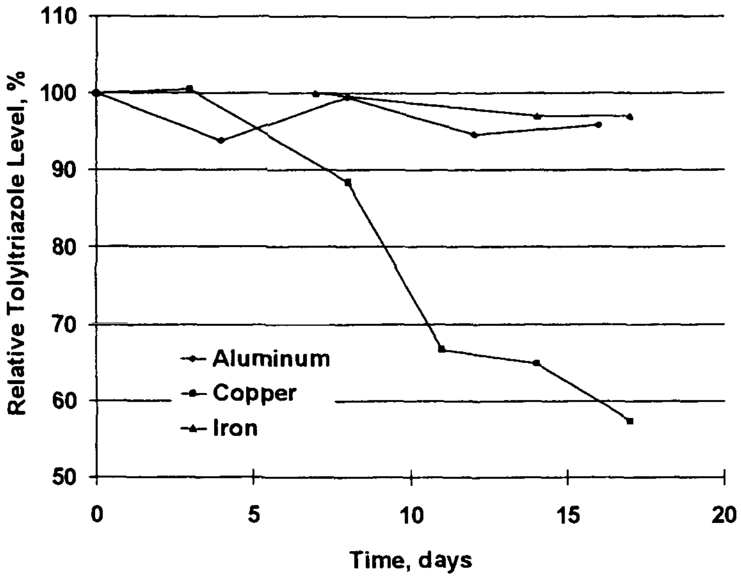


FIG. 5—*Effect of metal on TTZ depletion.*

figure, it can be seen that only the treatment with copper results in significant triazole depletion. TTZ levels remain essentially at their initial values in the presence of either iron or aluminum over the same time period where a 50% TTZ depletion occurs in the presence of copper. The data clearly indicate a role for copper in the disappearance of tolyltriazole in the aging experiments. TTZ depletion in the presence of copper could conceivably be due to a copper catalyzed decomposition reaction or to the formation of a protective TTZ/copper layer. Analysis of the solutions obtained from the copper aging test did not indicate the presence of any compounds which could be attributed to tolyltriazole decomposition.

X-ray photoelectron spectroscopy (XPS) provides further insight. XPS was used to obtain surface analysis of the powdered metals after the simulation experiments. XPS results indicate the presence of 12.6% nitrogen on copper powder surface but only 0.5 and 0.2% nitrogen on iron and aluminum, respectively. Results obtained from high resolution XPS are provided in Table 1.

Data obtained with pure tolyltriazole are also presented as a reference. The results show a very close correspondence between the nitrogen components adsorbed on copper following the simulation experiment and with pure TTZ, suggesting that rather than decomposing, TTZ is adsorbed intact on the copper surface.

TABLE 1—*High resolution XPS analysis of TTZ and of aged copper powder.*

Surface Nitrogen Species	TTZ Reference, XPS Binding Energies	Aged Copper Powder, XPS Binding Energies
Neutral organic nitrogen	399.7	399.1
Ammonium ion nitrogen	400.7	400.0
Aromatic N, II to II* transition	406.5	406.5

The aged copper powder was also analyzed by temperature programmed desorption/mass spectroscopy. Results of this analysis are presented in Fig. 6. Here the concentrations of desorbing components (in relative units) are plotted as a function of desorption temperature. Only two major components were observed to desorb from the copper surface, the carboxylic acid, and tolyltriazole. Although normalized to the same scale in Fig. 6, the amount of tolyltriazole desorbed was about twenty times the amount of desorbed carboxylates. TTZ desorption begins at 300°C and is complete only as temperatures approach 450°C. The high temperature of desorption indicates that tolyltriazole is very strongly bound to the copper surface consistent with the formation of a chemical bond between TTZ and copper as opposed to a purely physical adsorption. The formation of a strong copper-TTZ surface complex is consistent with literature reports [*6*] which have related complex formation to the TTZ protection mechanism.

These results, coupled with the fact that no nitrogen containing decomposition products were found in samples of the aged coolant, strongly suggest that tolyltriazole depletion in the simulated aging experiments is largely due to adsorption on copper and not due to decomposition. The characterization results reported here are entirely consistent with previously published findings for this layer formation. However, in the present study, the close correlation observed between the aging simulations and actual fleet experience strongly suggests that adsorption of TTZ on copper cooling system components plays a significant role in its depletion in the field.

The TPD/MS experiments described previously suggest that the TTZ adsorbed on copper during the simulation experiments is strongly and chemically bound to the copper surface and is not merely physisorbed. Insight into the corrosion protection properties of this layer has been obtained by additional experiments. Accordingly, several freshly polished copper electrodes were immersed in refluxing HELAC and maintained in the coolant under refluxing conditions for up to three weeks. Individual electrodes were periodically removed from the refluxing solution over the three week test period, washed with deionized water to remove coolant, im-

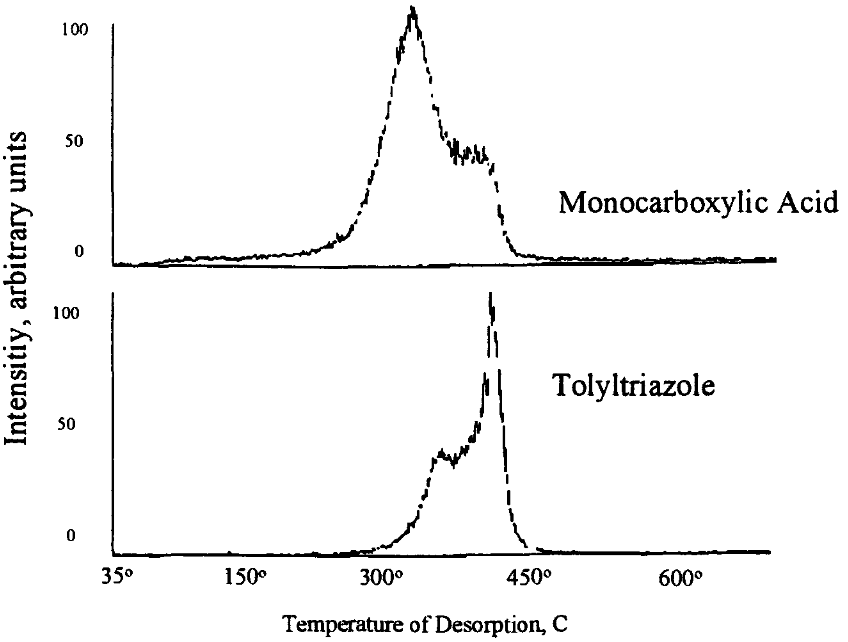


FIG. 6—*TPD/MS analysis of aged copper powder.*

mersed in ASTM corrosive water (free from any inhibitors including tolyltriazole), and analyzed by cyclic polarization. Polarization data were obtained as described in the experimental section, and results of this analysis are summarized in Fig. 7. For the purpose of comparison, a polarization scan was obtained using an untreated copper electrode immersed in an aqueous tolyltriazole solution dissolved in corrosive water. For this reference run, the toly level was adjusted to be equivalent to that of fresh Havoline Extended Life Coolant. However, unlike HELAC, all other inhibitors were omitted to emphasize copper protection afforded by TTZ.

From the figure, it can be seen that even after one day treatment in HELAC, the copper protection has increased relative to the untreated electrode. This is indicated by an increase in the open circuit potential, an even greater increase in the rupture potential and a ten-fold decrease in the passivation current. By 23 days, the protection afforded the treated electrode in TTZ-free water is nearly equivalent to that obtained in the reference scan with tolyltriazole present. Interestingly, the growth in protection in this simulation correlates with the depletion in tolyltriazole observed in the previous simulations. The combined experiments clearly show that the tolyltriazole layer formed is protective to copper.

It is noteworthy that the treated electrodes show good copper protection even in the complete absence of solution-(coolant)-phase TTZ. Results suggest that TTZ depletion observed in field use does not imply a corresponding loss of copper protection. Rather, the experiments suggest that after a protective coating is formed during the initial depletion stage, additional TTZ would only be required to replace adsorbed TTZ eroded away in use.

While laboratory experiments are suggestive, confirmation comes from examination of used copper components obtained after extensive field service. To this end a copper radiator was obtained from a field test after exposure to Havoline Extended Life Coolant/Antifreeze. The radiator was thoroughly washed with deionized water to remove used coolant and then cut to form electrodes suitable for electrochemical polarization characterization. As described previously, an electrode was immersed in corrosive water diluted to 33% with deionized water.

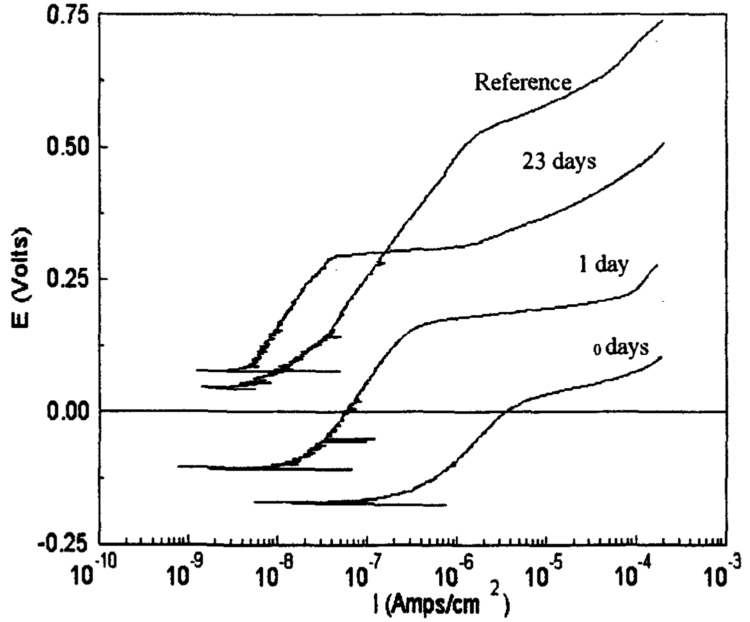
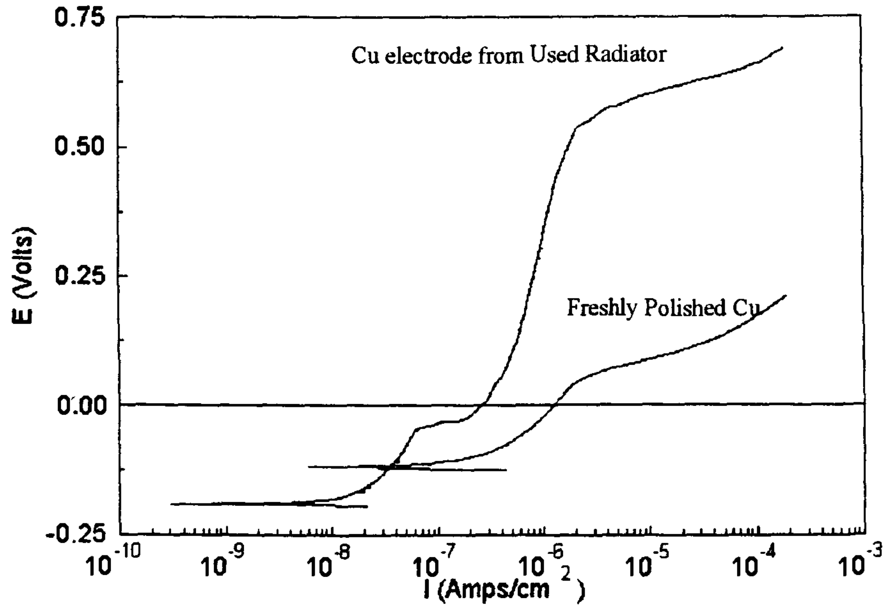


FIG. 7—*Polarization scans of copper following TTZ treatment.*



Electrodes immersed in corrosive water

FIG. 8—*Polarization scans on copper from used radiator versus fresh copper.*

Polarization scans determined the rupture potential and the passivation current for this material. Results of this examination are presented in Fig. 8. For comparison purposes, an additional electrode prepared from the radiator was given a exhaustive polish to remove all surface material prior to evaluation and then scanned under identical conditions to those described. These results are also presented in Fig. 8. From the figure, the lasting protection provided by prior exposure to TTZ is clearly demonstrated by a ten-fold decrease in its passivation current compared to the polished reference. The rupture potential also appears to be enhanced by this prior exposure.

Conclusions

The present study suggests that for Havoline Extended Life Coolant/Antifreeze, the formation of a protective TTZ layer on copper containing components contributes to tolyltriazole depletion. While other mechanisms may also be active, the formation of this protective layer is a significant contributor to the depletion observed. The study also shows that once this layer has formed, the covered copper component is protected even at very low (zero) TTZ coolant levels. In fact corrosion protection afforded TTZ-treated copper in the absence of additional TTZ, approaches that obtained at fresh tolyltriazole coolant levels.

The present study also suggests that the tolyltriazole depletion observed over the course of months to years in actual field experience can be simulated in bench top experiments in as little as two to three weeks.

Acknowledgments

The authors wish to thank Dr. Philip Dahlstrom for his X-ray photoelectron spectroscopic analysis and Dr. Donald Drinkwater for his temperature programmed desorption and mass spectrometry analysis. The authors are also grateful to Texaco Lubricants Company for permission to publish these results.

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Test Methods

Roy E. Beal[1]

Corrosion and Testing of Engine Coolants

REFERENCE: Beal, R. E., "**Corrosion and Testing of Engine Coolants,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335,* R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 89–112.

ABSTRACT: Corrosion protection is essential to any engine coolant. The wide range of metals and materials utilized in automobile engine cooling systems requires a complex of additives for corrosion resistance. A basic understanding of corrosion mechanisms and influences of individual metals is fundamental to successful formulation. Several types of corrosion can occur and these are addressed by different ASTM engine coolant testing methods. The desire for longer-life coolants emphasizes the need for newer testing methods to successfully simulate engine coolant requirements. Extension of current methods and new approaches to providing protection is discussed.

KEYWORDS: engine coolant, corrosion, pitting, galvanic, corrosion-fatigue, accelerated testing, long-life coolant, recycled coolant

Corrosion control of engine circuit metals and materials is the objective of ASTM engine coolant standards. Quality coolants in the marketplace rely on ASTM standards. Many states and authorities mandate ASTM engine coolant standards for customers. Development of improved performance standards for current coolants and new standards for long-life and recycled coolants requires knowledge, experience, and judgment. This paper presents available corrosion information for consideration in the preparation of new effective standards documents.

Corrosion

General

The Pourbaix diagrams [*1*] represent what is thermodynamically possible and are useful tools in corrosion research. They do not replace the need for chemical or kinetic studies, or practical observation by fluid analysis, microscopical examinations, etc.

Anodic or passivation protection is normal in an engine coolant, so that electrode potential is encouraged to move upwards in voltage. A nonporous passivation film is desirable. Anodic dissolution mechanisms are complex, particularly in the presence of inhibitors. Fluid flow is also an important parameter, especially where the protective mechanism is the formation of surface films. Active dissolution can occur at low current densities in high-flow-rate areas.

A review of the basic equilibrium diagrams for the main metals in engine circuits with respect to pH-water reveals the problem of carefully balancing inhibitor systems [*1*].

Vukasovich and Sullivan clearly showed how small changes in coolant composition can strongly influence corrosion results [2].

Aluminum is generally protected in a pH range of 4.5 to 8.5. Iron is more resistant to corrosion above pH 8. Copper has a wide passivation range of pH 7 to 12.5. Lead has no

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[1] Amalgamated Technologies, Inc., 13901 N. 73rd Street, Scottsdale, AZ 85260.

protection of its own, and zinc performs best in a pH range of 8 to 10.5. Galvanic effects provide a mixed potential situation between aluminum and steel, and copper alloys with solder that accentuates the material corrosion tendencies of metals. Depending upon the complexing found with fluid media components, these passivation boundaries can be moved to higher or lower pH values and to higher or lower potential values. As competent formulators of engine coolant realize, the situation is not simple and cannot be explained in simple terms. However, it is clear that coolants cannot thwart the basic thermodynamic and kinetic rules of chemical and metal interactions [*1*]. Media containing chlorides form porous films and are subject to pitting attack. Nitrites are an effective combatant in film formation.

Aluminum

Aluminum forms several hydroxides depending upon the particular environmental conditions. All of the oxide forms are white in color, including the hydroxide.

The potential pH diagram at 25°C considers hydrogillite $Al_2O_3 \cdot 3H_2O$ as the stable form. The hydroxide cations appear to be related to chloride complexes as presented in Fig. 1. A passivation range of pH 4 to 8.5 is shown [*1*].

Principal aluminum complexes are formed with organic compound anions such as acetic and oxalic, and fluorine compounds. Phosphates are sparingly soluble. Aluminum decomposes water to form hydrogen in acid solutions and aluminates in alkaline solutions. Between pH 4 and 9, an oxide film can usually be maintained.

Hydration and porosity of the oxide film control corrosion. Corrosion of aluminum therefore occurs in acid or alkaline conditions and passivation is very restricted and is a function of the fluid. Pitting due to chlorides is a well-known phenomenon. Neutral solutions have no action generally, except where pitting occurs in the presence of chlorides. Dissolution and attack are slower in acids than in alkaline.

Organic acids usually have low rates of attack on aluminum; notable exceptions are formic, oxalic and chloride containing acids. The relative corrosion rates of organic acids on aluminum are presented in Fig. 2. Most simple inorganic salt solutions have virtually no attack on aluminum except for aluminum, iron, copper chlorides or metals deposited from them [*3*]. Several abstracts were made from Shrier.

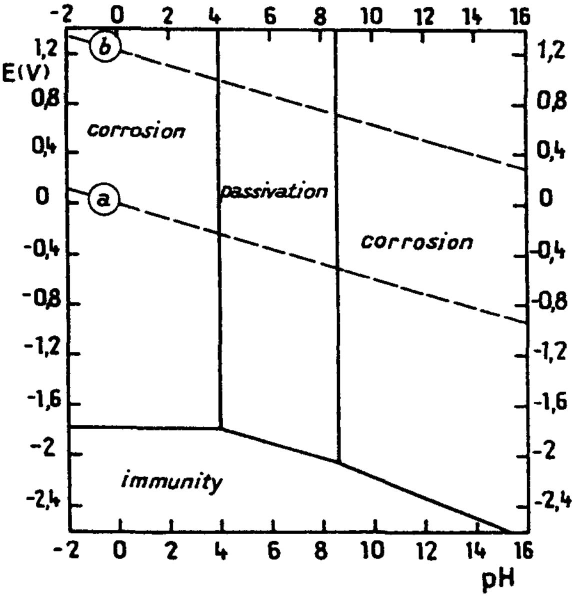
Barkley et al. demonstrated the importance of the aluminum alloy on corrosion response in a given coolant. Scott discussed new alloys for radiators [*4*]. Consideration must be given to the continued development of aluminum alloys for radiators and their performance in various coolant and inhibitor depleted environments.

Iron

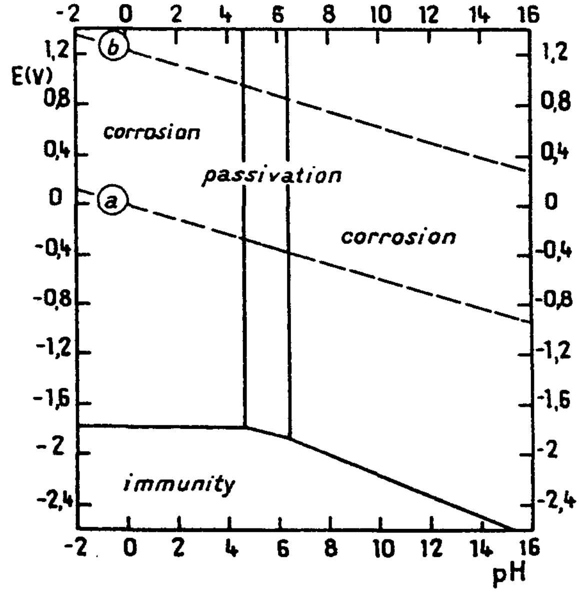
Iron corrosion is very vigorous in acid solutions, and progressively improves with increasing pH. Under conditions when the surface potential is lowered, corrosion can readily occur up to a pH of 10. Carbonates and phosphates are sparingly soluble. A yellowish color can indicate the presence of chlorides. Iron hydroxides are the dominant species in water, and passivation is very difficult below pH 8, and easier at moderately increasing pH values. A lack of oxygen potential can prevent the successful formation of a passive layer, since oxygen raises the electrode potential of iron. Chlorides prevent protection.

The influence of small amounts of salt or acid/alkaline on the surface potential and pH of iron is shown in Table 1. The natural electropotential of iron lies in the corrosion area at the left in the diagram, near to the boundary as shown in Fig. 3.

Iron corrosion can sometimes be encouraged during cooldown periods where the oxygen levels are higher, but the films formed are loose, according to Paine. The pH value at which



(*a*) **Passivation by a film of hydrargillite $Al_2O_3.3H_2O$.**



(*b*) **Passivation by a film of böhmite $Al_2O_3.H_2O$.**

FIG. 1—*Theoretical conditions of corrosion, immunity and passivation of aluminum at 25°C.*

general corrosion occurs for iron is higher at the lower temperature in the system exposure. In other words, problems can be aggravated during the time of vehicle inoperation, which produces ferrous or ferric ions depending on electropotential [5].

Sodium salts of carboxylic acids and other organics have been suggested as deicers in a

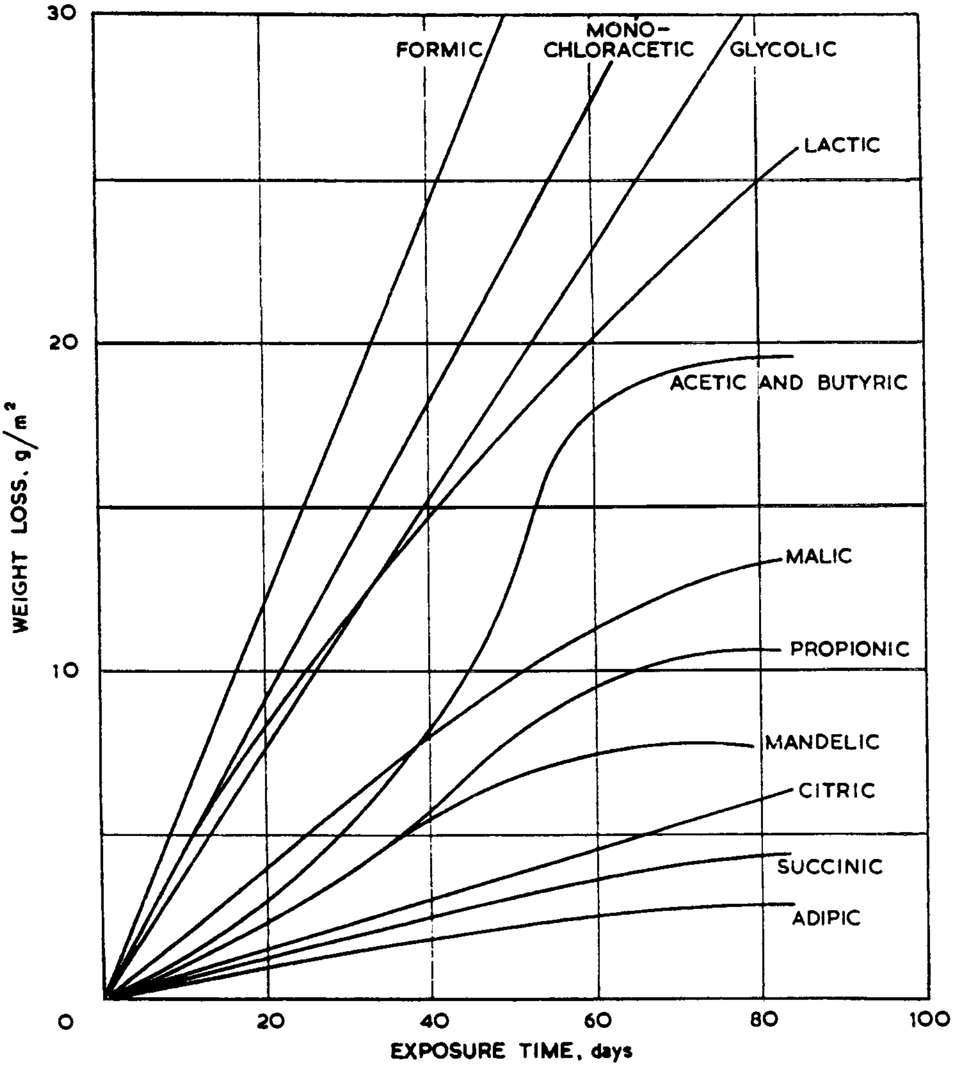


FIG. 2—*Action of dilute (0 · 1N) solution of organic acids on commercial-purity aluminum at 25°C.*

paper by Johnston and Huft. Investigations included a look at corrosion properties. It was found that sodium acetates and formates are mildly corrosive to steels, used in combination with pH adjustment. Higher corrosion tendencies were identified when tested separately without pH adjustment [*6*].

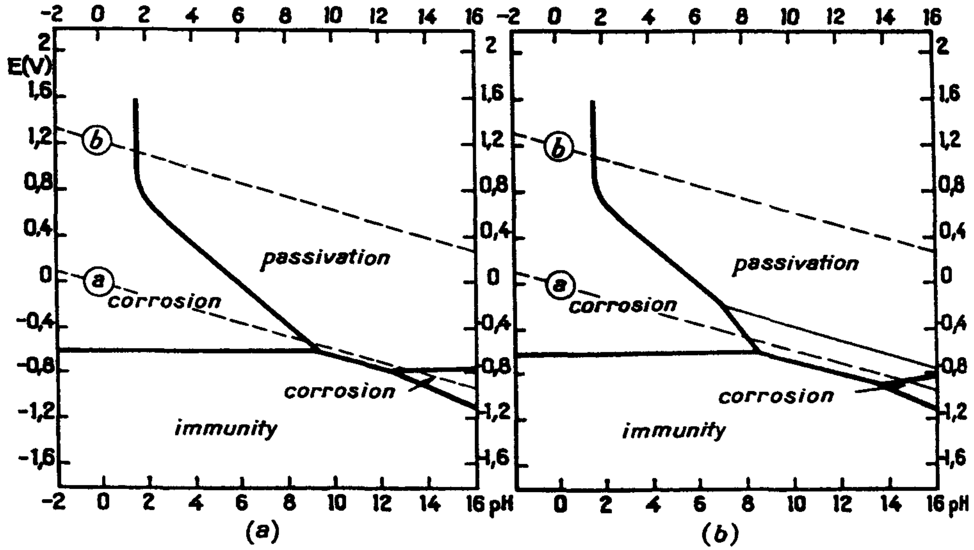
Copper

Copper is a relatively noble metal and generally the easiest one to protect in the engine coolant circuit. Copper is corroded by acid or strongly alkaline solutions containing oxidizing

TABLE 1—*Corrosion potential of iron in various solutions.*

No.	Insulated Iron	pH	*E* (volt)	
1.	Distilled water	8.1	−0.486	♦[a]
2.	NaCl, 1g/L	6.9	−0.445	♦
3.	H2SO4, 1 g/L	2.3	−0.351	♦
4.	$NaHSO_3$, 1 g/L	6.4	−0.372	♦
5.	NaOH, 1 g/L	11.2	+0.026	○[b]
6.	K2CrO4, 1 g/L	8.5	+0.235	○
7.	KMnO4, 0.3 g/L	6.7	−0.460	♦
8.	KMnO4, 1 g/L	7.1	+0.900	○
9.	H_2O_2, 0.3 g/L	5.7	−0.200	♦
10.	H_2O_2, 3 g/L	3.4	+0.720	○
11.	Brussels tap water	7.0	−0.450	♦
12.	Air-free NaOH, 40 g/L	13.7	−0.810	♦
	Iron Coupled to Another Metal			
13.	Tap water, iron-copper	7.5	−0.445	♦
14.	Tap water, iron-zinc	7.5	−0.690	○
15.	Tap water, iron-magnesium	7.5	−0.910	○
	Iron Used as an Electrode			
16.	0.10 M $NaHCO_3$, − ^{ve}pole	8.4	−0.860	○
17.	0.10 M $NaHCO_3$, + ^{ve}pole	8.4	−0.350	♦
18.	0.10 M $NaHCO_3$, − ^{ve}pole	8.4	−0.885	○
19.	0.10 M $NaHCO_3$, + ^{ve}pole	8.4	+1.380	○

[a] ♦ represents corrosion.
[b] ○ represents no corrosion.



(*a*) Assuming passivation by a film of Fe_2O_3.

(*b*) Assuming passivation by films of Fe_2O_3 and Fe_3O_4.

FIG. 3—*Theoretical conditions of corrosion, immunity and passivation of iron.*

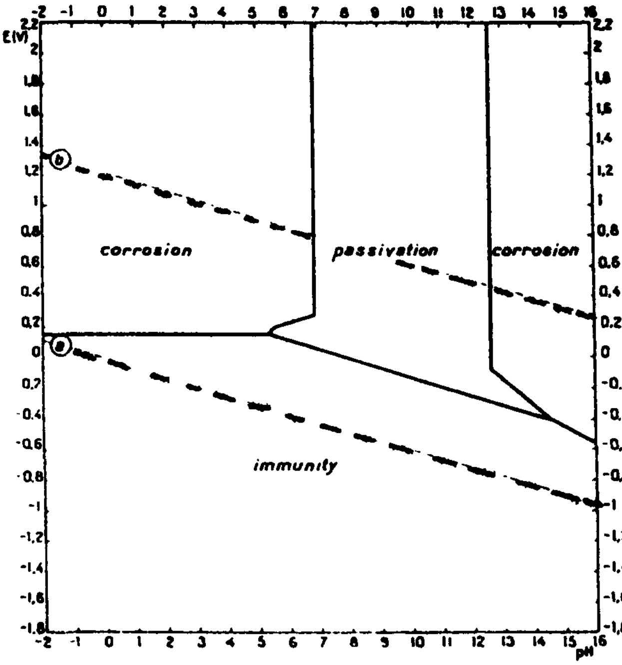


FIG. 4—*Domains of corrosion, immunity and passivation of copper at 25°C.*

agents. A copper corrosion diagram is shown in Fig. 4, revealing a passivation range from pH 7 to 12.5. The protective system used is passive films using organic compounds that form them by complexing with copper. Deaerated solutions do not corrode easily. When corrosion does occur, a brown-green layer is formed that is porous. Copper does not like ammonium salts.

Benzotriazole provides copper protection by film formation. Workers have shown that increased potential, increased flow and increased current all contribute to a weakening of the film and ultimately in the loss of protection. Ideally, it is best to have low values of all three. A dual film is present. The one nearest the parent metal is very thin, essentially a highly resistive solid-state polymer through which corrosion is controlled by diffusion. The second layer is quite porous and allows transport of solution ions. Film thickness appears to increase linearly with increased potential. The outer layer does add some resistance. A minimum amount of the azole is necessary to establish a satisfactory inner film that essentially nullifies corrosion.

At pH 7.9, copper can act as an effective electrocatalytic material for promoting CO_2 reduction to methane in a $KHCO_3$ aqueous environment. Evidence of the reduction reaction is observed by the presence of carbon at the copper electrode. Lead and tin can act in a similar manner.

High chlorides are detrimental to copper alloys in terms of direct pitting attack by film destruction, dezincification of brasses, and possible stress corrosion. Therefore less Cl^- is better. Chlorides also solubilize some Cu that will deposit on aluminum surfaces and cause pitting attack [*3*].

Copper alloys can pit and also suffer from dezincification when exposed to halide solutions containing Cl^- at lower pH values in a neutral to alkaline range. The presence of halide ions shifts the corrosion potential to a more negative value. As shown in Fig. 5, increasing Cl^- from 30 to 300 ppm will depress the corrosion potential of 70Cu-30Zn brass by 400 mV, which is substantial. The pH values also have a significant effect on lowering the pitting potential. A

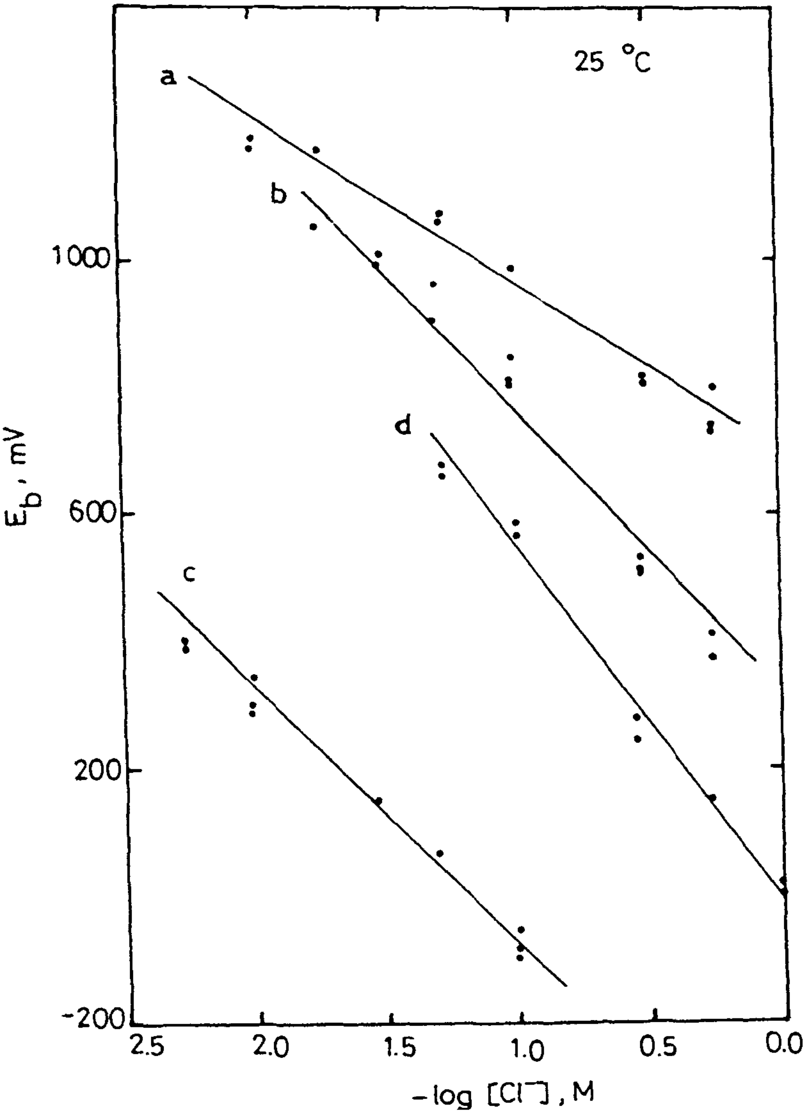
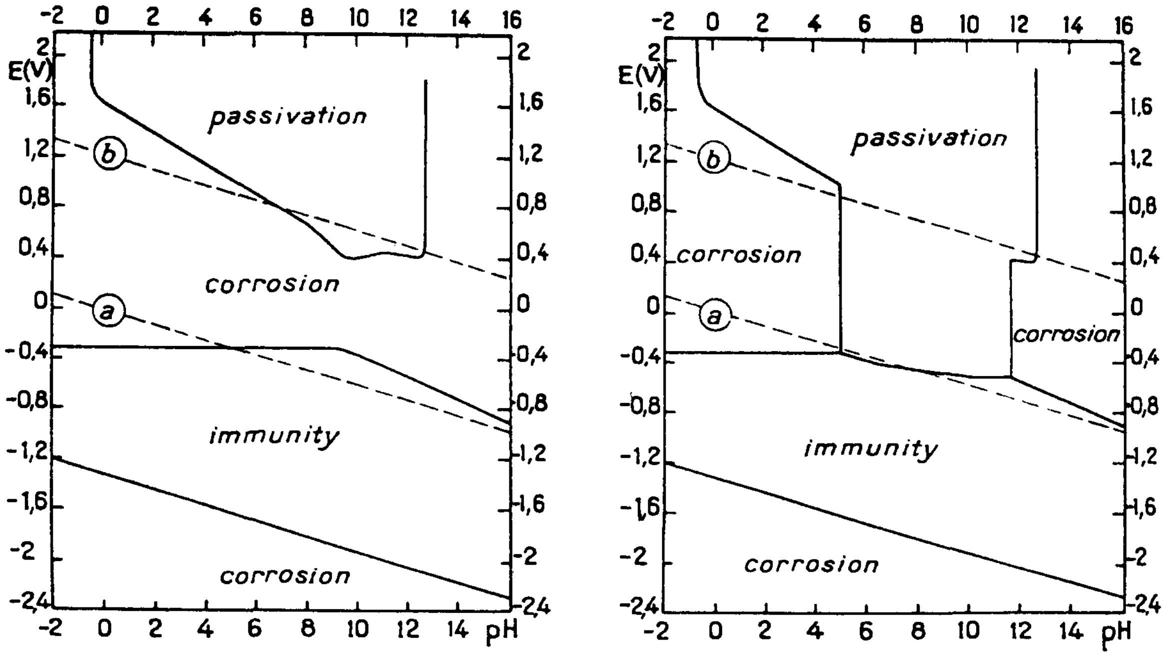


FIG. 5—*Pitting potential* E_b *versus logarithm of chloride ion concentration for Cu 70 at different pH values:* (a) *pH 12.0,* (b) *pH 9.00,* (c) *pH 7.05, and* (d) *0.001 M NaOH.*

reduction from pH 9 to pH 7 depresses the pitting potential by 800 mV. The pH values are therefore critical to copper alloy corrosion, especially in the presence of chlorides. These tests were performed in a borate buffered solution by El Rahman [7].

Lead

Lead is found in solder alloys used in copper-brass radiators. It is the most difficult metal to protect in the engine circuit. Any oxidizing action can cause lead to corrode, although carbon-



(a) In the absence of substances forming insoluble salts.

(b) In the presence of solutions containing CO_2. (Established for log $[(H_2CO_3) + (HCO_3^-) + (CO_3^{2-})] = 0$ and log $p_{CO_2} = 0$.)

FIG. 6—*Theoretical conditions of corrosion, immunity and passivation of lead at 25°C.*

ates have a beneficial effect in passivation. Lead oxide is too soluble to provide any protection. Neutral or alkaline solutions that are free from oxidizing agents provide stability for metallic lead. Corrosion activity can be seen across the entire pH spectrum as shown in Fig. 6. Passivation occurs only at high mV levels.

Solder alloys usually contain tin, and may be two-phase in character, producing localized galvanic action between the lead and tin if suitable protection is not given. Lead oxide (PbO) is amphoteric and dissolves in acid-neutral and slightly alkaline solutions. At higher potentials, PbO_2 is formed that is generally insoluble in engine coolants. It often complexes with chloride to form $PbOCl_2$ or solder bloom, which can be gelatinous or hard deposits depending upon oxidation conditions. Higher alkalinity will solubilize PbO_2 under very alkaline conditions above pH 9.5. Control of pH is therefore vital to lead protection.

Formic acid in the presence of oxygen rapidly corrodes lead. Carbonates tend to form protective films. Nitrites and nitrates are attackers of lead alloys and chlorides do not allow the successful formation of carbonate films [*3*].

Corrosion of lead in 10^{-4} to 10^{-1} M solutions of oxalic, tartaric and citric acids demonstrated that corrosion rate increases with higher acid concentration.

Oxalic acid is more aggressive than tartaric with citric showing the least damage, according to Gamal [*8*]. The corrosion mechanism is under anodic control due to complexing of lead ions with the acids. Corrosion of lead increases with pH in the range of 2.5 to 5.5. Addition of acetic acid will increase the amount of lead in solution. Oxide films on lead formed in aerated neutral solutions of corrosive salts are unstable; hence true passivation is not possible. Below pH 6, the metal surface is free of oxides. Alloying tin with lead alters the mechanism and rate of corrosion. The coupling enhances the corrosion of lead. Oxalic/acetic can get into engine coolant circuits from some flushing compounds or fluids [*8*].

Zinc

Zinc is sometimes found in cooling systems as a galvanized component and is included here for completeness. Zinc forms complexes with many anions and is usually sacrificial in engine systems. Zinc is unstable in aqueous media, although corrosion rates can be low at near neutral pH values. The influence of pH on the corrosion of zinc is illustrated in Figs. 7 and 8, covering potential ranges and actual corrosion data, respectively.

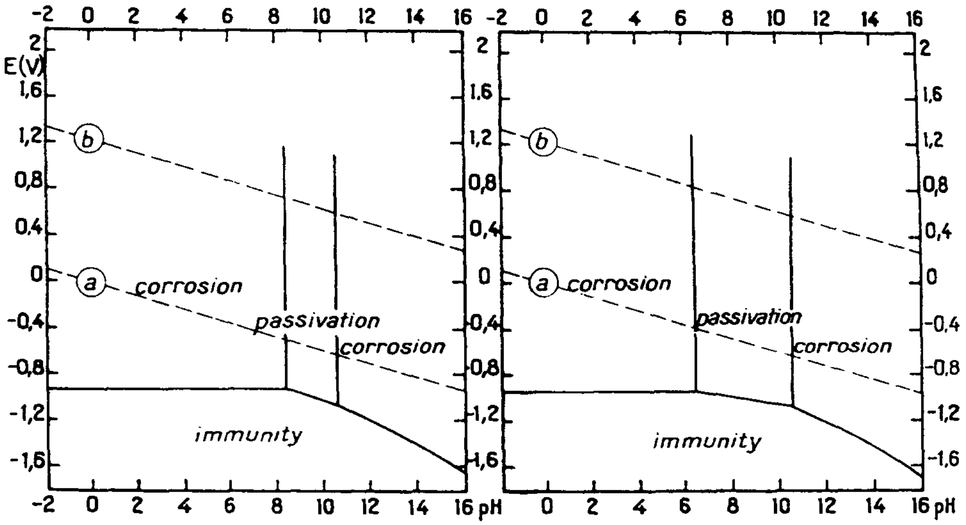
A reasonable passivation range is theoretically available in solutions containing CO_2. Hard waters can therefore help. Zinc works much better in a wet/dry situation. Zinc tends to be sacrificial because of the low electrode potential.

Pitting Corrosion

A study in the evaluation of corrosion inhibitors by Alexander and Moccari showed that as little as 1.5 ppm Cl^- requires additional inhibitors to prevent corrosion and pitting attack. The same article shows additive effects of sulfate and Cl^- ions on carbon steel corrosion [*9*].

Cl^- and SO4 ions are considered by Otero et al. as the main factors in prediction of pitting probability with Cl^- several times more powerful in causing problems [*10*].

- Sulfate ions in a coolant inhibit corrosion tunneling caused by chlorides on a free surface. The effect is to reduce the general corrosion rate, but increase the chances of gross pitting attack of aluminum alloys, especially in near neutral pH conditions. Chlorides are more apt to cause aluminum pitting in the presence of inhibitors and general corrosion when no inhibitors or depleted conditions are present.
- Self-catalytic pit growth is feasible once the pits have already formed. Pits tend to cause chloride concentration within them during the corrosive action, coincidentally with a drop in pH values.



(a) (b)

Solutions free from CO_2. **Solutions containing CO_2.**

FIG. 7—*Theoretical conditions of corrosion, immunity and passivation of zinc at 25°C.*

Chlorides and sulfates have a synergistic effect in pitting attack. Pitting frequency is described by

$$\log P = a + b \log t$$

Chloride is especially important in forming new pits or making deep pits grow.

Pitting potentials in chloride solutions are directly related to the logarithmic level of chloride as shown in Fig. 9. Any increase in chloride is therefore an increased risk. Buffering can help. Other ions may increase or decrease pitting. Pitting potential is relatively independent of pH.

Aluminum and its alloys can be susceptible to pitting by many ions, including the following:

- Chlorides
- Bromides
- Fluorides
- Nitrates

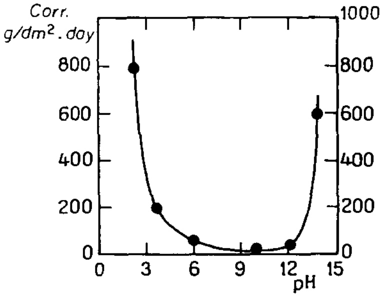


FIG. 8—*Influence of pH on the corrosion rate of zinc.*

Pitting potentials E_p in different solutions reveals Cl^- as most severe, accompanied by hydrogen evolution.

The strongest effect in corrosion of aluminum is the pitting potential E_p that is governed largely by the coolant environment, and secondly, by the aluminum alloy.

Note: The situation is complicated by the use of aluminum clad layers, so that E_p for the clad layer and the core is important to the corrosion situation.

- Aluminum alloys will not spontaneously pit when E_p is more noble than E_{corr}. Increasing chloride ions shifts E_p towards a negative value. A wide spread between E_{corr} and E_p in an inhibited coolant is valuable in defeating corrosion due to coolant depletion or chloride action.

In a pH range of 4 to 9, aluminum that was exposed with a wide-range concentration of nitrate, phosphate and benzoate inhibitors did not change pitting potential significantly in the presence of Cl^- ions.

Galvanostatic polarization has demonstrated itself as a method of pitting potential determination of candidate wrought aluminum alloys in coolants. Conversely, the method can be utilized to demonstrate the effectiveness of a coolant in protecting aluminum surfaces.

Work on the investigation of impurity elements by Breslin et al., on electrochemical activity of aluminum alloys, demonstrated that the addition of sulfate to chloride solutions can raise the E_{corr} value, changing galvanic relationships and pitting effects. A separate interesting feature is the effect of In on pitting attack of Al. Only trace amounts of In are required on surfaces to initiate attack. Copper and iron salts change the electropotential at the Al surface and therefore affect corrosion properties [*11*].

Copper and iron in trace amounts that are deposited on aluminum alloy surfaces act as an efficient cathode and thereby shift potentials to cause pitting. Temperature is clearly an important accelerant. The rate of pitting increase with temperature generally follows the Arrhenius law or equation, except when conflicting kinetics intervene. Specification of temperature in addition to other test conditions is vital to acceptable comparisons of data.

The pitting potential of iron is independent of Cl^- concentration, with no observable incubation period. Pitting also has been reported in iron at pH 8.45 in a buffered solution containing sulfates, although natural surface potentials, E_{corr}, are raised. It is suggested that sulfate anions

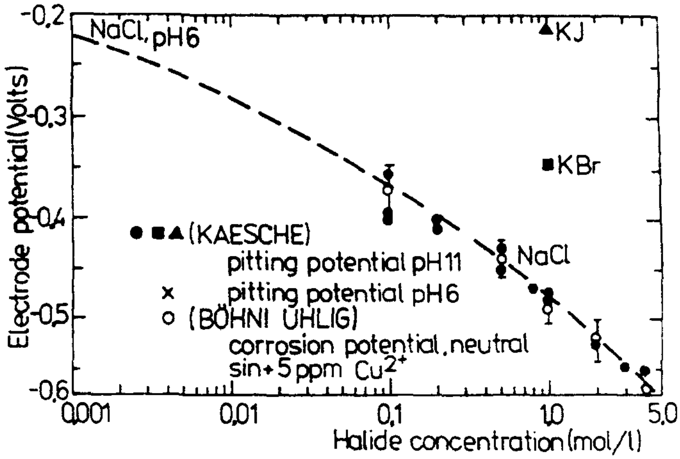


FIG. 9—*Pitting potentials for aluminum (99.99%) in different halide solutions and open circuit potentials of Al in* Cl^- *containing 5 ppm* Cu^{2+}.

are active in island formation of ferrous hydroxide at which pits develop. Pitting potential of pure iron in chloride solutions does not depend on pH in the range of pH 8 to 12.7.

Copper and copper alloys can be damaged by pitting in some natural waters and in chloride environments. Bicarbonates found in some waters are a problem. Ferrous ions deposited on copper surfaces can cause pitting. Organic substances are helpful in preventing the problem. Most organic inhibitors raise the pitting potential of the engine coolant, so that inclusion of a pitting potential test in the regimen of evaluation is a good idea.

An example of the cross current between protection and passivation is given in Fig. 10. There is an empirical equation proposed that indicates

$$\log c_s = a + b \log c_p$$

where c_s and c_p are aggressive and passive substances, respectively. The concentration of $NaNO_2$ necessary to combat Na_2SO4 in iron corrosion is presented as an example. Several inhibitive and aggressive ion relationships are log/log related. The two main mechanisms of corrosion protection are competitive adsorption and film formation, disruption or repair. Sulfates can act as inhibitors or aggressor ions, depending upon the fluid condition and the metal involved.

- Glassware tests are *not* adequate for identifying pitting attack or crevice corrosion, especially with aluminum alloys.

Pitting attack is not investigated by the ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384-96) because of the short time period involved, and yet pitting, especially of aluminum alloys is the most insidious form of corrosion. Although modern automobile radiators are designed to handle a wide range of environments, it still is encumbent upon engine coolants to provide protection.

- Simulated service tests with copper/brass radiators does not ensure good coolant conditions for aluminum.

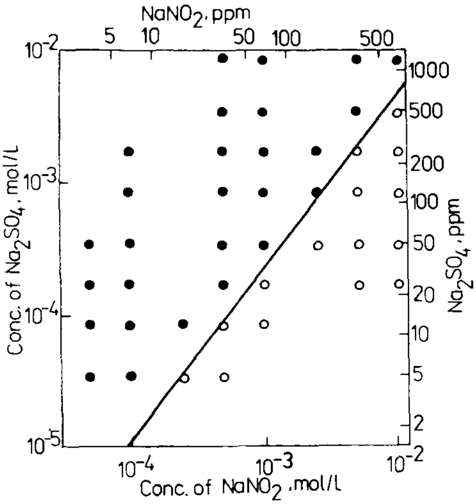


FIG. 10—*Effect of Na_2SO4 additions on the corrosion of iron in an air-saturated $NaNO_2$ solution at 25°C.*

TABLE 2—*Standard potentials of some metals.*

Metal-Metal Ion Equilibrium Unit Activity Range: Noble to Active	Electrode Reduction Potential Versus Normal Hydrogen Electrode at 25°C, V Range: Noble to Active
Au-Au^{+3}	+1.498
Pt-Pt^{+2}	+1.2
Pd-Pd^{+2}	+0.987
Ag-Ag^{+}	+0.799
Hg-Hg$_2^{+2}$	+0.788
Cu-Cu^{+2}	+0.337
H$_2$-H^{+}	0.000
Pb-Pb^{+2}	−0.126
Sn-Sn^{+2}	−0.136
Ni-Ni^{+2}	−0.250
Co-Co^{+2}	−0.277
Cd-Cd^{+2}	−0.403
Fe-Fe^{+2}	−0.440
Cr-Cr^{+3}	−0.744
Zn-Zn^{+2}	−0.763
Al-Al^{+2}	−1.662
Mg-Mg^{+2}	−2.363
Na-Na^{+}	−2.714
K-K^{+}	−2.925

Galvanic Corrosion

Galvanic corrosion is an important factor in engine cooling circuits. It can be simply defined as one metal in contact with another in a corrosive environment. The corrosion is accelerated by the difference in potential between the two metals, resulting in corrosion of the more active or electronegative metal. The rate of corrosion is determined by kinetics of reaction, between the environment and the metals involved. A galvanic series describes the relationship of metals in a given environment. Potentials can change and the relative order can also change in different environments. Generally, however, the majority of relationships are maintained, even in different fluids. The standard potential of some metals is presented in Table 2. Between two particular metals in engine coolant, the relationship can be described by a mixed potential corrosion diagram, Fig. 11. Factors influencing galvanic corrosion are presented in Fig. 12.

In summary, the main galvanic effects can be categorized as follows:

1. Electrode potentials and reaction kinetics.
2. Alloy composition and protective film characteristics.
3. Bulk solution properties and environment.
4. Galvanic couple geometry and joint fabrication.

In addition to the direct effect of the metals in the system that are galvanically coupled by vehicle construction and the engine coolant, the ions displaced into the fluid by corrosion occurrences also become important sources of galvanic coupling.

Work has been done on galvanic corrosion caused by corrosion products, quantifying galvanic currents and potentials between iron, copper, and aluminum in oxygen-containing environments. The galvanic interactions can be described as electronic, being either insulators, n-type junctions, p-type junctions, or metallic junctions of various thickness.

Examples of the dielectric properties of corrosion products are presented in Table 3. Aluminum and its oxides act as insulators. Iron and lead are n-type (oxygen deficient) and copper p-type (metal ion deficient) semiconductors that essentially furnish a galvanic couple at the

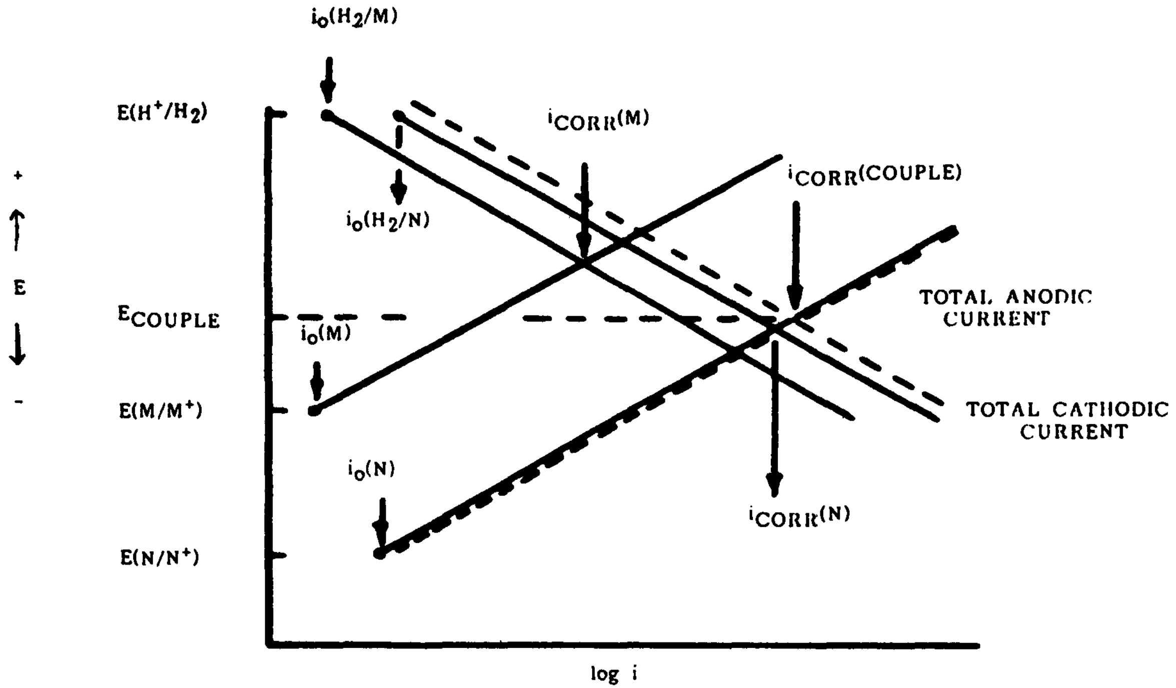


FIG. 11—*Galvanic couple between two corroding metals.*

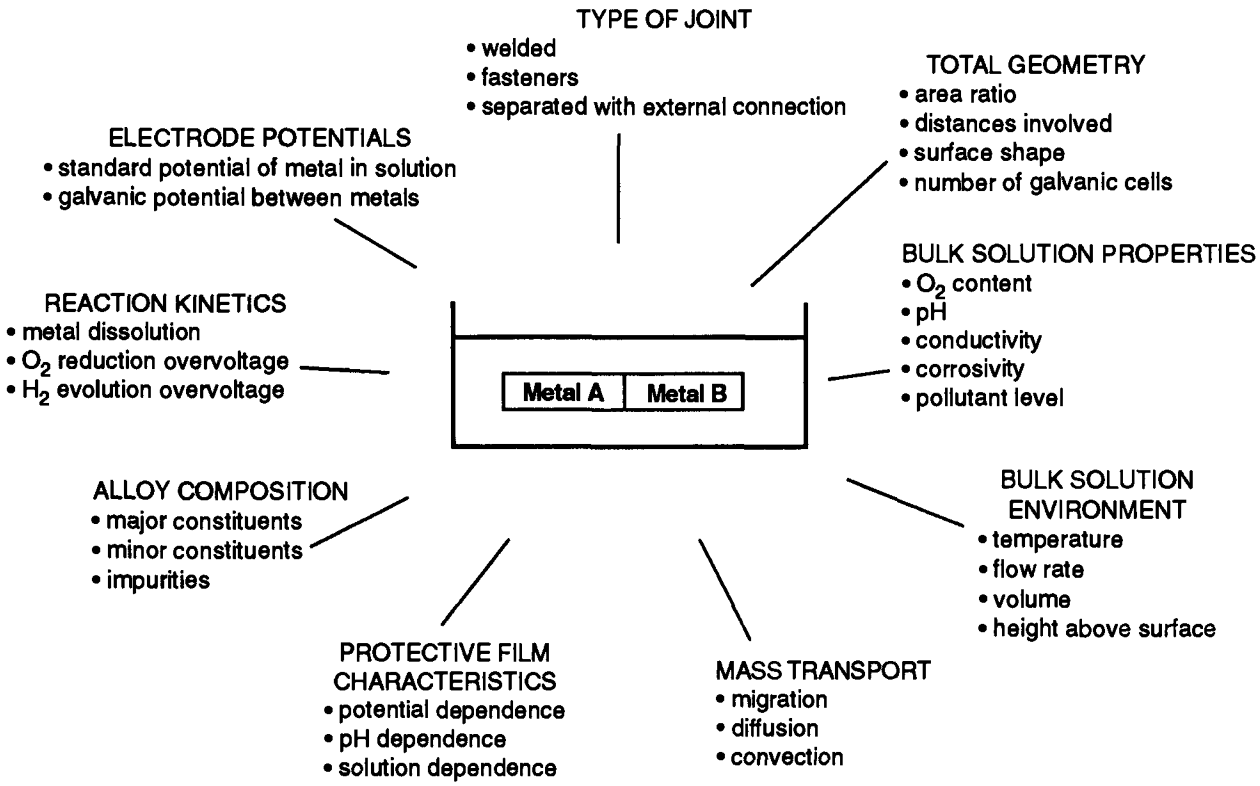


FIG. 12—*Factors affecting galvanic corrosion.*

TABLE 3—*Dielectric properties of corrosion products.*

Type	Metal	Product	E_g eV[a]	V_f,[b] Volts Versus SCE
Insulator	Al	Al_2O_3	8.7	. . .
Insulator	Zn	ZnS	3.7	. . .
Insulator	Zn	ZnO_2	5.0	−1.60
Insulator	Ta	Ta_2O_5	4.6	+0.90
Insulator	Hf	HfO_2	5.6	. . .
n-type	Ti	TiO_2	3.5	−0.30
n-type	Fe	Fe_2O_3	2.2	+0.10
n-type	Sn	SnO_2	3.6	−0.14
n-type	Zn	ZnO	3.3	−0.22
n-type	Cd	CdS	2.5	−0.65
n-type	Pb	PbO	2.7	+0.10
p-type	Ni	NiO	3.7	+0.93
p-type	Cu	Cu_2O	1.6	+0.26
p-type	Cu	CuO	2.0	+0.50
Conductor[c]	Cr	Cr_2O_3	1.7	. . .
Conductor	Co	CoO	0.7	. . .
Conductor	Pt	PtO	0.2	. . .
Conductor	Fe	FeS_2	1.2	. . .
Conductor	Ni	NiS	0.1	. . .

[a] E_g = band (mobility) gap.
[b] V_f = flat band potential.
[c] Degenerate, or n-type.

surface. Galvanic currents developed with iron and copper can be substantial as shown in Table 4, with electrode potentials presented in Table 5. These data show that copper or aluminum have the widest potential range, but iron tends to develop the highest current levels.

Clearly, both iron and copper can be a problem, and these species are used to create accelerated testing conditions for aluminum alloys in radiators [*12*].

Stress-Corrosion Cracking and Corrosion Fatigue

Environmental fracture susceptibilities of commonly used metals in the engine coolant circuit are dependent upon the metal and fluid. For example, Dean et al. showed that copper alloys are severely affected by high nitrate contents and aluminum alloys by high chloride contents [*13*]. Although rarely seen in vehicles, fracture of steel can occur under highly caustic conditions. Beal demonstrated that increased levels of chloride in hot engine coolant aggravate and increase the cracking tendencies of radiator brasses. The effect of chloride on cracking tenden-

TABLE 4—*Galvanic current.*

			Current, $\mu A/cm^2$		
Metal	Oxide	Oxide Conduction Type	TOE AAE	PFE AAE	TOE PFE
Al	Al_2O_3	I	4	5	0
Ti	TiO_2	N	2	1	3
Fe	Fe_2O_3	N	49	−1	205
Ni	NiO	P	1	16	−11
Cu	CuO/Cu_2O	P	30	36	1
304SS	Cr203	C	135+	120[c]	0

TABLE 5—*Electrode potentials.*

Metal	Oxide	Oxide Conduction Type	Potential, Volts Versus SCE PFE	TOE	AAE
Al	Al_2O_3	I	−0.627	−0.606	−0.767
Ti	TiO_2	N	−0.268	−0.156	−0.468
Fe	Fe_2O_3	N	−0.642	−0.601	−0.682
Ni	NiO	P	−0.151	−0.372	−0.420
Cu	Cu_2O/CuO	P	−0.082	−0.075	−0.269
304SS	Cr_2O_3	C	−0.116	−0.369	−0.262
Pt	PtO	C	+0.365	...	...

cies is shown in Fig. 13 [*14*]. Introduction of Type 409 stainless steel oil coolers is a new factor to consider, and these can be particularly vulnerable in chloride environments.

A combined elastomer compression and crevice corrosion test should be considered. Stress-corrosion cracking and corrosion fatigue cannot be ignored since they are strongly affected by the environment. A slow-strain-rate test will accommodate stress corrosion suscep-

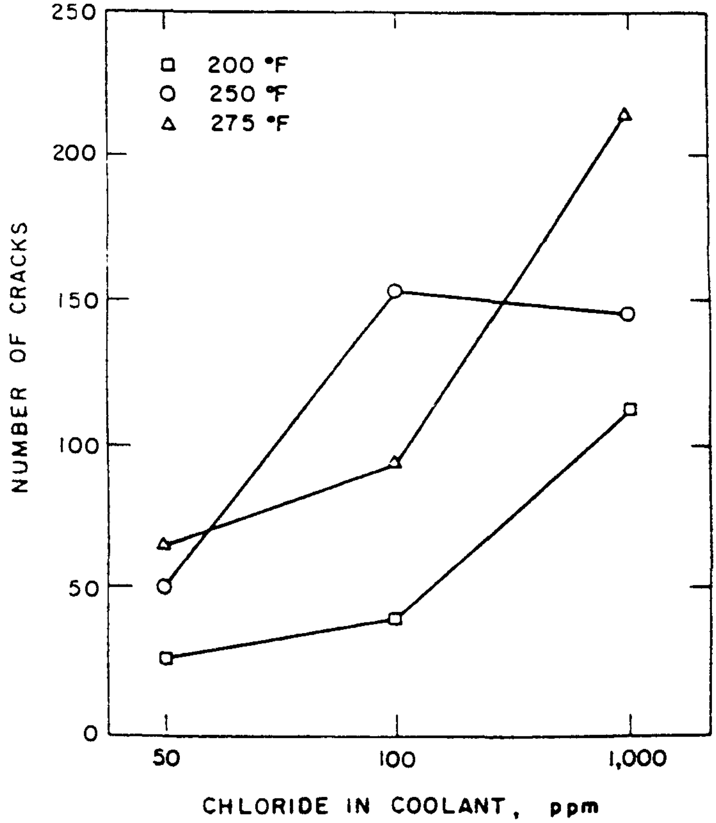


FIG. 13—*Effect of chloride content on cracking tendency in Alloy C26000 in slow-strain-rate test at three temperatures.*

tibilities and can be executed on the copper and aluminum alloys involved. Temperature is a dominant effect. Tests at 250°F (121°C) will essentially cover the engine coolant situation.

Galvanostatic Pitting Test

Wiggle [*15*] describes a galvanostatic pitting test for rapid evaluation of aluminum pitting propensities that has a background of correlation with service experience and test values. From his work it was determined that using a A7072 alloy, a pitting potential of −400 mV, represented the borderline between good and bad results. Good coolants can have a potential up to 0 mV. The −400 mV value relates to AA7072 and AA3003 materials only at the present time. Data need to be established for other alloys. Because of the valuable nature of this test it is included as a Ford standard method. The test is recommended for inclusion in recycled engine coolant standards, initially using the AA7072 material for comparison purposes. Figure 14 is taken from the paper by Wiggle. Twenty-five percent coolant was selected as the standard because it gave the best correlation. Wiggle also states that depletion rates of each inhibitor may be different. The complex interactions involved, with synergistic and antagonistic effects on aluminum pitting potential, must be considered. Whether recycled coolants follow the results of Wiggle by depleting 50% in 50 000 miles (80 500 km) remains conjectural until tested with each system. The 25% coolant selection for recycled coolants therefore needs further consideration to establish mileage equivalency. A similar consideration is needed for long-life judgments. Maybe a 15% solution of new coolant should satisfactorily indicate likely service response of a long-life coolant for 80 000 miles (128 744 km).

Acceptable pitting potential values for currently used automobile radiator materials should be developed to allow better control of engine coolant acceptability. Szklarska-Smialowska presents much useful information on metal pitting in her book [*16*].

New Organic Acid Coolant Technology

New inhibitor technology using monoacid/diacid inhibited ethylene glycol engine coolant is prevalent in Europe and is being introduced to the U.S. This technology was covered by Maes

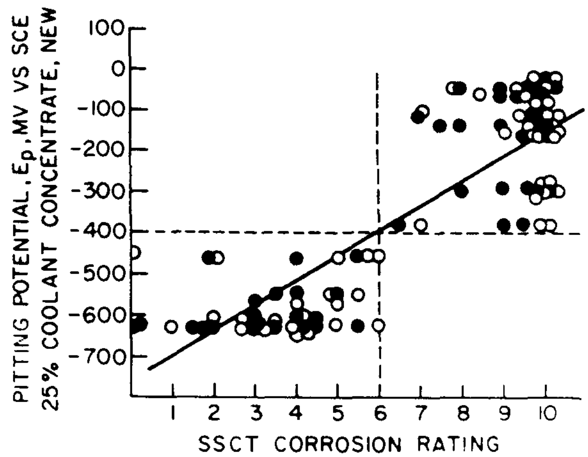


FIG. 14—*Relationship of pitting potentials of AA7072 for 25 vol.% fresh coolant mixtures with long-term SSCT corrosion ratings. Open circles are pitting attack ratings and filled circles are crevice attack ratings.*

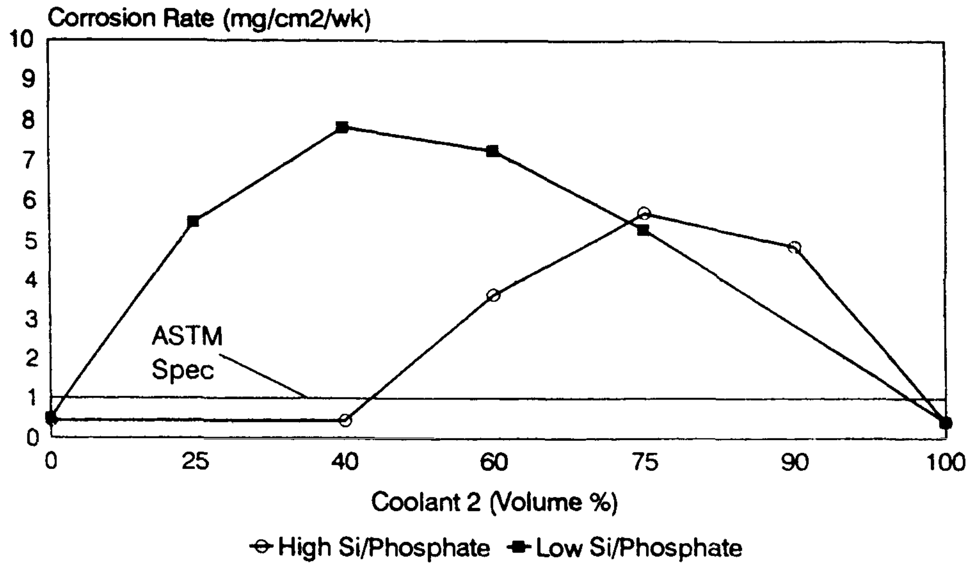


FIG. 15—*Coolant mixture corrosion rates in ASTM D 4340.*

and Van De Ven, and Darden et al. [*17,18*], who concentrated on effectiveness with aluminum alloys. These materials are claimed to be satisfactory in pitting protection of aluminum. A question is whether these fluids are compatible with recycled coolant additive packages with some treatment systems and this needs to be resolved so that ASTM standards can reflect practices. Some controversy still exists as to whether the carboxylic acid coolants protect high-lead solders in copper/brass radiators, according to Burns [*19*].

Mixed coolant effects were studied by Mercer [*20*] and found to cause failure in the ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants under Heat-Rejecting Conditions (D 4340-96) where carboxylic acids are mixed with conventional coolants as shown by Fig. 15.

Accelerated Corrosion Testing

Accelerated testing with valid results is the "holy grail" of the quality engineer. There are obvious valid arguments in the reduced cost of testing with shorter time periods involved with a particular method. For engine coolants, since the main criteria are general corrosion of the metals in the engine circuit, and pitting attack of the more vulnerable alloys, there are two ways to accelerate testing that can be immediately implemented. First is temperature. The test temperature of the ASTM Test Method for Simulated Service Corrosion Testing of Engine Coolants (D 2570-96) can be raised to 240°F (115°C) from the present 190°F (88°C). This will more severely stress the fluid, yet still be within the normal engine coolant operating temperature range. The second approach is to saturate the fluid with oxygen during the cooldown periods in the test. Also, retaining the 1064 h test period is questionable with longer-life coolants, since the test was originally designed for a 2-year-life coolant. A four-year-life coolant should be tested for over 2000 h for equivalency in testing. Assuming the original 1064 h was valid for the 2-year coolant, this is obviously necessary. A reasonable question to ask is, How long is the recycled coolant product supposed to function, and what ASTM standard criteria should be used to satisfy quality requirements? An important consideration is the overall test program.

A vital question is possible degradation effects in service of different recycled products. The standards for recycled products, traditional coolants, and new long-life coolants should therefore include new measures, or tests or other criteria of acceptable stability or longevity of corrosion protection.

A combination of chloride and organic acids is sometimes used as a synthetic corrosion medium, because of their synergistic effects which may also be pH related. All references to corrosion relate to the importance of the Cl^- ion in enhancing corrosion.

Test solutions to accelerate corrosion generally containing Cl^-SO4, iron, and copper species were studied by Francis and Lee. The presence of copper and iron increases corrosion rates and pitting, which are not affected by oxygen content in a chloride-containing solution [*21*].

Advanced Test Methods

British standards on engine coolant performance use higher test temperatures, and European standards in general allow less metal loss on glassware tests. Mercer [*20*] of England's National Physical Laboratory concluded in 1979 that performance under higher heat flux would be appropriate and that more rigorous pitting behavior tests are needed. Mercer used test temperatures up to 248°F (120°C). Currently, the ASTM Coolant Committee is lagging in both coolant technology and coolant requirements in the form of new or revised test methods and standards that are applicable to the modern vehicle.

Schulmeister and Speckhardt concluded that differentiation between antifreeze/coolant capabilities in relating to valid service behavior predictions requires that test temperatures be increased and that concentrations below recommended service levels must be used. From an accelerated test standpoint, the level of coolant percentage is therefore an important consideration. Increased test predictions may require 30% or even 15% solutions, rather than the current ASTM D 2570 standard dilutions.

O'Brien et al. discussed electrochemical techniques by use of galvanic couples, using aluminum/cast iron, solder/brass, and aluminum/steel. They concluded that the test identified inhibitor relationships that the standard glassware test does not cover. Choinski and Maxwell question the ASTM D 2570 test as a qualifying method.

Dorward proposed a boiling ASTM D 1384 procedure with modified ASTM water that included 10 ppm iron and copper ions as chloride and sulfate salt additions. Metallographic cross sections were included, since simple weight loss does not give sufficient information. Beynon reported that aluminum is particularly vulnerable to chloride ions, and that water low in chlorides and sulfates is preferable, because these ions compete for sites on metal surfaces and will lower protection [*22*].

The consensus of the ASTM D15 committee appears to indicate that the ASTM D 4340 test should be performed in duplicate. Experience over many years of testing with all kinds of coolants provides support for this, especially where any marginal results can be expected. The test for recycled coolant should also be performed in duplicate. Each test result must pass the 1.0 $mg/cm^2/week$ test limit for acceptance of the product.

Inclusion of the solder bloom coupon into the ASTM D 1384 test bundle for evaluation of this phenomenon is very helpful. There are no specific inhibitors for lead and the solders used in radiators are generally of high lead content. The special coupon design allows for galvanic effects, since the back of the coupon is brass and in direct contact with the solder. Any solder bloom tendencies are shown by a white deposit on the solder surface after the test period [*23*].

Material concerns should be more prevalent in ASTM with relation to aluminum alloys, because of the changes being made over the years of these alloys in service. Materials and coolants work together and should be tested together. ASTM standards therefore should reflect modern usage of aluminum alloys in radiators to be current with vehicle usage conditions.

The simulated service test D 2570 with an aluminum radiator is a realistic approach in appraisal of fitness for service. This can be used as an alternative radiator to the standard copper/brass unit when copper alloy protection is not needed in the coolant, or sensitivity of the coolant to aluminum alloys is more critical.

Rowe covered the measurement and evaluation of pitting corrosion, demonstrating that statistical methods are very useful in developing pitting probabilities. Estimates are made of maximum pitting depths and pit growth relationships with time are established [*24*]. The purpose of the discussion is to introduce pitting measurement after the simulated service test as a criterion for acceptance of a recycled coolant. Obviously, some experience is needed before standards can be introduced. However, if pit measurement is required, then data will gradually become available. Testing to failure may not be practical or necessary when this technique is used. From our own experience, for example, an estimated maximum pit depth of 0.05 mm after a D 2570 test can be used, including Weibull plots of selected tubes with 50 designated examination areas [*25*].

For example, measuring pit depth and numbers on every fourth tube in the radiator: this approach will give a twofold advantage. First is the development of acceptance criteria, and second, a basis for improvement in all coolants by whatever method or process, whether new or recycled. The ASTM Guide for Applying Statistics to Analysis of Corrosion Data (G 16-95), using extreme probability plots, appears to be most appropriate.

Liebold and Starke discussed European test methods. The Forschungsvereinigung Verbrennungskraftmaschinen e.V. Frankfurt (FVV) test attempts to cover a wider range of practical engine conditions within one test and has been successful in testing coolants for automobile use. Consideration should be given by ASTM to adopting this approach, perhaps in the area of long-life coolants where tests that include degradation and aging factors are important to verification of coolant quality on some kind of accelerated basis [*26*].

Current Coolant Testing Methods

Less fluid is doing more work in the modern engine cooling circuit. Proportionately, the inhibitive capabilities need to be better, because the total areas of metallic surface exposure have not reduced as much as the volume of fluid available. More highly stressed coolant needs more careful consideration, and recycling presents a responsibility in addition to an opportunity. Rowe also confirms that coolant temperatures of 250°F (121°C) can occur. In this regard, present ASTM testing is remiss in not including tests that cover this situation, except for the ASTM D 4340 hot surface test.

Current coolant test methods need some changes to accommodate new vehicle construction and operation. The following test changes are recommended. The ASTM D 2570 test should be modified to include temperatures up to 250°F (121°C) in order to stress the coolant more. Consideration should be given to reduce the metal loss allowances, because good-quality coolants on the market have much lower losses than the standards require. In addition, with the internationalization of ASTM, weight losses can readily be brought in line with current European practices.

Other countries, such as Japan, use a consistent engine coolant concentration in test methods. Current ASTM practices should be reviewed to determine whether the present coolant percentages for each test should be retained or made more universal.

Long-life Coolant Testing Methods

Vehicle manufacturers and major coolant suppliers are introducing engine coolants with significantly longer life expectancy. Methods of testing these coolants in an accelerated manner are needed to reflect the longer life with realism. The current ASTM coolant test methods are insufficient. The following test method changes should be introduced. The ASTM D 4340 test should be extended in time, and possibly increased in temperature. The ASTM D 2570 test should be raised in temperature and extended for at least twice the current exposure period. A galvanostatic pitting test should be coupled to ASTM D 2570 with tests before and after on the coolant used for simulated service. Test solution concentration can be used for stressing the system by lowering the percentage of coolant used in the simulated service test.

Aluminum radiators should be mandatory, since these long-life coolants are generally designed to work with aluminum and iron systems, and therefore the ASTM D 2570 test for long-life coolants should include all the above factors and aluminum radiators. Inclusion of two radiators will allow progressive removal of tubes for pitting analysis from one radiator, with the second radiator performing the complete test.

A further consideration is to introduce an FVV-type test for long-life coolant quality determination. This test could be used in conjunction with some of the ideas presented to provide a simulated service test of value in a reasonable time period.

Recycled Coolant Test Methods

The ASTM D 1384 test is well-established method of screening potentially good coolants from poor ones. It never was designed as an overall *acceptance* test for new coolants, although the test is valuable in quality control. The test is also based on new or virgin coolant and a known history of correlation with service experience over many years. The normal vehicle usage rate and accompanying coolant degradation with time is therefore well documented.

There is clearly insufficient experience with recycled coolants to make a universal judgment of a similar nature, based on the new processes involved. The D 1384 test is still applicable as a *screening* test but dangerous as an acceptance test until more knowledge concerning the degradation rates of the various recycled coolants is acquired. The currently proposed tests by ASTM Committee D15.15 for assessment of recycled coolants are essentially the same as those proposed by Rowe in 1979, for general purposes, even though requirements in engine cooling systems have, if anything, become more stringent.

Recycled coolant requires the inclusion of some form of accelerated test to make up for the deficiency in addition to the normal procedures involved with ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light Duty Service (D 3306-94). The best way to approach the problem is to raise the temperature of the test solution for an artificial aging period exposed to test bundles for metal ion interaction in a simulated service-type environment.

Engine coolant analysis should be used as one of the degradation criteria. A comparable test using the ASTM D 1384 technique with the fluid that has been exposed to the accelerated vehicle aging tests would enable some logical decisions on the most appropriate testing methods to be applied to the recycled products [22].

A cyclic polarization electrochemical profile of the synthetic used coolant will allow comparison with a similar profile taken after recycling, with a new additive package included, to demonstrate improvements in pitting potentials and corrosion. The galvanostatic pitting test is also appropriate to the recycled coolant product and gives valuable information on the capability to resist pitting attack in service.

The simulated service test should include an aluminum radiator to represent most newer vehicles in service. The pitting analysis concept should also be included. Examination of every fourth tube of the radiator for pit depth and numbers should be performed after the test. A bloom specimen attached to the test bundles will cover possible solder corrosion.

Discussion

Recycling of different types and formulations of engine coolant can also be a concern, depending upon the methodology used and the removal of various constituents from the glycol-water solution by the particular supplier and subsequent reconstitution. A combination of chemical species or physical property limitations that appears sensible from the available knowledge base on the subject and performance testing to ensure that the consumer has a good coolant is desirable for a recycled product. Obviously ASTM D 3306 is a minimum standard. However, because of present imponderables regarding stability of solutions, degradation of a recycled product over time, and influence of allowable contaminants or impurities, further testing of adequacy is needed. The solder bloom coupon, the galvanostatic pitting test, and constituent or property limits are steps in the right direction. Degradation, or life assessment, appears to be one of the major remaining questions.

The ASTM D 1384 test protocol is designed for use in conjunction with ASTM corrosive water as a means of stressing the fluid and producing, in effect, an accelerated test. Since the new coolant standard has a chloride standard of 25 ppm maximum, and the water quality standard recommends 40 ppm Cl^- maximum, this represents an increase in chloride level by a factor of 2 for testing purposes. Therefore, to use the same protocol for testing a desired standard of 100 ppm chloride maximum in the recycled coolant, a chloride level of 200 ppm is needed for the necessary acceleration effect. Even with the argument that domestic water supplies nearly all contain chlorides up to 75 ppm, a *maximum* of 50 ppm chloride in the vehicle is expected, and a testing acceleration factor of two is accommodated.

Conclusion

The challenge in preparing adequate ASTM standards for engine coolant performance requires an understanding of the metals involved and their corrosion characteristics. The information presented is based on available corrosion data to assist in new and improved standards development for engine coolants. Some changes to current standards are recommended and ideas put forward for test methods for long-life and recycled coolants.

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Predictive Tools for Coolant Development: An Accelerated Aging Procedure for Modeling Fleet Test Results

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REFERENCE: Gershun, A. V. and Mercer, W. C., "**Predictive Tools for Coolant Development: An Accelerated Aging Procedure for Modeling Fleet Test Results,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 113–132.

ABSTRACT: The objective of this study was to develop an accelerated aging test (AAT) for conventional and extended life coolants that will predict coolant composition and performance after 100 000 or more miles (160 930 km) of use. The procedure was developed by examining the effects of a series of cooling system metals, their surface area and the amount of each used, test temperature, glycol concentration, and test time on important chemical and physical properties of the test coolant. The chemical and physical properties evaluated included the accumulation of glycol degradation products, the depletion rate of active inhibitors, the pH drop, and the presence of corrosion products in solution. In addition, the test coolant performance was evaluated in ASTM D 1384 and D 4340. The effects of variation in the test procedure on the coolant were compared to actual coolant from extended duration fleet tests. The test procedure selected gave test coolant with composition, physical properties, and performance that compared favorably with the fleet test fluid. The test performance was validated by comparing the properties of a series fluids after this test to corresponding fluids removed from vehicles after extended use. An example of fluid development using this procedure is presented. Further areas of investigation are suggested. It is recommended that the general test procedure be considered for adoption as an ASTM test method for evaluation of the extended performance of fluids in automotive and light duty cooling systems.

KEYWORDS: extended life coolants, conventional coolants, performance tests, organic acids, inhibitor depletion, glycol degradation, accelerated aging test

As automobile and light duty truck manufacturers demand coolants with extended useful lifetimes [*1–3*], coolant manufacturers respond with improved coolant formulations [*4,5*]. In the past five years several coolant suppliers have introduced coolants with extended time and mileage intervals. Development of extended-life coolants has been a time-consuming process because performance of proposed formulations could be evaluated only through extended-duration fleet tests. Current laboratory tests were developed to represent the shorter drain intervals recommended for conventional coolants and are not fully predictive of extended-life performance. The development and evaluation of experimental formulations in a more reasonable time and at a more reasonable cost require an accelerated test procedure.

While there has been a need for such an accelerated procedure for a number of years, development of such a test has been hampered by a dearth of coolant performance data from actual extended duration fleet tests. Without the knowledge of how coolants performed in

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vehicles under actual extended use conditions, any prediction of end of test properties was an uneducated guess. Over the past decade we have run a series of extended-duration fleet tests on both conventional and organic acid based coolants. This testing provided us with information on the performance of each of the coolants, the chemical properties of the coolants after fleet testing, and how those properties changed as a function of time and mileage. Most important, we retained the actual used coolant for a variety of evaluations. With the actual fleet data on a variety of coolant types, the development of an accelerated aging test protocol was possible. The properties and performance of coolants exposed to a series of test protocols could be evaluated and compared with those of the fleet test coolants. Thus, the information from extended life fleet tests was leveraged into further test development.

There are two basic types of information available from coolants which have been used in vehicles. One type is direct information on the chemical and physical properties of the coolant. Evaluation of the chemical and physical properties tells the researcher about what has happened to the coolant during use, how well the corrosion inhibitors have worked, and how much of the corrosion inhibitors are left. This information, combined with evaluation of cooling system components, tells what has happened in the past. The second type of information tells the researcher more about the reserve inhibition the formulation has for protecting the cooling system at higher mileage and gives an idea of how the inhibitor package would respond to upsets in the cooling system such as the introduction of poor water, the replacement of parts, or low coolant levels. This information can be gathered by evaluating the performance of the used coolant in laboratory tests with new metal specimens. The new metal specimens do not have the benefit of the barrier to corrosion established from the beginning of the fleet test. Thus, protection or lack thereof is an indication of the amount of reserve protection included in the formulation.

The goal of accelerated aging test development was to provide a test that could rapidly mimic the effects of extended fleet testing on coolant formulations. Our experimental procedure uses the standard laboratory glassware apparatus and takes two weeks to provide coolant with the chemical, physical, and performance characteristics of coolant which has been in vehicles for 100 000 miles (160 930 km). We used the chemical, physical, and performance characteristics of authentic used coolant to develop this test. Once the test was developed, it was validated by comparing the same properties of other artificially aged coolants with the properties of the same coolants after extended fleet testing.

We also have used the test to evaluate candidate formulations. This test is combined with the other standard laboratory tests to provide a snapshot of the expected performance of candidate formulas in a vehicle. We are currently using the test as part of the screening of candidate formulas. It has not yet replaced extended fleet testing but has reduced the need for extensive testing on a number of candidate formulas. The test has allowed a much higher degree of confidence in the candidate coolants as they begin fleet testing.

Experimental Procedures

Test coolants prepared in the laboratory were analyzed before and after all tests. Analyses included inductively coupled plasma emission spectroscopy (ICP) for inorganic ions, gas chromatography for the organic acids, and ion chromatography for sodium nitrate, sodium tolyltriazole, and sodium mercaptobenzothiazole.

Fleet Tests

Selected coolants were evaluated in fleet tests. Coolant 1 was tested as factory fill in new vehicles. The coolants were evaluated during the course of the fleet test by metal specimen weight loss and solution analysis. Fluid performance was analyzed at the conclusion of the fleet test by selected ASTM and proprietary test procedures.

A bypass (heater circuit) specimen capsule was used as in ASTM Practice for Testing Engine Coolants in Car and Light Truck Service (D 2847-94). The specimen bundles contained the same seven metals used in the ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384-96). New radiators were put in all test vehicles at the beginning of the test. These radiators were tested to determine their thermal and flow characteristics before and after the test. The fleet test ran for four years and 160 000 km. The vehicles were factory filled with a 50 volume percent solution of the test coolant and deionized water. Coolant dilution was maintained at 50 volume percent throughout the test. Specimen bundles were removed at 19 000 km intervals and coolant samples were removed at 16 000 km intervals.

Laboratory Tests

Standard Tests—Laboratory tests included ASTM D 1384 and the ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions (D 4340-96). There were several deviations from the ASTM D 1384 standard. These included the addition of a high lead solder specimen (97.0% lead, 2.5% tin and 0.5% silver), a modified beaker, and the use of fine pumice for cleaning the aluminum specimens. The results presented for ASTM D 1384 are averages of triplicate runs and those for ASTM D 4340 are averages of duplicate runs.

Accelerated Aging Tests—The accelerated aging tests were carried out in our modified ASTM D 1384 beaker. The test coolants were diluted with deionized water to the selected volume percent. Experimentally it was found that any fluid loss at test conditions was due to loss of water so initial coolant levels in the beakers were marked accurately and coolant makeup during the test was with Type IV water to the indicated pre-test level. This assured a constant coolant concentration from the beginning to end of the test. Metals used in the test were copper, aluminum and cast iron alloys specified in ASTM D 1384 unless otherwise stated. These metals were added to the beaker at the beginning of the test in the form of standard metal test coupons, granular beads (average particle size = 5 to 30 mesh), metal shavings, or powder (average particle size = 100 to 325 mesh). The metal test coupons were prepared according to standard ASTM procedures before the test. The other test metals were prepared by J. T. Baker Inc. and Metaspec Co. All accelerated aging tests were carried out in triplicate beakers.

Results and Discussion

Fleet Test Results

While several coolants, including conventional and organic acid coolants, were the subject of fleet tests and accelerated aging tests in our laboratory, the results for a single organic acid coolant were used in the evaluation of the accelerated aging test protocol and will be discussed in detail. This coolant was an early development effort and presented the opportunity to test several formation concepts as well as to provide the necessary background information for accelerated aging test development. This coolant is not and has not been commercially available. Results from fleet tests of other coolants are discussed briefly in the validation section below.

Metal Specimen Weight Losses—The fleet test was run for 160 000 km over a four-year period. At 19 000 km intervals metal specimens were removed from the vehicles and the weight difference from the original was determined. As can be seen in Table 1 the 160 000 km weight loss indicated that the coolant was still protecting the cooling system metals adequately at the

TABLE 1—*Coolant 1 fleet test weight losses.*

Specimen Interval, km	Copper	Solder	Brass	Steel	Cast Iron	Aluminum
19 000	38	1	11	1	1	2
38 000	43	1	15	2	1	2
57 000	48	4	14	3	7	5
76 000	52	5	18	4	5	5
95 000	49	2	15	13	4	3
114 000	53	5	16	19	2	5
133 000	55	9	20	21	2	6
160 000	58	10	24	33	3	3

end of the test. The increase in steel weight losses indicated that the fluid may be reaching the end of its ability to protect that metal. The absolute weight loss for steel is still low.

Solution Chemistry—The fleet test was monitored by examining solution chemistry of the coolant in addition to the metal specimen weight losses. The solution chemistry gives another way of evaluating the ability of the coolant to protect the metal surfaces. Important parameters monitored were the presence or absence of cooling system metal ions in solution, the amount of corrosion inhibitors remaining in solution, the pH of the solution and the presence of contaminants such as glycol degradation products.

There were no cooling system metals observed in solution. This supports the conclusion derived from the metal specimen weight losses that there was no significant corrosion of cooling system metals and therefore that the coolants were providing adequate corrosion protection to the cooling system.

The predominant corrosion inhibitor in the organic acid formulation is the organic acid. There was about 75% of the original organic acid remaining in solution at the end of the fleet test. At this point, the cause of the decrease remains unknown although some is certainly on the metal surfaces, some was probably oxidized during the course of the fleet test, some may be tied up with lead from the Modine solder, and some may have precipitated due to solubility losses associated with the decrease in pH. The inorganic inhibitors remained in solution at the original level. Tolyltriazole achieved an equilibrium level, approximately 60 ppm, within the first 48 000 km.

The level of glycol degradation products is shown in Table 2. The observed glycol degradation products were formate and glycolate. There were essentially no other contaminants observed in the organic acid system.

TABLE 2—*Coolant 1 fleet test accumulation of EG degradation acids.*

Interval, km	Formate	Glycolate
24 000	33	72
32 000	82	182
40 000	105	227
48 000	99	285
56 000	120	349
64 000	142	429
72 000	128	454
80 000	169	625
88 000	201	840
96 000	158	796

TABLE 3—*Coolant 1 ASTM D 4340 test results.*

Original Coolant 1	Coolant 1 After 160 000 km in Vehicle
0.3	0

Post Fleet Test Performance—The end-of-test fluid was evaluated in two basic ASTM tests, D 1384 and D 4340, as is now required in two domestic OEM specifications. Testing coolants, according to virgin coolant tests and to virgin coolant standards, does not necessarily tell much about the ability of the coolant to continue protecting an already passivated system. Because the tests are run on virgin metal coupons, the coolant is being asked to do a much different job than it has been doing in the vehicle. The metals that the coolant has been protecting are those that were passivated by the virgin coolant, not brand new metal surfaces. These tests strain a system that has been strained already by 160 000 km in the vehicle. End-of-test evaluations do give an idea of the available corrosion protection reserve of the coolant.

A comparison of the D 4340 results for Coolant 1 is shown in Table 3. Coolant 1 was able to protect heat rejecting aluminum in this test to essentially the same level as virgin coolant. This is undoubtedly due partially to the ability of organic acid fluids to protect cast aluminum heat rejecting alloys, but is also partially due to the decrease in pH over the course of the fleet test. The end of the fleet test fluid pH is within the range of aluminum passivity. In addition, there remains in solution a large percentage of the original organic acid to protect aluminum.

Table 4 also shows a comparison of the ASTM D 1384 results for virgin and fleet aged samples. The performance is similar to the original in all metals but cast iron. This fluid was unable to protect cast iron. Our initial inclination was to associate the loss of ferrous metal protection with the decrease in pH of the fluid; the same compositional parameter that is thought to protect heat rejecting aluminum since the end of test pH was one where cast iron is expected to freely corrode. Since there are reports in the literature that proclaim the ability of organic acid based coolants to protect ferrous metals, we decided to determine which of the changes in coolant composition and properties were implicated in ferrous metal corrosion.

Determination of Composition/Properties Effects—To evaluate the effects of the changes in composition and properties, experiments were designed to isolate individual changes as much as possible. This was done to the authentic end of the test fluid in most cases. However, in some cases model fluids with desired composition and properties were prepared. The fluids were then tested in ASTM D 1384 to determine the effects of the changed composition or property. The addition of sufficient organic acid to bring the amount in solution to pre-test levels had the greatest effect on the protection of steel and cast iron as tested in ASTM D 1384. There was some improvement in protection of the ferrous metals when either the pH or TTZ level was adjusted back to initial levels. Adjustment of any two of the examined parameters at the same time resulted in further improvement. Essentially the same ASTM D 1384 perfor-

TABLE 4—*Coolant 1 ASTM D 1384 test results.*

	Original Coolant 1	Coolant 1 After Fleet Test
Copper	2	1.3
Solder	7	3.3
Brass	2	1.4
Steel	0	1.0
Cast Iron	3	161
Aluminum	6	5.8

mance as with the virgin fluid was achieved by adjusting pH, organic acid and TTZ levels to pre-test levels while leaving the acid degradation products at the post-test levels. High ferrous metal weight losses could be achieved by preparing synthetic versions of the post-test fluid.

Conclusions—The fleet test of Coolant 1 was successful in a variety of ways. It demonstrated that this test coolant could adequately protect the cooling system metals for at least 160 000 km. It also showed that there was some loss in performance as compared with the virgin fluid. The end-of-test fluid allowed us to probe the effects of the various compositional and property changes and determine which of those were important for future coolant development efforts. Most importantly it provided us with the information that we needed to develop a fast screening test for evaluating the ability of a coolant to protect the cooling system without having to test each and every candidate fluid in extended fleet tests.

Accelerated Aging Test Development

Any test to accelerate the aging of candidate coolants and allow the prediction of the results of extended testing must meet certain requirements. The test must be relatively fast. The faster the test can be run the better because a large number of test fluids can be evaluated in a short period. It should be possible to run the test on small scale samples, but also scale up the test so that sufficient amounts of the aged fluid can be generated for aged coolant performance testing. Ideally, the test would not require much capital investment and more ideally would use equipment already in the laboratory. The test must yield aged fluid that has both composition and properties similar to those of the authentic used fleet test fluid. These could, for instance, be the amount of ethylene glycol degradation products, pH, and corrosion inhibitor level. Most importantly, the performance of the laboratory-aged fluid must mimic the performance of the fleet-aged fluid.

There have been some studies related to the concept of accelerated aging reported in the literature and even some reported accelerated aging tests [*6–10*]. Some of these have focused on the degradation of ethylene glycol in the absence of corrosion inhibitors or have not specifically looked at the effects of the entire cooling system on coolant. None of the reported tests have had authentic aged coolant, and organic acid based coolant was used as the baseline for test development.

Parameters Evaluated—The parameters evaluated for the development of the accelerated aging test were the type of metal used, ratio among the metals, metal surface area, coolant concentration, test temperature, and thermal cycles. Various tests were run to explore the effect of each of these variables on the composition and properties of the coolant. Early work in the Union Carbide laboratory on the breakdown of ethylene glycol provided a great deal of useful information on this subject and allowed us to reduce the number of required experiments [*6,7*]. The objective of the Union Carbide study was to understand ethylene glycol breakdown under conditions found in the cooling system. This extensive work explored a large number of the variables that we felt were important, but focused on only a portion of the problem that we were trying to solve. While a large number of experiments were performed to develop the test, only a select few of these will be described.

A number of potential variables were fixed for ease of experimentation. The desired maximum test time was fixed at two weeks to coincide with glassware tests. This also allowed information to be generated and evaluated quickly. Intermediate solution samples were taken so that rate information was available. The intermediate information allowed us to probe for data on induction effects, changes in rate, and the like. We decided to carry out the test in the glassware apparatus if at all possible. This meant that we could evaluate large numbers of experiments in a short period of time without having to invest in additional equipment and without having to use large amounts of coolant and metals. The use of the glassware test

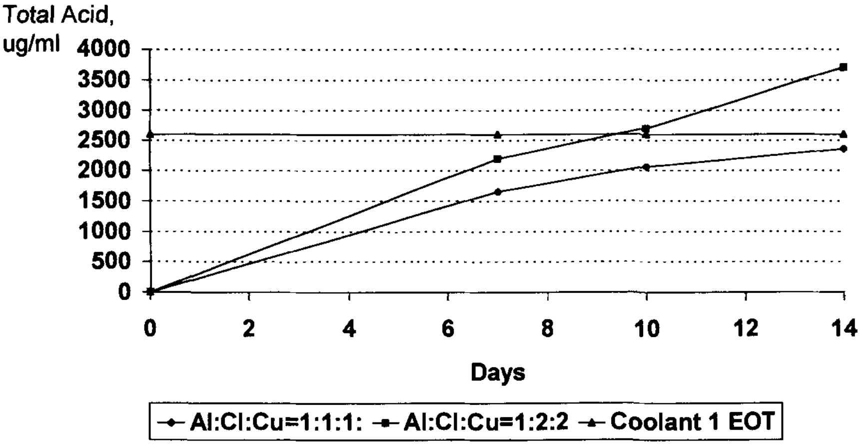

FIG. 1—*Ethylene glycol degradation product as a function of metal ratios.*

apparatus limited the amount of aged coolant that could be generated. Some of this disadvantage was overcome by the use of multiple glassware apparatus.

Metal Selection—The metals available for evaluation included all of the metals commonly found in light duty cooling systems. These included high and low lead solders, copper, brass, steel, cast iron, and aluminum. Early work in Union Carbide laboratories on the effects of different metals on the breakdown of glycol suggested that the most important metals for the oxidation of ethylene glycol were iron and copper [6,7]. Other common cooling systems metals and alloys were found to have no effect nor to inhibit glycol oxidation. We included these metals in our evaluation based on these results. Aluminum would not have been included based on the Union Carbide evaluation but was included in our tests because of the current importance of aluminum in cooling systems.

Figures 1 and 2 show the effect of varying the amount of the copper and iron while holding the amount of the aluminum constant on the amount of glycol degradation products generated and on the depletion of organic acid. Equal amounts of the metals, by weight, gave amounts

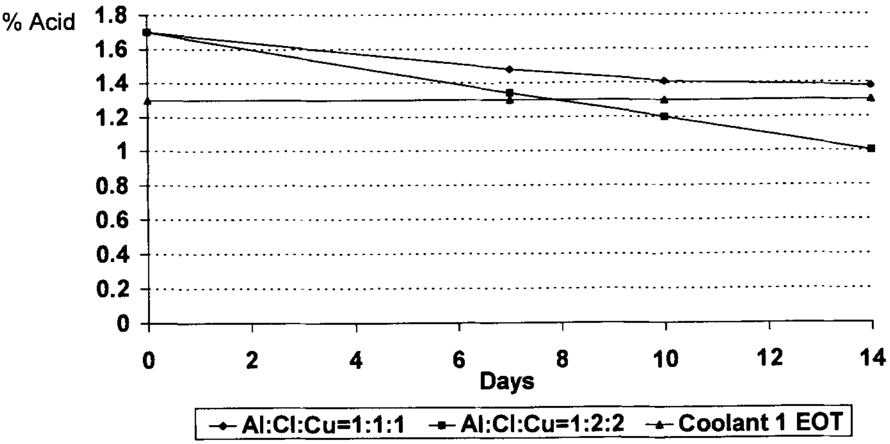

FIG. 2—*Inhibitor acid depletion as a function of metal ratio.*

TABLE 5—*Metal surface area.*

Metal Sample Used	Surface Area, cm^3
ASTM specimens	154
Granules	226
Shavings	379
Powder	781

of total degradation acids and that more closely approximated the desired result at the desired test increment than greater amounts of copper and cast iron.

The rate of glycol degradation, as measured by the increase in degradation acids present is nearly linear over the period for the test with larger amounts of cast iron and copper (Fig. 1). The oxidation rate appears to be slowing down during longer test periods for the lower levels of cast iron and copper. The distribution of the glycol oxidation products matched that observed for the end of test Coolant 1. There was no change in the ratio of the glycol oxidation products as the ratio of the metals changed.

Similar results are observed for the organic acid inhibitor depletion (Fig. 2). The amount of remaining inhibitor acid is lower in the solution with the larger amount of copper and iron. Consistent with the rate of ethylene glycol breakdown, the test solution with lower amounts of iron and copper shows a decreasing acid degradation rate with increasing time on test. The depletion rate with the larger amounts of copper and iron is linear over the test period.

The presence of the larger amount of aluminum may inhibit glycol oxidation due to copper and cast iron as shown in the Union Carbide work. The test solution with the 1 : 1 : 1 metal ratio has both a lower metal loading and a different ratio among the metals. The initial rate difference is consistent with either an inhibitory effect due to the relatively larger amount of aluminum or a reduced amount of active sites. The decrease in rate with time of the solution with the 1 : 1 : 1 ratio is consistent with a loss in active oxidation sites.

Metal Surface Area Evaluations—The effect on pH, accumulation of ethylene glycol degradation products, and inhibitor acid depletion as a function of surface area was studied. We used ASTM metal specimens, granular ASTM metals, shavings of the same metals, and metal powders. Extreme care was exercised in handling of the metal powders because their high surface area made them quite reactive. Equal weights of the metals were used. Approximate surface areas are shown in Table 5.

The effect of the different metal surface area on loss of inhibitor acid is shown in Fig. 3. As expected, the highest surface area resulted in the greatest loss of inhibitor acid. The level of organic acid in the test solution was below the desired target level seven days into the test. The level at the end of test was unacceptably low for the metal powder. Surprisingly, the next most active type of metal for inhibitor acid degradation was the metal specimens. The granular metals came the closest to the desired level of inhibitor acid. The metal shavings appeared to be the least active for degradation.

The oxidation of ethylene glycol was most pronounced with the powdered metal, Fig. 4. As with the depletion of the inhibitor acid the powdered metal appeared too active, with the target level exceeded very early in the test. The other forms of the metals were far less active. The amount of degradation acids formed with each of these species was similar to the desired level at the end of 14 days. There was much less difference in activity between these species than that seen in inhibitor depletion. The rate of ethylene glycol oxidation appeared linear for all but the powdered metal which showed a decrease in rate at longer test times.

The effects of metal surface area on pH, Fig. 5, were as expected based on the surface area

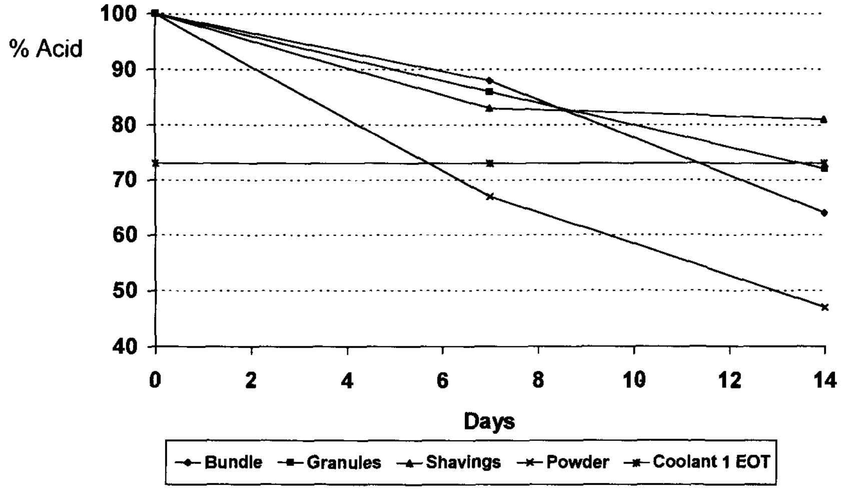

FIG. 3—*Inhibitor acid depletion as a function of metal type.*

of the metals used in each test solution. Higher surface area led to lower end of test pH. This result was not expected based on the amount of degradation acids and inhibitor acid depletion observed with bundles, granules, and shavings. As expected from the amount of glycol degradation products formed and the decrease in inhibitor acid, the pH drop for test solutions containing the powdered metal was the largest. The next largest pH drop was observed in test solutions containing metal shavings. Similar drops were observed for both the granules and the bundles. It appears that there are other contributions to the decrease in pH than just the amount of degradation acids formed and the loss of inhibitor acid. These other contributions have not yet been identified.

pH Variation—The effect of pH on glycol oxidation also was considered. The Union Carbide workers reported that glycol oxidation rates were high in both highly acidic and highly basic

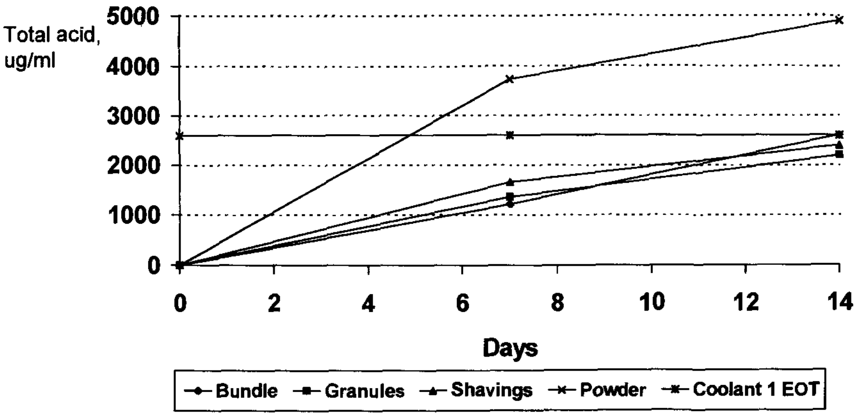

FIG. 4—*Ethylene glycol oxidation as a function of metal surface area.*

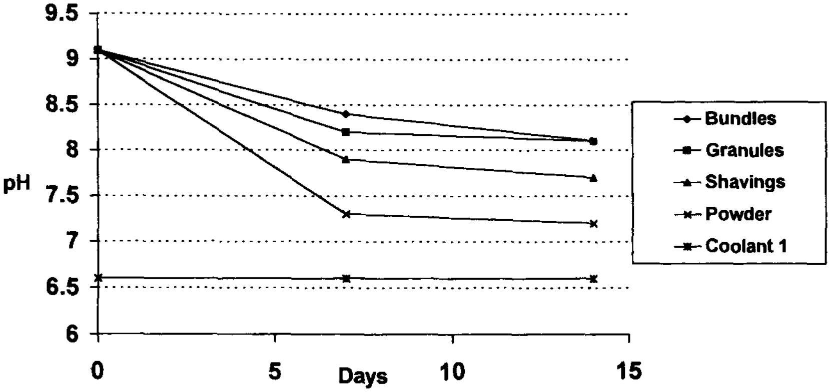

FIG. 5—*pH changes as a function of metal surface area.*

solutions and that slightly basic solutions were more prone to glycol oxidation than neutral or slightly acidic solutions [*6,7*]. As we were going to use the final pH of the test solution as an indicator of success there was no attempt to modify the pH of the initial solutions for test purposes. The coolant was tested at the normal pH of the formulation.

Test Coolant Concentration—Glycol oxidation was reported to increase as the concentration of glycol in an ethylene glycol/water solution increased [*6,7*]. This, combined with our observation that there is little ethylene glycol oxidation in typical laboratory coolant tests, suggested that we should try increased concentrations. In Figs. 6 and 7 the results of glycol oxidation and inhibitor acid depletion over the test period are plotted. The amount of glycol oxidation and inhibitor acid depletion obtained with the 50% solution was much lower than that with the 85% solution. The results at 50% do not approach the levels observed in the end-of-fleet-test fluid. The rate of ethylene glycol degradation and inhibitor acid depletion appears to slow at longer test times for the 85% solution. In the 50% solution the ethylene glycol degradation rate is fairly linear over the test period. There is an induction period that lasts most of the test period in the 50% solution. It is only after 10 days of testing that ethylene glycol

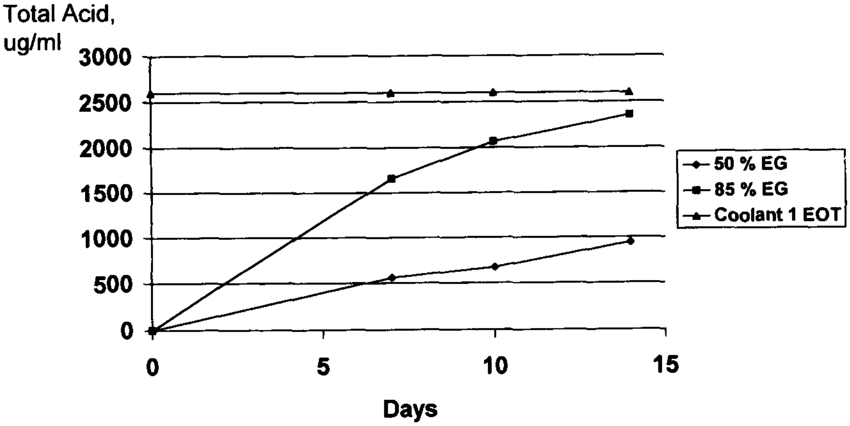

FIG. 6—*Degradation acid concentration as a function of coolant concentration.*

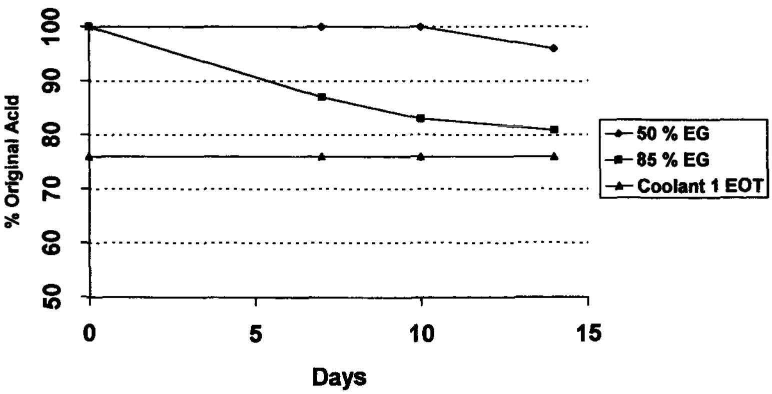

FIG. 7—*Inhibitor acid remaining as a function of coolant concentration.*

degradation is observed. Preliminary results using 100% coolant provided unacceptably high levels of degradation of the ethylene glycol and the inhibitor acids.

Test Temperature Effects—The Union Carbide study found that the rate of ethylene glycol degradation doubled for every 15°C increase in temperature under their test conditions. This work suggested that temperatures in the range accessible with the glassware apparatus would be appropriate for our study. We wanted to investigate temperatures that were representative of relatively high ones actually observed in cooling systems and selected 100 and 120°C for investigation. As shown in Figs. 8 and 9 there was too much activity at 120°C for the selected test period. The rate of both inhibitor acid depletion and ethylene glycol degradation was significantly greater at 120°C than at 100°C. The most appropriate temperature selected for the test protocol was 100°C. In addition, the rates of reaction at the lower temperature slowed at longer test times indicating a deactivation of the system.

Conclusions—A series of tests was carried out to determine optimum accelerated aging test conditions. The results of these tests suggested that test validation studies proceed with a test that lasted two weeks, had a 1:1:1 ratio of aluminum, cast iron, and copper, used metal shavings, used an 85% coolant concentration, and ran at 100°C. This provided a test that yielded

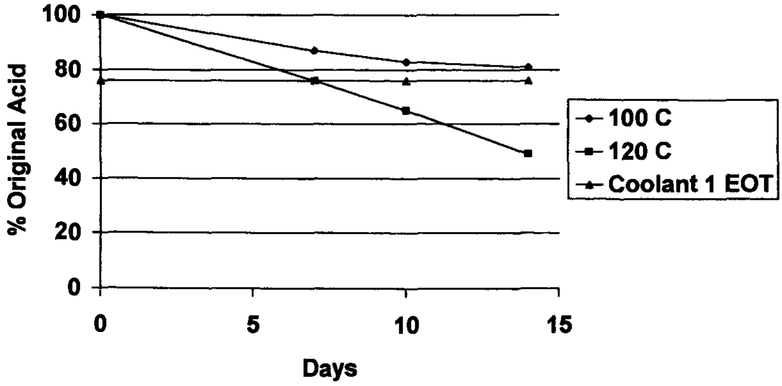

FIG. 8—*Percentage of inhibitor acid remaining as a function of test temperature.*

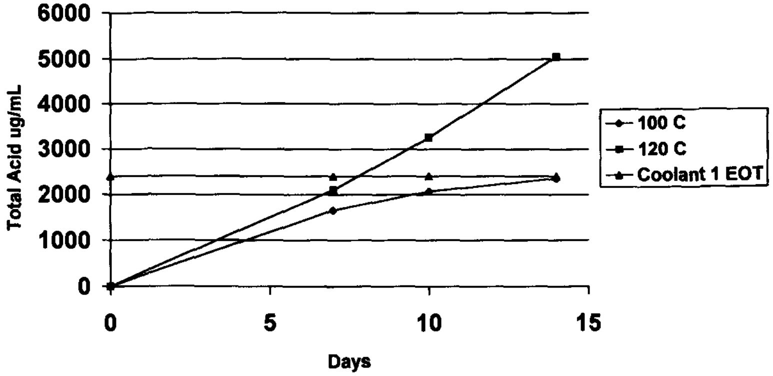

FIG. 9—*Degradation acid concentration as a function of test temperature.*

a coolant with essentially the same physical and chemical properties as the authentic end-of-test 100 000 mile (160 930 km) coolant.

Accelerated Aging Test Validation

The next step in the test development was to validate the test by comparing the corrosion inhibition performance of the aged fluid with that of the authentic 100 000 mile (160 930 km) fluid. In addition, we wanted to compare results obtained by aging other types of coolants with the authentic used coolants. The evaluation was divided into two parts: (1) determination of the physical and chemical properties of three fluids evaluated in long-term testing, and (2) evaluation of the corrosion inhibition properties of the coolants. These were the three fluids—one conventional silicated fluid and two organic acid fluids—discussed above.

Physical/Chemical Properties—The three coolants were aged via the proposed procedure. The chemical and physical properties of the aged coolants were examined to compare them with the authentic end of test values. The test would pass the first validation step if the chemical and physical properties of the test fluids matched those of the authentic fluids. The three physical/chemical properties chosen for this part of the validation were those used for test development: pH, percentage of major corrosion inhibitor lost, and generation of ethylene glycol degradation products. Since Coolant 3 was a conventional North American coolant, the major corrosion inhibitor examined was silicate. As discussed previously, our fleet testing of the conventional North American coolant showed normal silicate depletion over the course of the fleet test and no depletion of the buffer.

The pH of the test solutions is shown in Fig. 10 as a function of the time on test. As observed in the fleet testing, Coolant 1 has the lowest pH from the earliest test times. Coolant 2 pH is intermediate and Coolant 3 has the highest. These values are reflective of the buffer ranges for each system. The pH values for the organic acid coolants, Coolant 1 and Coolant 2, are much higher than expected. The end-of-fleet-test pH values for these coolants were slightly acidic to neural. The pH for Coolant 3 was slightly higher than that of the end-of-fleet-test samples.

Initially, we were skeptical of the pH values but dilution studies confirmed that the organic acid coolant pH values were far more sensitive to dilution than conventional coolants. Thus, dilution of each of the aged coolants resulted in a pH decrease, essentially to the observed end-of-fleet-test values. The decrease for the organic acid coolants was much larger as a function of the dilution amount than the conventional coolant, reflecting the differences in the buffer and buffer capacity between the coolants.

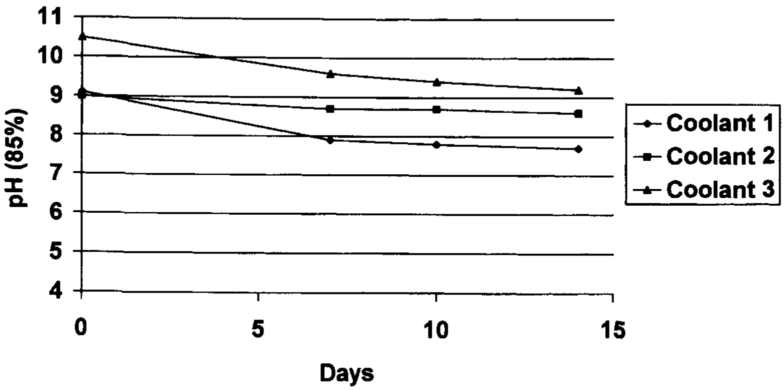

FIG. 10—*Test coolant pH.*

Similar results were obtained for the coolant corrosion inhibitors. The percentage of decrease in organic acid concentration for Coolants 1 and 2 is shown in Fig. 11 and Coolant 3 silicate depletion is shown in Fig. 12. As shown in the fleet testing, Coolant 1 retains approximately 70% of the initial acid level. Coolant 2 retains nearly all of the initial level of organic acid. The small (Coolant 1) or very small (Coolant 2) amount of organic acid depletion is consistent with that reported in the literature. There is a gross excess of organic acid over that required to completely cover and inhibit the metal surfaces in a cooling system. This is reflective of the dual role, inhibitor and buffer, that organic acid coolants play in these systems. The loss of organic acid from the solution is most probably not reflective of the formation of a protective coating on the metal surface but rather reflects a degradation of the organic acid. The difference in behavior of Coolants 1 and 2 is the subject of current research and may be the subject of a future paper.

The drop in silicate concentration from the Coolant 3 parallels that seen in fleet tests. The high initial level quickly drops as the protective metallo-silicate layer is formed on the surface. The level of silicate in solution continues to drop even after the rapid formation of the protective layer as a reserve silicate layer forms on the surface. The amount of silicate remaining in solution is just the equilibrium-soluble amount. Thus, in the aging test, equilibrium solubility is achieved between the third and seventh day and remains at essentially the same level for the

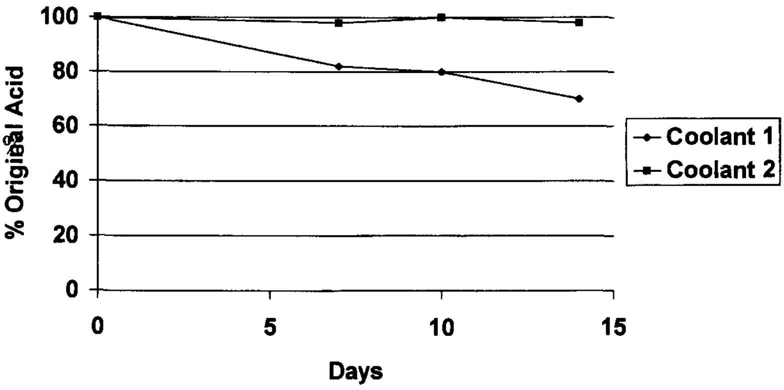

FIG. 11—*Test coolant inhibitor acid concentration.*

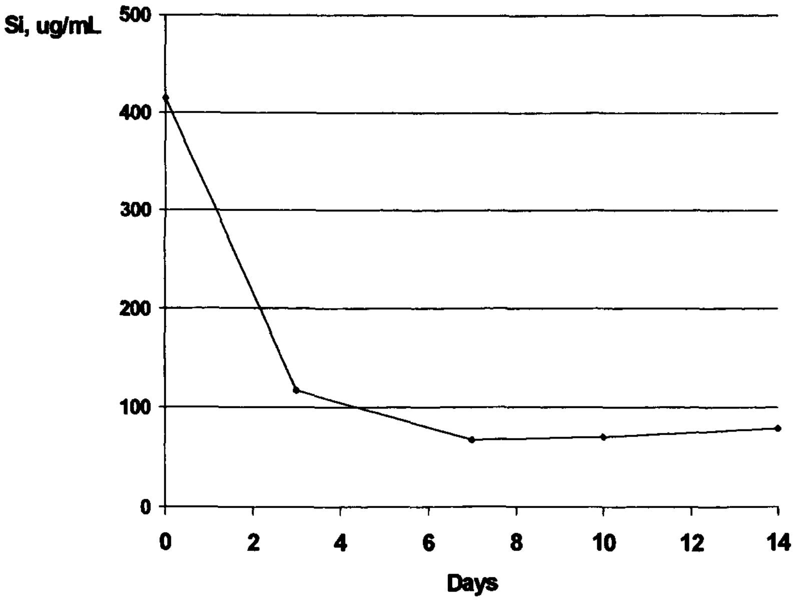

FIG. 12—*Silicate depletion in Coolant 3.*

remainder of the test. Similarly, in the fleet test the silicate level reaches the equilibrium level within the first 5000 miles (8000 km) and remains at that level throughout the test. The equilibrium solubility is nearly the same in the 85% solution as in the 50% solution. The silicate level at the end-of-test coolant is well represented by that in the aged coolant.

Laboratory Corrosion Tests

The next stage of validation for the accelerated aging test was to compare the laboratory test results for end-of-fleet-test coolants and the aged coolants. As discussed above, testing of used coolants is less a function of how the coolant would continue to function in the original cooling system than a measure of the reserve ability to prevent corrosion. The major test used was ASTM D 1384. The amount of coolant that can be generated in the accelerated aging test is limited by the size of the glassware beakers used and the number of test stands. The generation of enough coolant to perform such tests as the simulated service or pump test is time consuming and was not pursued although it is possible. ASTM D 4340 was evaluated but not reported because the end-of-test organic acid coolants passed this test quite easily and often showed improved performance over the virgin coolants.

Figure 13 shows the results of the ASTM D 1384 tests for the aged and end of test organic acid coolants. As indicated earlier, Coolant 1 showed a reduced reserve for the protection of the ferrous metals as compared with Coolant 2. The reduced reserve was shown in the high cast iron weight losses in ASTM D 1384 testing of the end of test Coolant 1. Aged Coolant 1 was unable to protect either ferrous metal tested. It appears that accelerated testing may result in a slightly more degraded coolant than fleet testing. The general conclusion is that Coolant 1, whether artificially aged or aged in a vehicle has lost its reserve for protection of ferrous metals while retaining reserve protection for the other test metals. The ability of the end-of-

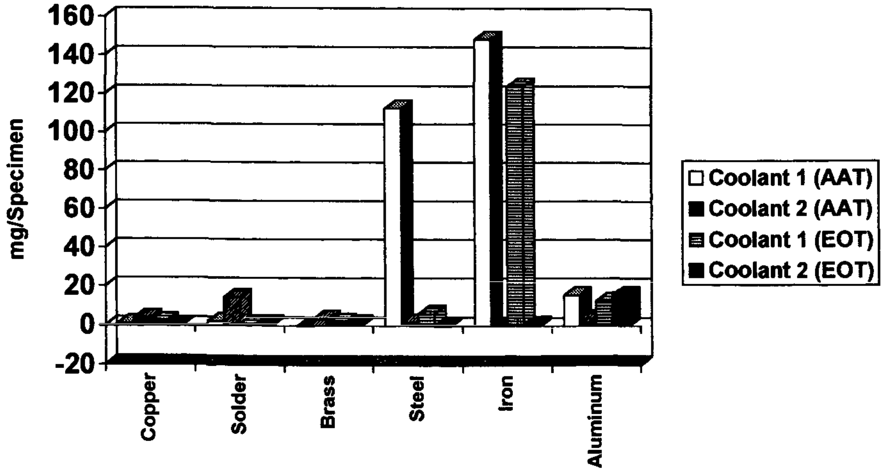

FIG. 13—*ASTM D 1384 test of aged and end-of-test coolants.*

test Coolant 1 to protect the other test metals is reflected in the aged fluid. The results for aged Coolant 2 are very similar to those of the end-of-test fluid.

Coolant 3 was also tested in ASTM D 1384 after aging and the results compared to those obtained for the end of fleet test fluid. Figure 14 compares the ASTM D 1384 test results for the virgin, end of test, and aged coolants. Like the tests comparing the results with the organic acid fluids, the tests with Coolant 3 showed that the general trend observed with the end of test fluid was observed in the aged fluid. Both coolants were able to protect all metals except cast iron. Unlike results with the organic acid fluids, the magnitude of the cast iron weight loss was less for the aged fluid than with the end-of-test fluid. It is anticipated that this difference is more a function of the variation in absolute weight losses seen in freely corroding systems than a function of a weakness in the test. Both possibilities continue to be pursued.

Test Validation Conclusions—The similarity in the chemical and physical properties of the aged and end-of-test fluids provides the first part of the evidence needed to validate the accelerated aging test. The second part is provided by comparison of the performance testing. These

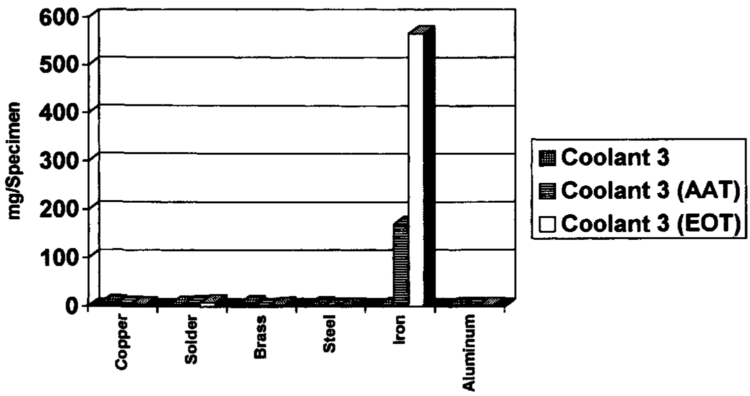

FIG. 14—*ASTM D 1384 test of Coolant 3.*

comparisons demonstrate that this test is capable of predicting in a very short time the results generated in extended fleet testing. This is a very useful tool. Of course, it cannot be used to completely eliminate the need for extensive fleet testing but does provide the researcher with an additional tool in coolant development.

The accelerated aging test provides the ability to leverage the knowledge gained in fleet tests for more extensive coolant development. Thus, candidate formulas can be evaluated in conventional laboratory tests as well as the accelerated aging test before fleet testing. The inclusion of the accelerated aging test allows a larger number of formulas to be screened than would be possible using fleet tests and can prevent fleet testing of marginal formulas.

Coolant Development Efforts Using Accelerated Aging

The final stage in the development of this test was to utilize it to develop advanced organic acid formulas. The goal of this section of the research was to put to use what we had learned in the testing and evaluation of Coolants 1 and 2 and formulate a better product. There appeared to be several areas where we could improve these formulas just in the parameters that we investigated. In addition to trying to improve end-of-test performance, degradation of ethylene glycol, pH drop, and loss of inhibitor acids, we also were trying to prepare formulas that would have cost and manufacturing advantages over Coolants 1 and 2. The evaluations include the use of new combinations of organic acids and modified inhibitor levels. Initial results of this development are shown next.

Chemical/Physical Properties—The chemical and physical properties of interest were those that we used to develop the test. Coolant 4 is one of a series of formulations developed, building on the knowledge gained in testing of Coolants 1 and 2. This formula offers cost and manufacturing advantages over both of the latter formulas as well as the performance advantages shown below.

A comparison of the amount of glycol degradation products formed during the course of the accelerated aging test is shown in Fig. 15. Both Coolant 2 and Coolant 4 show improved performance relative to Coolant 1. A significantly smaller amount of ethylene glycol degradation products is present in each solution after the accelerated aging test. In addition, Coolant 4 offers a slight performance edge over Coolant 2 because it has slightly fewer degradation products than Coolant 2. The large difference in the amount of ethylene glycol degradation products between Coolant 1 and Coolants 2 and 4 is attributed to differences in the corrosion

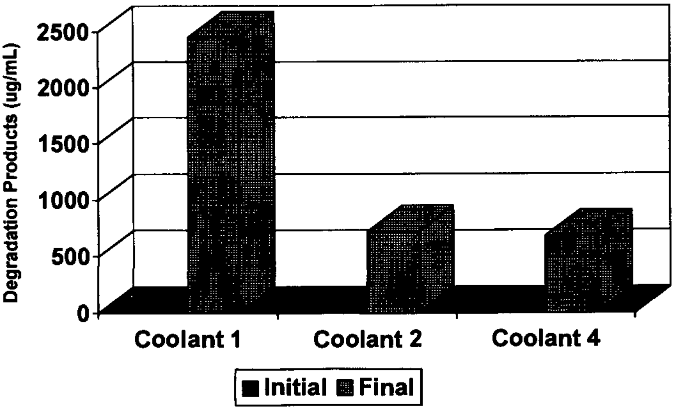

FIG. 15—*Ethylene glycol degradation products after accelerated aging.*

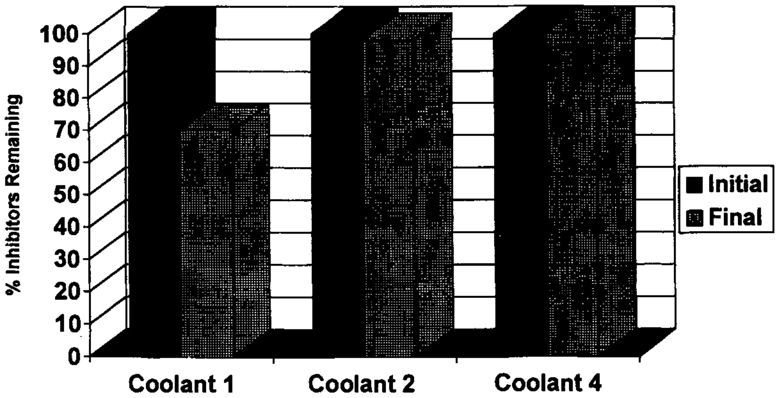

FIG. 16—*Percentage of organic acid inhibitors remaining after accelerated aging.*

inhibitor package. The ethylene glycol degradation in Coolant 1 was due to a combination of the effects due to the presence of cooling system metals and effects due to part of the corrosion inhibitor package. Neither Coolant 2 nor 4 uses these corrosion inhibitors.

Coolants 2 and 4 retain considerably more of the initial level of corrosion inhibitors than Coolant 1. Again, there is a small advantage of Coolant 4 over Coolant 2. The difference between Coolant 1 and the other two coolants is probably due to the removal of the same corrosion inhibitors which led to greater degradation of ethylene glycol in Coolant 1. There may also be differences associated with the selection of the organic acid used that led to the observed differences between Coolant 2 and Coolant 4.

As discussed above, the observed pH drop is primarily a function of the organic acid inhibitors remaining in the solution after a test, the type of organic acid used, and the amount of ethylene glycol degradation products generated during the test. There is a dramatic difference in the observed pH drop between Coolant 4 and Coolants 1 and 2. All of the above parameters play a role. The difference in the organic acids used alters the buffer range of the coolant. In addition, as shown above, there are fewer degradation acids generated and a greater amount of remaining organic acid in solution at the end of the test. The differences between Coolants 2 and 4 are attributable to the different organic acids used in the formulations.

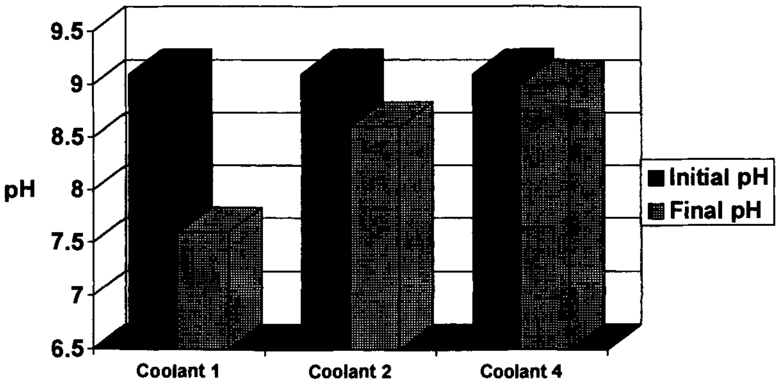

FIG. 17—*Test coolant pH.*

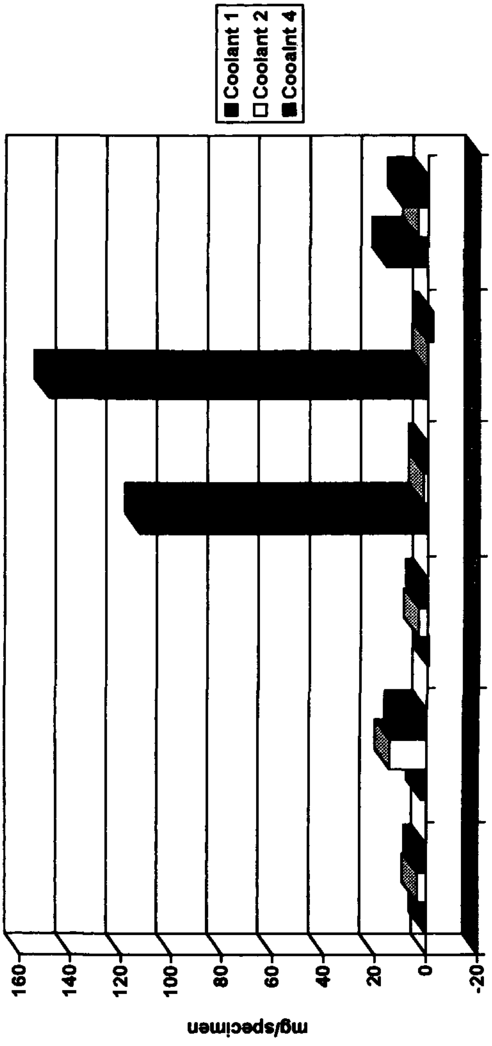

FIG. 18—*ASTM D 1384 testing of aged coolants.*

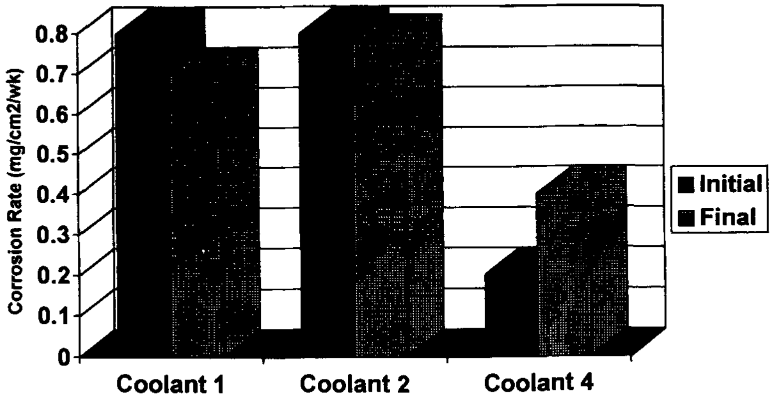

FIG. 19—*ASTM D 4340 testing of aged coolants.*

Performance Tests—As part of the performance evaluation of candidate formulas the post-accelerated aging test fluid is tested in D 1384 and D 4340. As discussed previously, the use of these tests on aged coolant allows a measure of the reserve in the coolant and allows a prediction of the performance at higher mileage intervals. It was clear from the evaluation of Coolant 1 that it was able to protect the cooling system metals for the entire fleet test but had a limited reserve, especially for the protection of the ferrous metals. Coolant 2 offered an improved reserve compared with Coolant 1. It was anticipated that Coolant 4 would have better performance than Coolant 1 based on the comparison of physical and chemical properties after accelerated aging, and it was hoped that Coolant 4 would offer advantages over Coolant 2, as well.

Figure 18 shows the performance of the three aged fluids in ASTM D 1384. The lack of reserve in Coolant 1 for ferrous metals is clearly shown by the large weight losses for both cast iron and steel. The anticipated performance advantages of Coolant 4 over Coolant 1 were demonstrated in this test. However, there were no performance advantages observed for Coolant 4 over Coolant 2.

Coolant 4 does offer performance advantages over both Coolant 1 and Coolant 2 with respect to the protection of heat-rejecting aluminum as measured in D 4340. The advantages are apparent in both the virgin and aged coolant. There is a small increase in the corrosion rate as a result of the aging protocol with Coolant 4. Unlike Coolant 4, both Coolants 1 and 2 show small improvements in the performance in D 4340.

Coolant Development Conclusions—The accelerated aging test has allowed the rapid evaluation of candidate formulas and the development of Coolant 4. It is expected that Coolant 4 will offer significant advantages over Coolants 1 and 2 in use and have a more substantial inhibition reserve at high mileage intervals. This should allow Coolant 4 to protect more effectively against cooling system upsets and also allow extension of the coolant drain interval. Coolant 4 is currently being fleet tested to confirm the results of the accelerated aging test.

Conclusion

An accelerated aging test has been developed. This test uses standard laboratory glassware and immerses common cooling system metals in a concentrated aqueous solution of coolant for a two-week period. The resulting coolant has chemical, physical, and performance properties which mimic those of a coolant that has been in the cooling system for an extended time. The development of the accelerated aging test allows a rapid evaluation of the ability of a coolant to protect cooling systems at the end of 100 000 miles. The coolant generated in the accelerated aging test can be tested in other performance tests. We believe that this test will be a useful addition to the repertoire of performance tests available to coolant development scientists.

Acknowledgments

The authors wish to acknowledge the efforts of all of the Prestone Products laboratory staff. Without their efforts none of this work would have been possible.

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Rapid Electrochemical Screening of Engine Coolants. Correlation of Electrochemical Potentiometric Measurements with ASTM D 1384 Glassware Corrosion Test

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REFERENCE: Doucet, G. P., Jackson, J. M., Kriegel, O. A., Passwater, D. K., and Prieto, N. E., "**Rapid Electrochemical Screening of Engine Coolants. Correlation of Electrochemical Potentiometric Measurements with ASTM D 1384 Glassware Corrosion Test,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 133–141.

ABSTRACT: Engine coolants are typically subjected to comprehensive performance evaluations that involve multiple laboratory and field tests. These tests can take several weeks to conduct and can be expensive. The tests can involve everything from preliminary chemical screening to long term fleet tests. An important test conducted at the beginning of coolant formula development to screen the corrosion performance of engine coolants is described in ASTM D 1384. If the coolant formula passes this test, it is then subjected to more rigorous testing. Conducting the test described in ASTM D 1384 takes two weeks, and determining the coolant corrosion performance under several test parameters can take resources and time that users seldom have. Therefore, it is very desirable to have tests that can be used for rapid screening and quality assurance of coolants.

The purpose of this study was to conduct electrochemical tests that can ultimately be used for quick initial screening of engine coolants. The specific intent of the electrochemical tests is to use ASTM D 1384 as a model and to attempt to duplicate its results. Implementation of the electrochemical tests could accelerate the process of selecting promising coolant formulas and reduce coolant evaluation time and cost.

Various electrochemical tests were conducted to determine the corrosion performance of several engine coolant formulas. The test results were compared to those obtained from the ASTM D 1384 test. These tests were conducted on the same metal specimens and under similar conditions as those used in the ASTM D 1384 test. The electrochemical tests included the determination of open circuit potential (OCP) for the various metal specimens, anodic and cathodic polarization curves for the various metal specimens, corrosion rate for metal specimens involved in a galvanic triad, and critical pitting potential (CPP) for aluminum (pitting of aluminum engine components and cooling systems is a cause for concern).

The details for the methods and the correlation of the results to ASTM D 1384 tests results will be presented.

KEYWORDS: coolant, corrosion, engine, electrochemical testing

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Test Setup

Test Apparatus

Apparatus for the electrochemical tests consisted of a Solartron 1284 potentiostat with a computer interface and controller, a glass test cell (1 L) with water jacket, and a Luggin Probe equipped with a saturated calomel reference electrode (Fig. 1).

Metal Test Specimens

The metals used in the tests were aluminum, brass, cast iron, copper, lead, and steel. The alloy compositions are those recommended in ASTM Standard Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384).

Test Solution

The test solution consisted of 25% coolant and 75% corrosive water conforming to the requirements of ASTM D 1384. The solution was altered from 33⅓% coolant to have sufficient solution conductivity for electrochemical measurements.

Heating/Aeration of Solution

The test cell was filled with coolant test solution and kept heated at a temperature of 88°C. The solution was aerated in accordance with ASTM D 1384 during the tests.

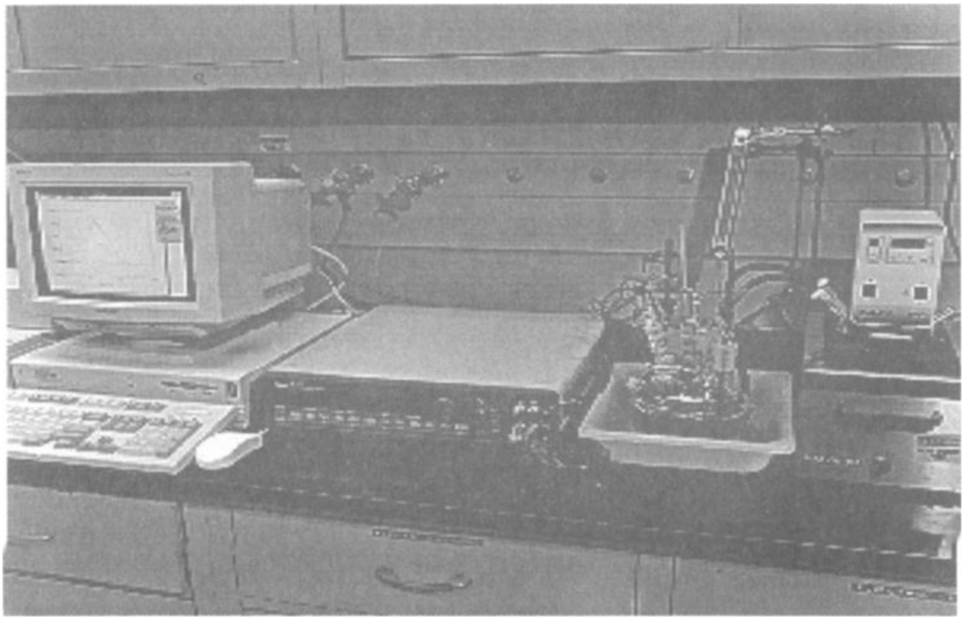

FIG. 1—*Test setup.*

Test Procedures

Comparison to ASTM G 5

To ensure that the electrochemical equipment was operating properly, the electrochemical tests were compared to the reference test methods in ASTM Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements (G 5).

Number of Tests Performed

Every electrochemical test was run at least three duplicate times. Fresh solution and new coupons were used in every test to ensure repeatability. The standard ASTM D 1384 tests were run in triplicate, and the results were compared to those of the electrochemical tests.

Open Circuit Potential

Low silicate ($\leq$250 ppm Si) engine coolant was used to determine the open circuit potential (OCP) of the metals. The OCP was determined by immersing the metal specimen in the heated solution and monitoring the potential for a minimum of 12 h. This ensured that a stable OCP had been reached. Typically, stable OCPs were reached after 3 h. The OCP was measured relative to the saturated calomel electrode (SCE) reference electrode. The OCPs were used to develop appropriate working and experimental parameters for the other electrochemical tests.

Anodic and Cathodic Polarization Curves

Low silicate coolant was used in generating the anodic and cathodic polarization curves of the metal specimens. Scan rates of 0.1667 mV/s were used from the OCP to potentials up to 1 V from the OCP.

Galvanic Triad Corrosion Rate

Because ASTM D 1384 requires the coupling of three different metals, a galvanic system is created. The combination of the three test metals in contact is referred to as a galvanic triad. Polarization and OCP studies were necessary to support galvanic testing.

Low silicate engine coolant was used to determine the galvanic triad corrosion rate. Corrosion rate was determined for metals in two sets of galvanic triads (1) aluminum, steel, and cast iron and (2) lead, copper, and brass.[6] The potentiostat was used in the zero resistance ammeter mode. Equal electrode areas were maintained. The potential of the triad was measured relative to the SCE reference electrode.

Critical Pitting Potential

Low silicate, high silicate ($>$250 ppm silicon), and organic acid type engine coolants were used to determine CPPs of aluminum.[6] The CPP was measured relative to the SCE reference electrode. Anodic polarization was conducted on aluminum from OCP at 1 mV/s up to 1 V above OCP.

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TABLE 1—*OCP of metal specimens.*

Metal	V (SCE)
Cast iron	−0.297
Aluminum	−0.580
Brass	−0.327
Copper	−0.172
Carbon steel	−0.326
Solder	−0.627

Test Results and Discussion

Open Circuit Potentials

The OCPs that were determined for the metal specimens are shown on Table 1.

Accurate OCP measurement was critical for the validity of this study. The relationship of the OCPs of the individual metals is essential to understand galvanic relationship (Figs. 2 and 3).

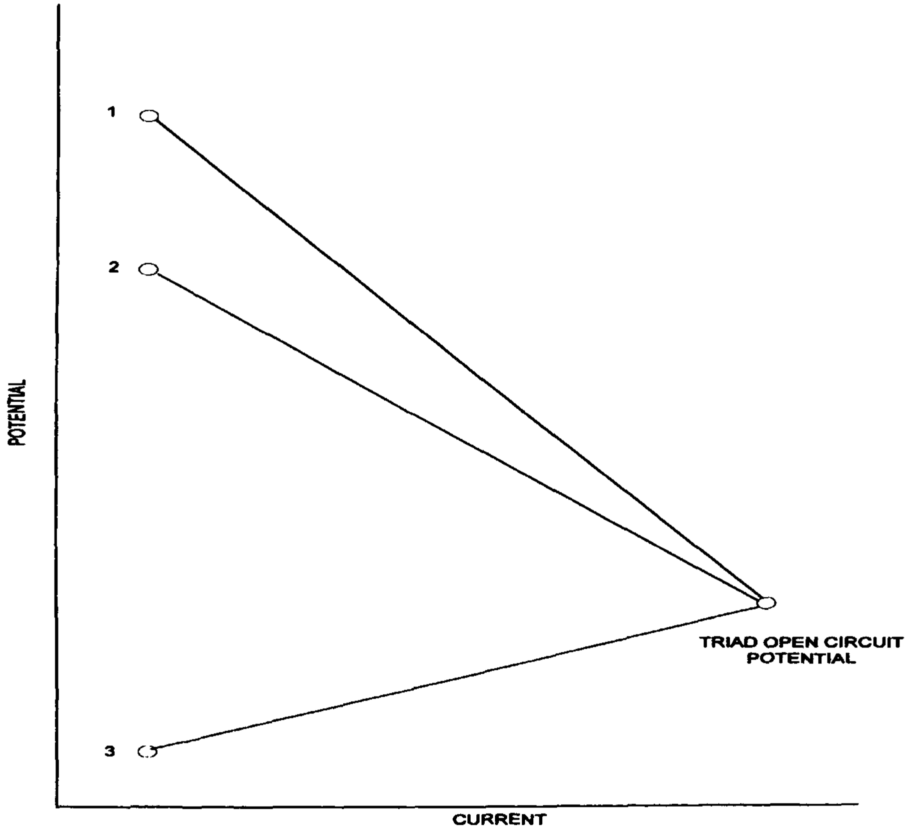

FIG. 2—*Example of galvanic triad with one anodic metal.*

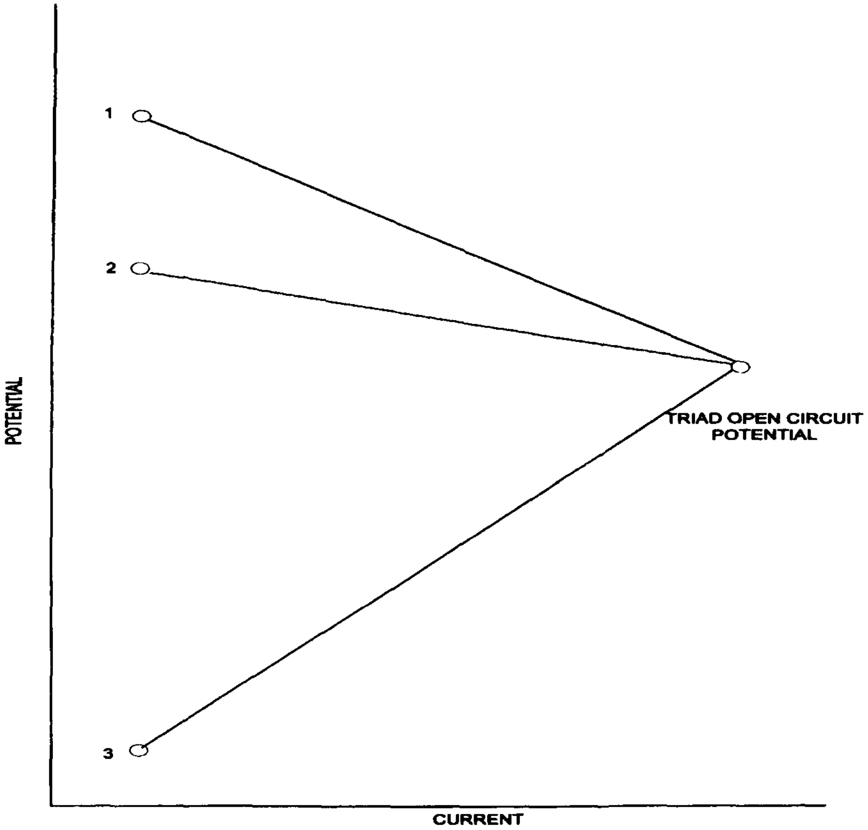

FIG. 3—*Example of galvanic triad with two anodic metals.*

Anodic and Cathodic Polarization Curves

The anodic and cathodic polarization curves generated for some of the metal specimens are shown in Figs. 4 and 5. Polarization curves can be used to determine corrosion rates for individual metals using Tofel extrapolation. This was of little use for the intent of this study because ASTM D 1384 uses coupled metals and corrosion rates measured via coupling do not correlate to those generated via polarization. However, these curves proved valuable to determine corrosion rates when two metals acted as anodes in a triad. The potential of the triad was used to determine the corrosion current from the polarization curves of the individual metals. The polarization curves were also used to determine the current required to be applied to individual metals in order to achieve the same potential as their triad. This current can be used to calculate the corrosion rate of the metals that are not in the triad.

Galvanic Triad Corrosion Rate

The potential and corrosion rates that were determined for the galvanic triads are shown on Table 2.

Two methods were used to determine the corrosion rate.[6] The first method was used when

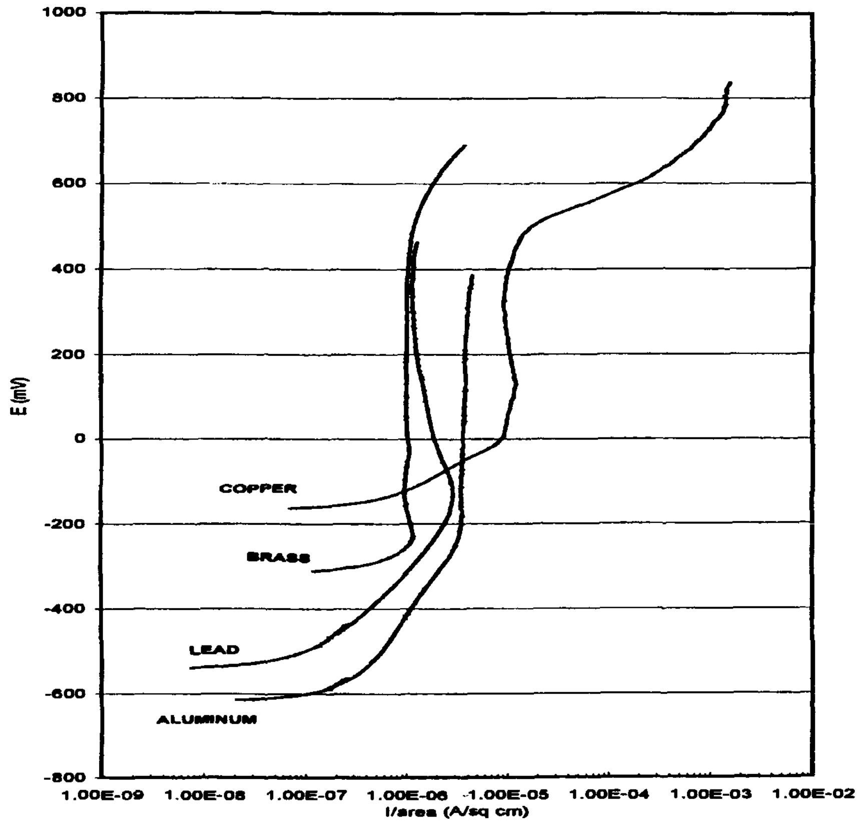

FIG. 4—*Anodic polarization curves.*

two metal specimens were cathodic to their OCPs. The measured current was used to calculate the corrosion rate for the one metal that was anodic to its OCP (see Fig. 2). The second method was used when two metal specimens were anodic to their OCPs (see Fig. 3). In this case, corrosion occurred on two of the metals; therefore, the measured current could not be used to calculate corrosion rate. The following additional step was required to determine the corrosion rate. Either the two anodic metals were individually polarized to the triads potential and the measured current was used to calculate the corrosion rate, or the corrosion rate was calculated from polarization curves. These two methods of calculating the corrosion rate are essentially equivalent and can be used as a quality check on the data. Conducting this additional step required only nominal additional time.

ASTM D 1384 test procedures require electrical contact of three different metal specimens. Therefore, galvanic type experiments are deemed the most appropriate method for simulating this procedure. Rapid results were obtainable in the first case discussed in the OCP section (two cathodic metals). Both of the galvanic triads corresponded to this type of triad. Measured current corresponded to the corrosion rate of the anodic material. Metal specimens were determined to be anodic or cathodic based on their individual OCPs as compared to that of the triad.

A comparison of the corrosion rate determined from the galvanic triad and the corrosion rate determined from the ASTM D 1384 test is shown on Table 3.

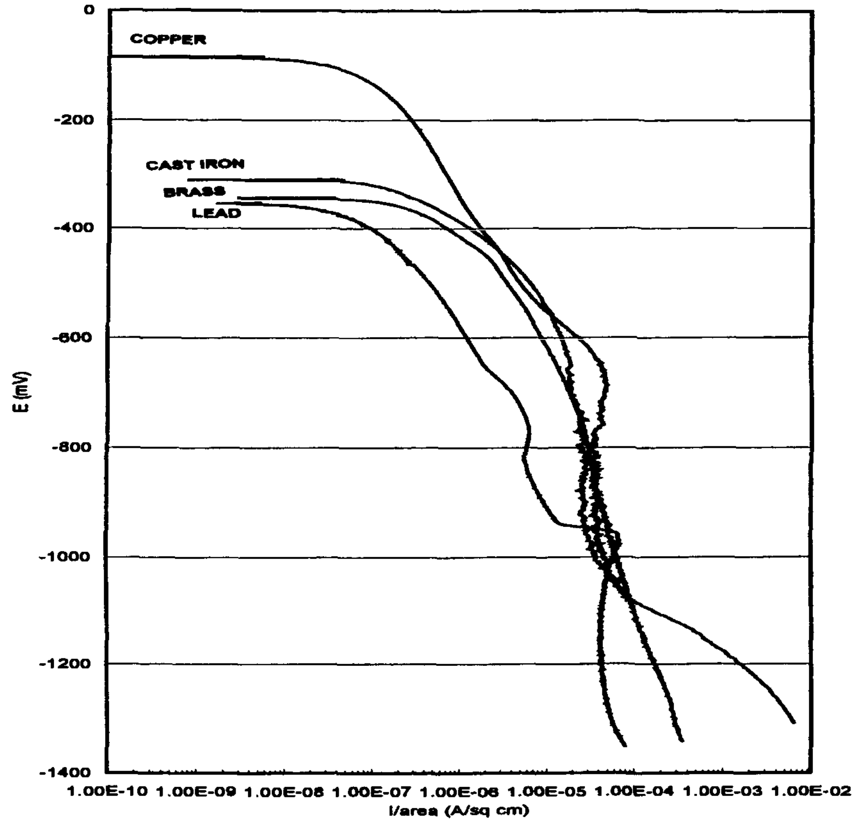

FIG. 5—*Cathodic polarization curves.*

TABLE 2—*Galvanic triad results.*

Triad	Potential	Corrosion Rate
Solder, copper, and brass	−0.3950	solder 0.48 MPY
Cast iron, carbon steel, and aluminum	−0.4320	aluminum 5.78 MPY

TABLE 3—*Comparison of galvanic triad and ASTM D 1384 results.*

Metal	Corrosion Rate for Galvanic Triad, MPY	Corrosion Rate for ASTM D 1384 Test, MPY
Cast iron	N/A[a]	. . .
Steel	N/A[a]	. . .
Aluminum	5.78	8.24
Solder	0.48	0.28
Brass	N/A[a]	. . .
Copper	N/A[a]	. . .

[a] These metals acted as cathodes in the triad; therefore, corrosion rate could not be determined.

TABLE 4—*Aluminum CPPs.*

Coolant Solution	CPP	Δ Between OCP and CPP
Low silicate	−0.58	0.2
High silicate	−0.5	0.0
Organic acid	1.0	N/A

The electrochemical test could determine corrosion rate only for the metals acting as anodes. While some corrosion occurs to the cathodic metals in the ASTM D 1384 test, the anodic metals always provide some protection to the cathodic metals. Thus, the results of the electrochemical tests are expected to be consistent with a pass/no pass criteria.

Critical Pitting Potential

The CPPs for aluminum with different engine coolant solutions are shown on Table 4.

The importance of the CPPs can be understood by examining Fig. 6. This figure shows the relationship of current versus potential for a conventional coolant and for an organic acid type coolant. The curves follow classical paths. After the point where passivation breaks down the current increases rapidly with small increases in potential. The potential at the point where passivation breaks down is called the CPP. The test results showed that organic acid type coolant is the most effective coolant tested in preventing onset of pitting in aluminum. Note

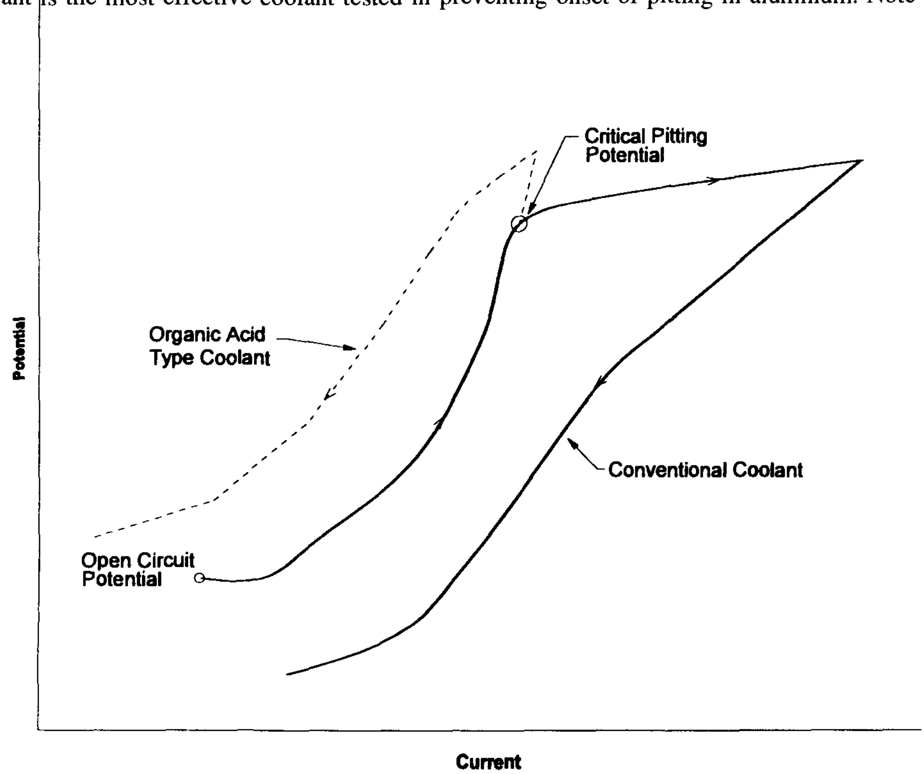

FIG. 6—*Example of critical pitting potential curve.*

that there is not a rapid rise in current as potential is increased, indicating that no pitting has occurred. The reverse scan is behind the original curve, indicating that the metal remains passive, which is expected as passivity did not break down.

Significance of the coolant CPP can be interpreted using various techniques. A common technique is to run galvanostatic tests that require the coolant to pass a certain minimum break point. Though this technique can provide some useful information, another technique that can provide more useful information is comparing the OCP to the CPP. This difference between the two potentials (called Δ in the table), gives a relative indication of the ability of the coolant to prevent pitting. Since the potential of metals in inhibited solutions tends to become more positive with time as inhibitor components break down, the difference between the two potentials can indicate a coolant's ability to prevent corrosion over a longer time frame.

Another possible shortcoming of galvanostatic tests can be caused by the fact that the OCP for the same grade of aluminum is different in different coolants. Therefore, a specific potential value that has been established as a pass/fail criteria may require only a minimal increase in potential for one coolant and a large increase in potential for another coolant, that is, one coolant may actually provide better long term service and not pass a screening galvanostatic test.

Conclusions

1. Results of the electrochemical tests were reasonably consistent with results from the ASTM D 1384 test.
2. The metal loss determined by averaging the results of three electrochemical tests was within a factor of two of the metal loss determined by ASTM D 1384.
3. The average time, including setup time, required to conduct an electrochemical test is one day. This can mean significant time savings compared to traditional tests.
4. Electrochemical tests show promise for screening and quality assurance applications.
5. Results of the galvanic triad corrosion rate test seemed to correlate best with the ASTM D 1384 test.

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Long-Term Serviceability of Elastomers in Modern Engine Coolants

REFERENCE: Bussem, H., Farinella, A. C., and Hertz, D. L., Jr., "**Long-Term Serviceability of Elastomers in Modern Engine Coolants,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335,* R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 142–180.

ABSTRACT: The aging of elastomers in engine coolants after extended periods of service can be both a physical process (stress/strain relaxation) and/or a chemical change. Engine coolants are essentially aqueous and non-aqueous electrolytes coupled with inorganic inhibitor systems, as well as new organic acid systems. The long-term effects of this environment are reviewed. Chemical and functional tests are utilized to model these aging processes. This review will offer a better understanding of the long-term suitability of typical candidate elastomers.

KEYWORDS: coolants, aging, inorganic inhibitors, organic acid inhibitors, elastomer

The long-term suitability of elastomers in heavy-duty engine coolants is a function of both oxidative resistance (atmospheric environment) and coolant effects (reductive environment). Seals will be subject to both environments. The test program includes tests that will give adequate long-term data on both the physical and chemical shifts that might lead to premature failures.

The basic function of coolant inhibitor agents is to prevent corrosion. "Corrosion is the process of surface deterioration of metals and related materials. The alteration occurs by the metal, *M*, losing *m* electrons and becoming a positive ion" [*1*] as in the equation

$$M^0 \rightarrow M^{m+} + me^- \qquad (1)$$

To prevent this electron loss (oxidation) the inhibitor must supply an electron to the ion (reduction). The reductive environment must be necessity dominate, thus any related materials must be resistant to this same environment. The electro-chemistry involved is that of Lewis acid-base concepts, simply defined as:

Acid: "Any species that can accept a share in a pair of electrons during a chemical reaction" [*7*] (electron pair acceptor, or EPA).

Base: "Any species that can donate a share in a pair of electrons during a chemical reaction" [*7*] (electron pair donor, or EPD).

"Neutralization is the coordinate bond formation between the acid and the base:" [*7*]

$$A + {:}B = A{:}B \qquad (2)$$

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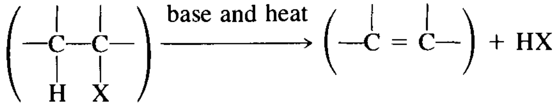
Certain elastomers or their crosslinking systems will eventually be attacked by these electron pair donors (EPDs). For example, vinylidene fluoride based fluoropolymers may be attacked via two mechanisms:

1. Crosslink scission via hydro-alkoxy elimination.
2. De-hydrofluorination of the polymer backbone (which consists of geminal difluorides) by a strong base (EPD) as shown [*4*]



$$\left(\begin{array}{c} | \quad | \\ -\mathrm{C}-\mathrm{C}- \\ | \quad | \\ \mathrm{H} \quad \mathrm{X} \end{array}\right) \xrightarrow{\text{base and heat}} \left(\begin{array}{c} | \quad | \\ -\mathrm{C}=\mathrm{C}- \end{array}\right) + \mathrm{HX} \qquad (3)$$

where X is a halogen.

Acrylonitrile copolymers may also be attacked. Acrylonitrile (RCN) is a reaction product of propylene, oxygen and ammonia as shown [*4*]

$$2CH_2 = CHCH_3 + 3O_2 + 2NH_3 \rightarrow 2CH_2 = CHCN + 6H_2O \qquad (4)$$

The degradation mechanism is [*4*]

$$RCN \xrightarrow{\text{EPD}} RH \qquad (5)$$

which is the reverse of the reaction of Eq 4.

Experimental Method

Test Procedure

Four candidate elastomers were tested: NBR (nitrile rubber), HNBR (hydrogenated nitrile rubber), EPDM (ethylene-propylene terpolymer) and FEPM (tetrafluoroethylene-propylene copolymer) formulations. Standard AS568-214 O-rings were tested in a fixture as shown in Fig. 1[4] in accordance with ASTM D 1414. The following parameters outline the test matrix used:

(*a*) Aging for 100, 500, 1000, and 1500 h at 150°, 175°, and 200°C while under approximately 22% compression.

(*b*) Aging in both inorganic inhibited coolant, subsequently referred to as IIC (Fleetguard Compleat with DCA4)[5] and organic acid inhibited coolant, subsequently referred to as OAC (CAT EC1).[6]

Conventional dry-heat aging of the elastomers at similar time and temperatures was also performed. Dry heat aging tests were in conformance with ASTM D 395 and ASTM D 412.

Additional tests included:

(*a*) Monitoring pH shifts of aged test fluids compared to control fluid.

(*b*) Calculating strain energy density at 20% extension for both aged and original test specimens.

(*c*) Monitoring fluoride ion (F^-) activity for indication of nucleophilic attack on the fluoroelastomer.

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[4] For test fixture specifications, see drawing SK 1483 in the appendix.

[5] Trademark of Cummins Engine Company.

[6] Trademark of Caterpillar, Inc.

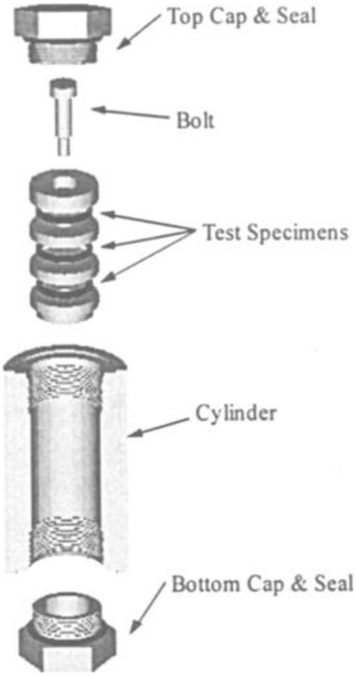

FIG. 1—*Test fixture, exploded view.*

The test fixture SK1483 (see the appendix for dimensions of the test fixture) is designed to simulate a realistic application of O-rings subjected to oxidative/vapor phase conditions on the top seal (Fig. 2). The bottom seal is subject to liquid phase/oxidative processes. The coolant to seal volume ratio was approximately 30:1 (in service there is typically an infinite amount of

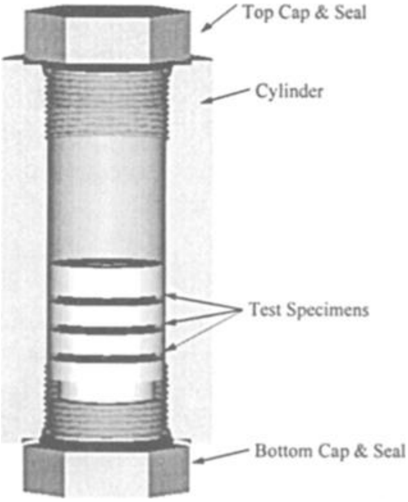

FIG. 2—*Test fixture assembly.*

fluid and a finite amount of seal material). As some elastomers degrade, fluid pH may be driven down, eliminating the fluid as an electron donor. Laboratory testing usually considers infinite seal volume and finite fluid volume, and thus often leads to flawed conclusions.

Calculations

Reported variables include: compression set; load, displacement, stress and strain to break; strain energy density at 20% elongation; and Shore M and A durometer.

Compression set, C, was calculated as the ratio of permanent strain to imposed strain. The equation used for an O-ring is

$$C = \frac{\varepsilon_p}{\varepsilon_i} = \left(\frac{t - t_{\text{final}}}{t}\right) \div \left(\frac{t - t_{\text{fixture}}}{t}\right) = \frac{t - t_{\text{final}}}{t - t_{\text{fixture}}} \tag{6}$$

where

ε_p = permanent strain (set),
ε_i = imposed strain,
t_{final} = thickness of O-ring after aging
t_{fixture} = distance between plates of test fixture (2.77 mm or 0.109 in.), and
t = original wall thickness.

Maximum load and displacement data are simply read from the data recorded by the Instron testing machine.

The cross sectional areas of an O-ring as shown in Fig. 3 is

$$A = \frac{1}{2}\pi \cdot t^2 \tag{7}$$

Engineering stress then is

$$\sigma = \frac{P}{A} \tag{8}$$

where P is the load measured by the tension testing machine.

Engineering strain (as per ASTM D 1414) is based on the inside circumference of the

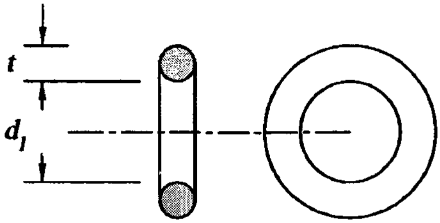

FIG. 3—*O-ring measurements.*

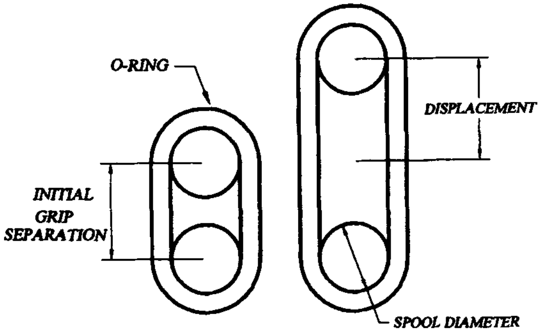

FIG. 4—*Grip configuration.*

O-ring. Initial inside circumference, l_o (Fig. 4) is used as the gage length; current inside circumference is used as current length, l_c. Thus engineering strain is

$$\varepsilon = \frac{l_c - l_o}{l_o} \tag{9}$$

Strain energy density at 20% elongation, $W(20\%)$ (work per unit volume), is calculated as the integral of the stress versus strain curve from 0 to 20% strain. Since the tension testing machine takes data at discrete points, the integral is approximated

$$W(20\%) = \int_0^{\varepsilon=20\%} \sigma \cdot d\varepsilon \approx \sum_{i=1}^{n} \frac{(\sigma_i + \sigma_{i-1})}{2} \cdot (\varepsilon_i - \varepsilon_{i-1}) \tag{10}$$

where

σ = engineering stress (as previously defined),
ε = engineering strain (as previously defined), and
$\varepsilon_{n+1} \cong 20\%$

Results

Fluid Aged O-Rings

Charts of fluid pH, compression set, maximum stress, maximum strain, and Shore M durometer versus aging time are presented for each of the candidate elastomers. Data at 0 h aging time corresponds to original material or fluid properties. The O-ring tension tests were performed in accordance with ASTM D 1414; compression set tests were performed in accordance with ASTM D 395.

Material failure (brittle or completely degraded material) is indicated by an unreported value; that is, charts may not show data for all aging times.

The legend on each chart indicates the elastomer, test temperature, and fluid used. For example, "FEPM @ 200°C, IIC" indicates FEPM aged in Fleetguard Compleat with DCA4 fluid at 200°C.

Figures 5 through 10 are charts of the EPDM process.

Figures 11 through 16 are charts of the HNBR process.

Figures 17 through 22 show charts of the FEPM process.

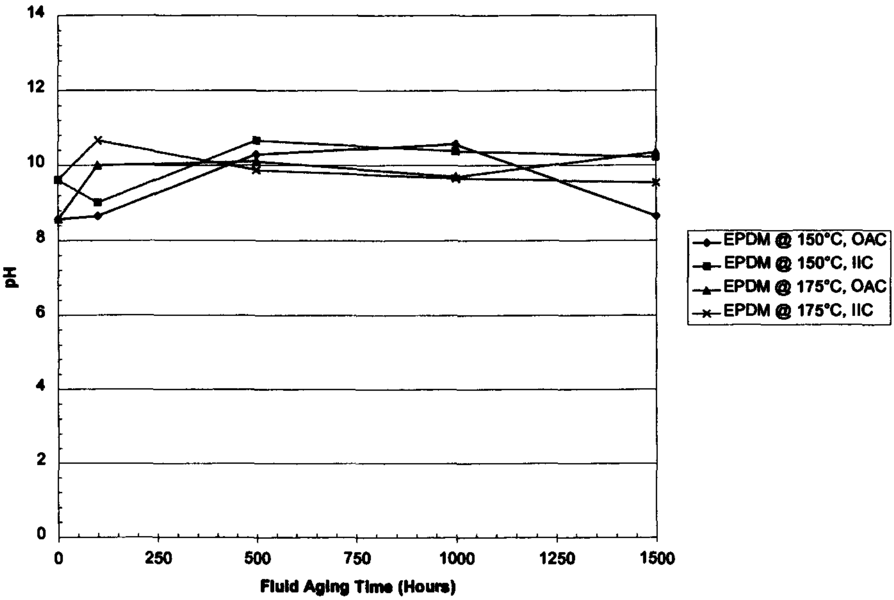

FIG. 5—*Fluid pH versus aging time for EPDM.*

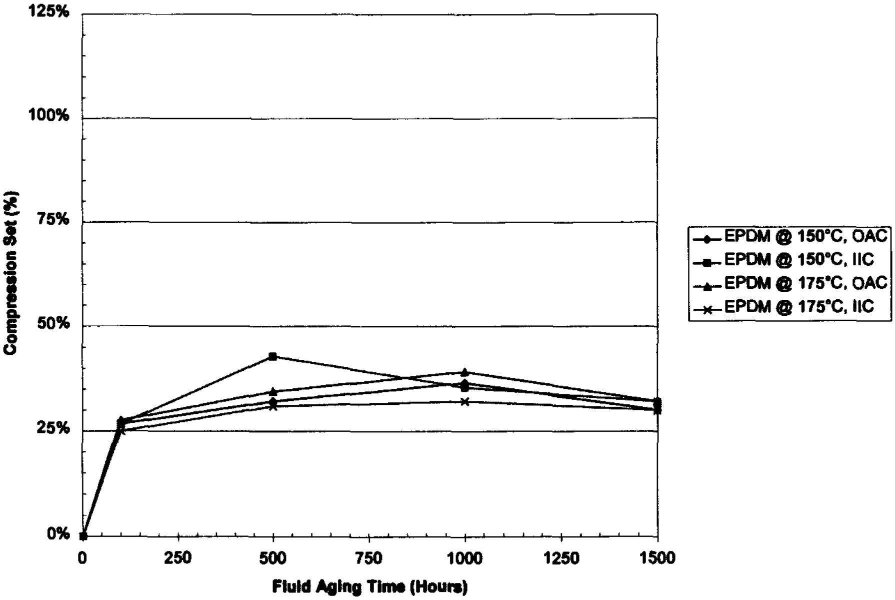

FIG. 6—*Compression set versus aging time for EPDM.*

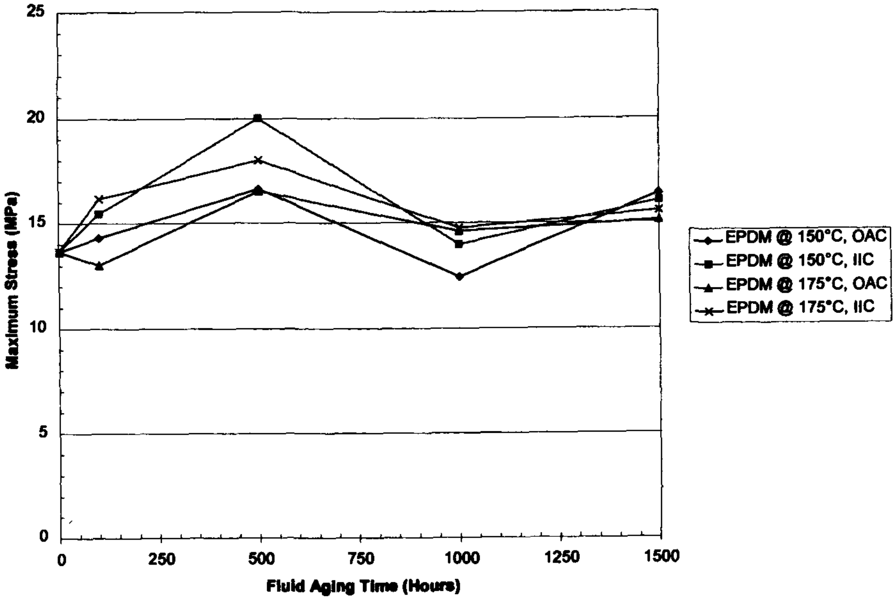

FIG. 7—*Maximum stress versus aging time for EPDM.*

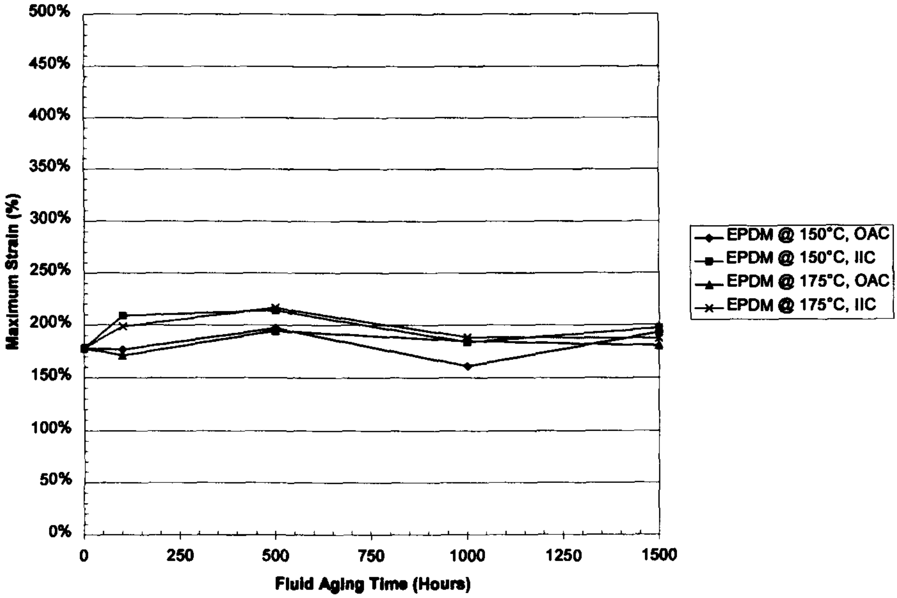

FIG. 8—*Maximum strain versus aging time for EPDM.*

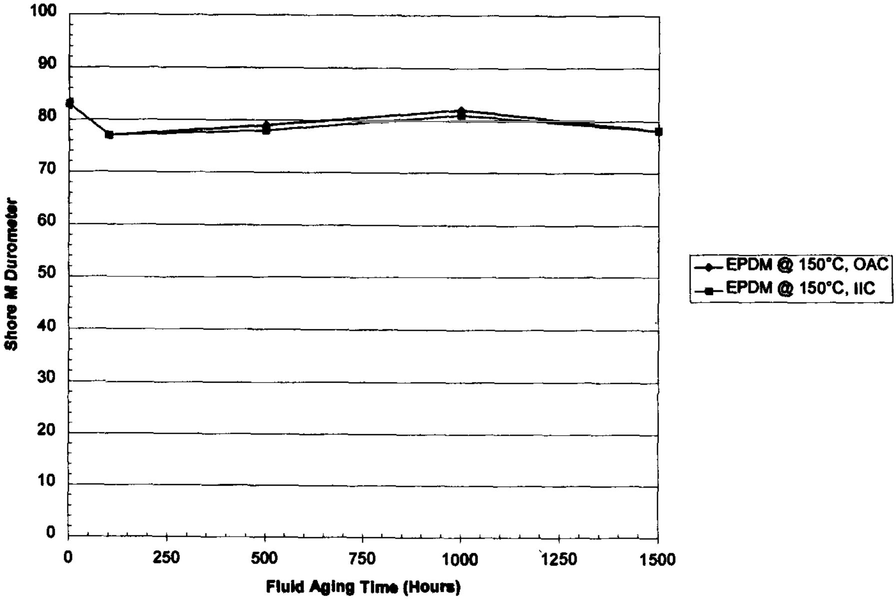

FIG. 9—*Shore M durometer for EPDM at 150°C.*

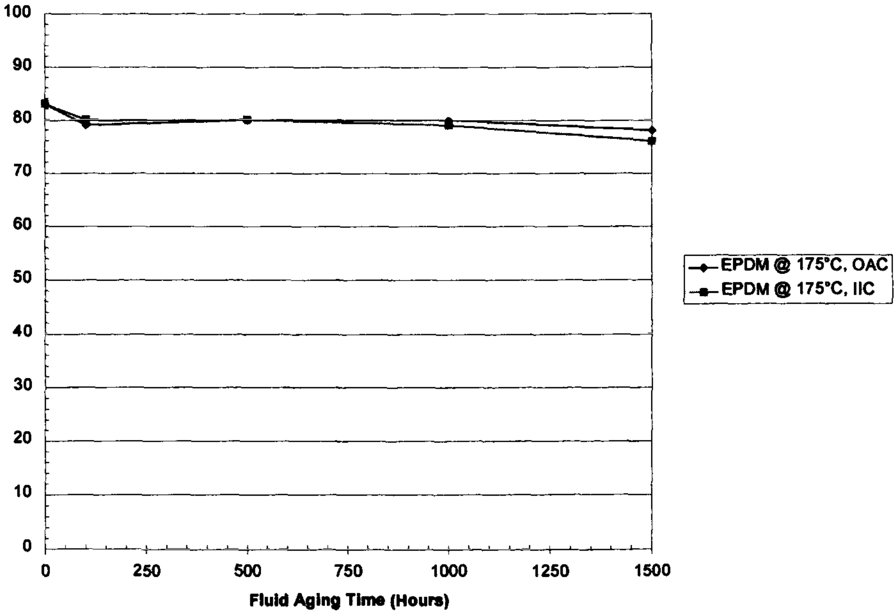

FIG. 10—*Shore M durometer for EPDM at 175°C.*

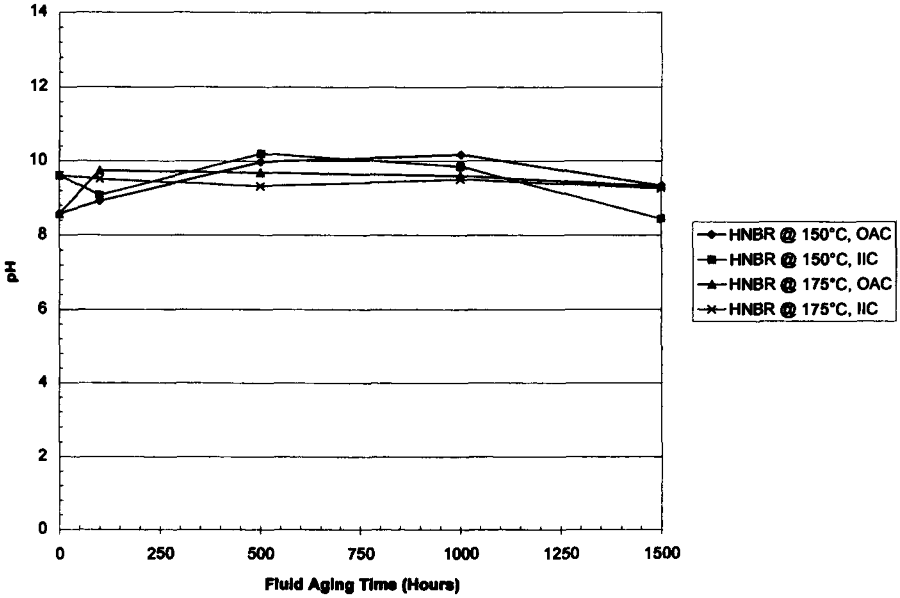

FIG. 11—*Fluid pH versus aging time for HNBR.*

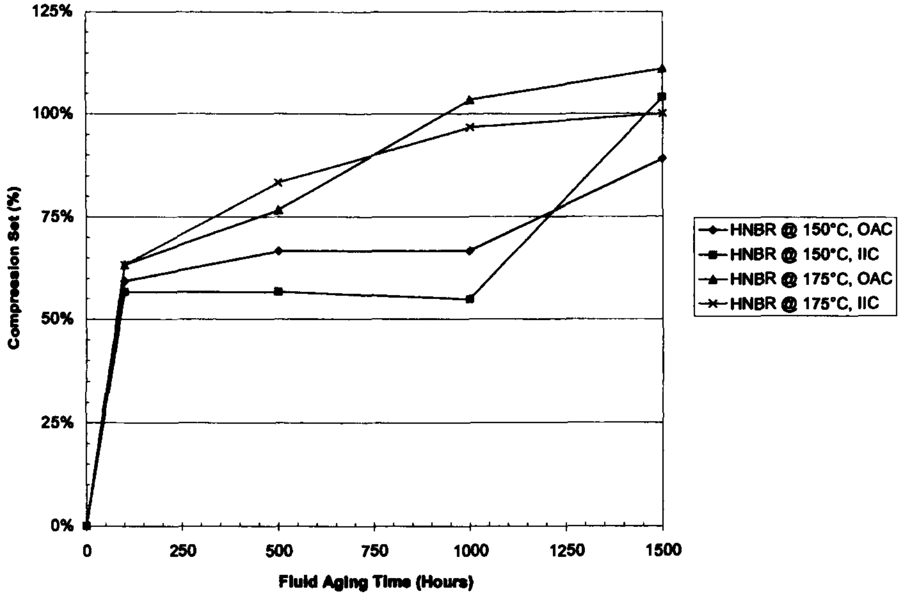

FIG. 12—*Compression set versus aging time for HNBR.*

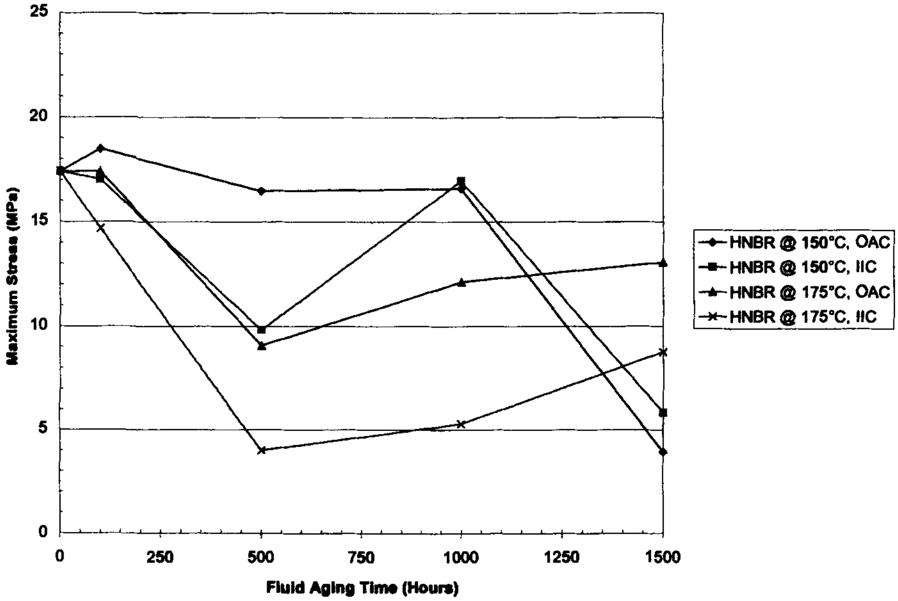

FIG. 13—*Maximum stress versus aging time for HNBR.*

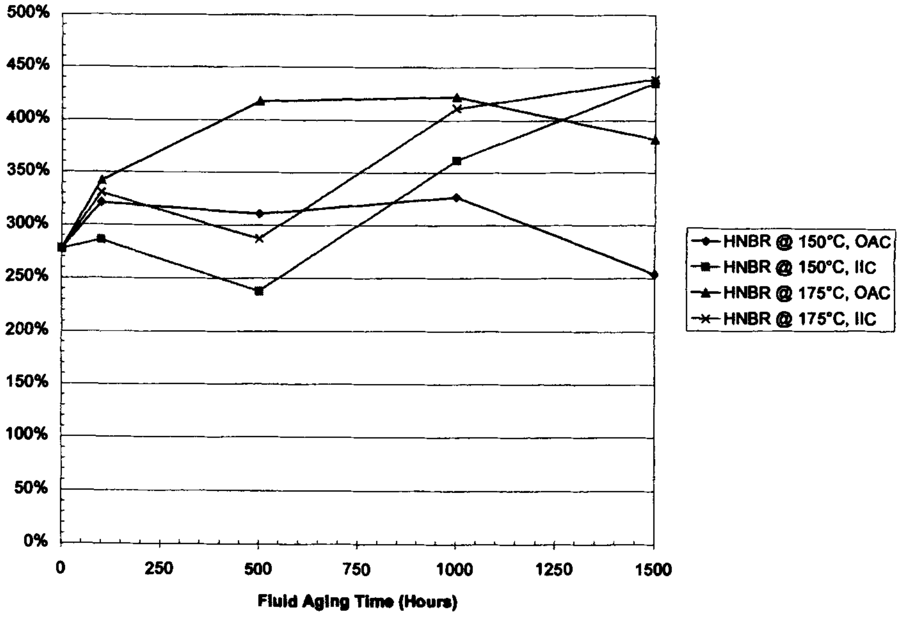

FIG. 14—*Maximum strain versus aging time for HNBR.*

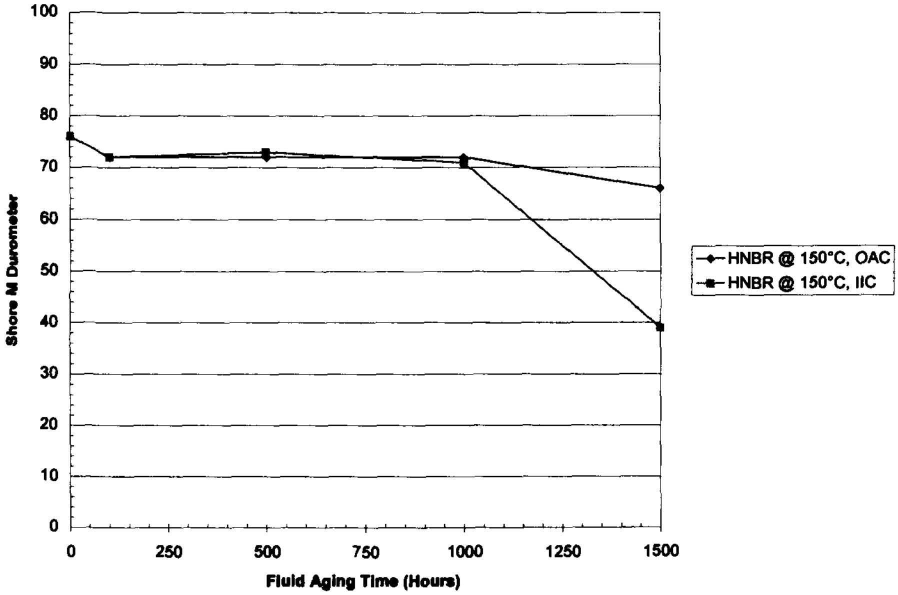

FIG. 15—*Shore M durometer for HNBR at 150°C.*

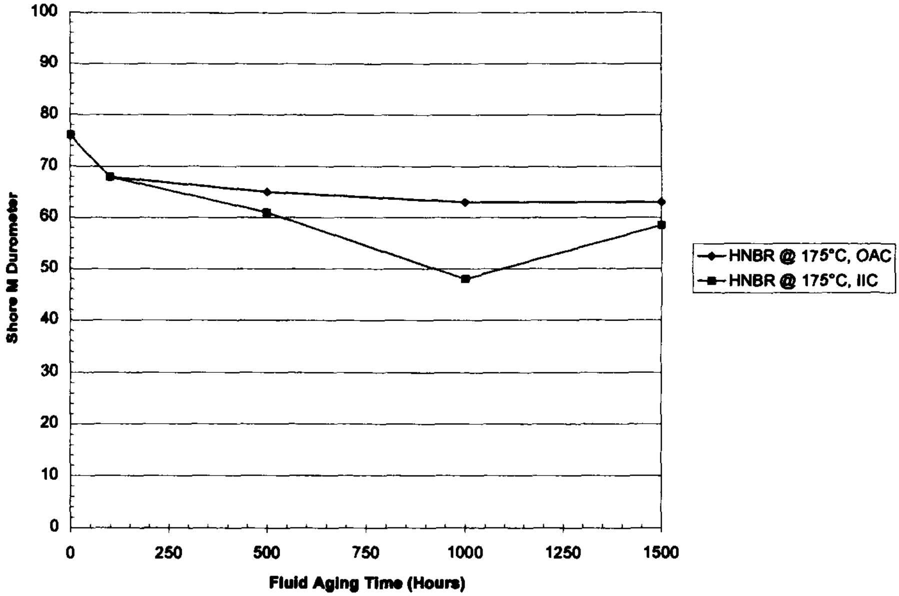

FIG. 16—*Shore M durometer for HNBR at 175°C.*

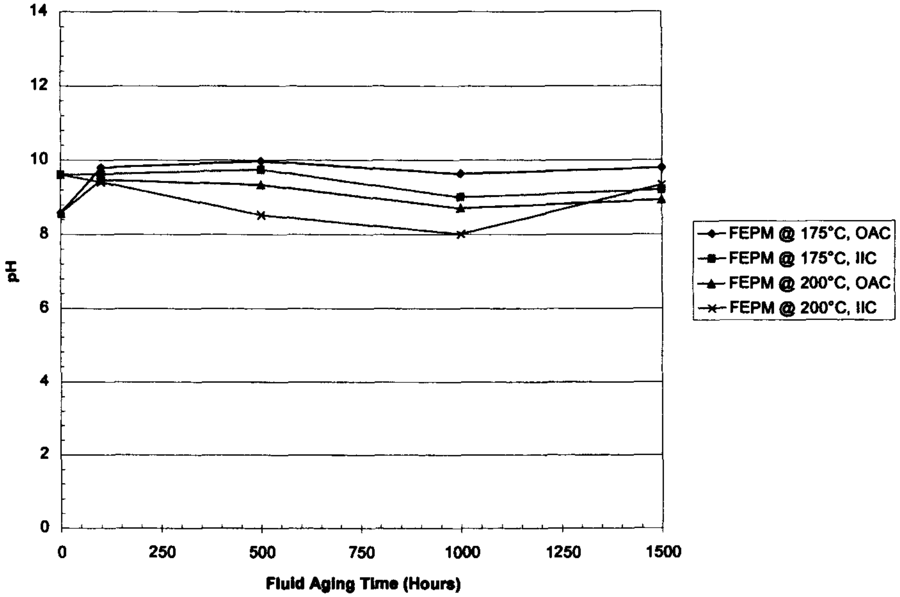

FIG. 17—*Fluid pH versus aging time for FEPM.*

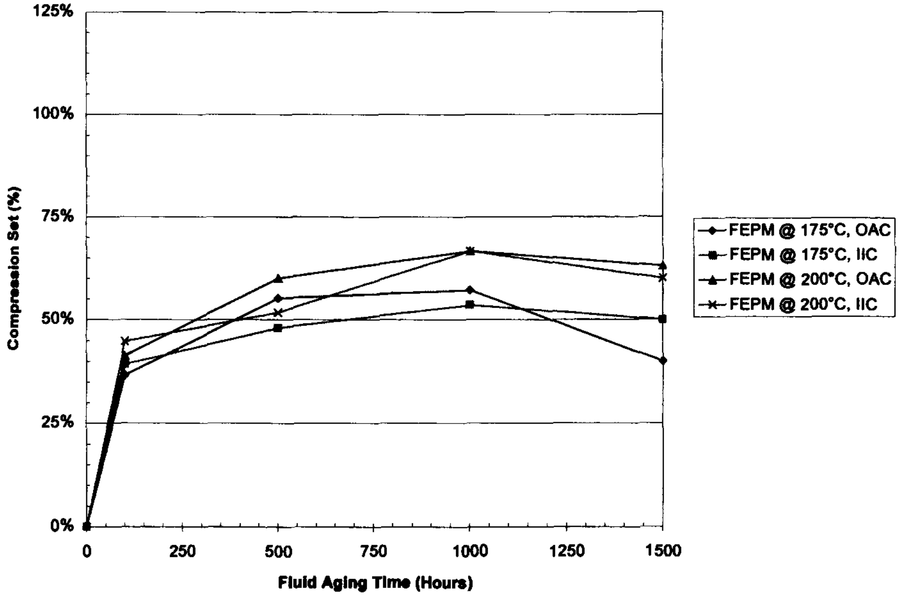

FIG. 18—*Compression set versus aging time for FEPM.*

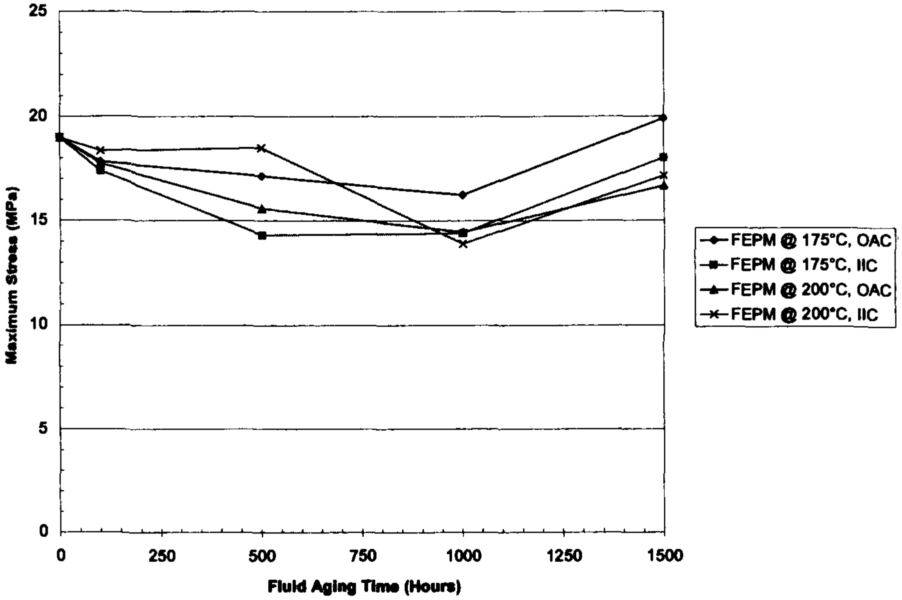

FIG. 19—*Maximum stress versus aging time for FEPM.*

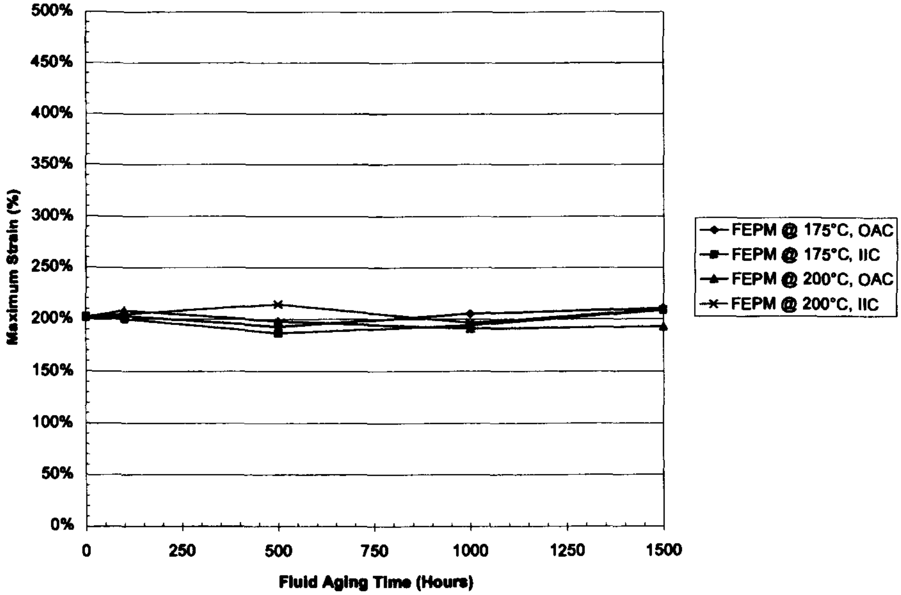

FIG. 20—*Maximum strain versus aging time for FEPM.*

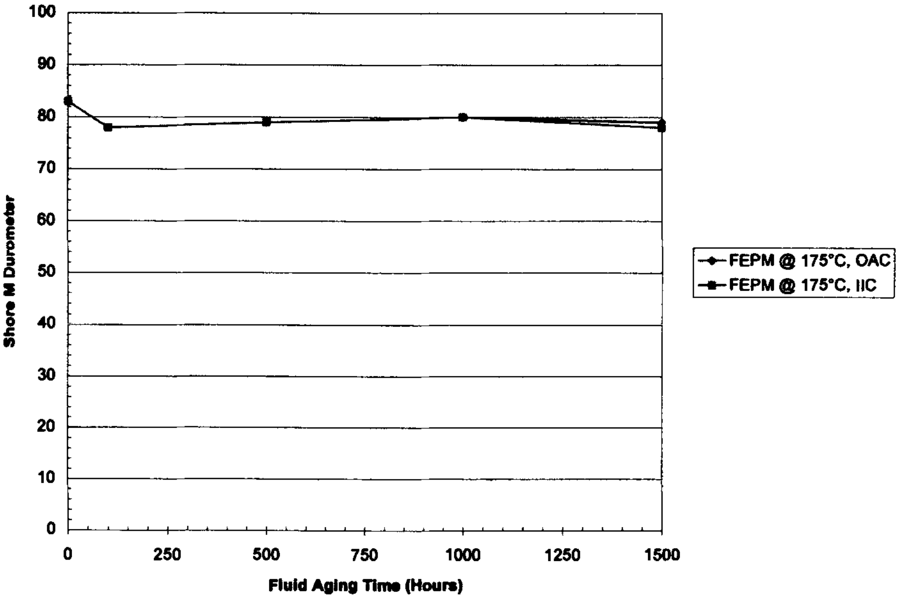

FIG. 21—*Shore M durometer for FEPM at 175°C.*

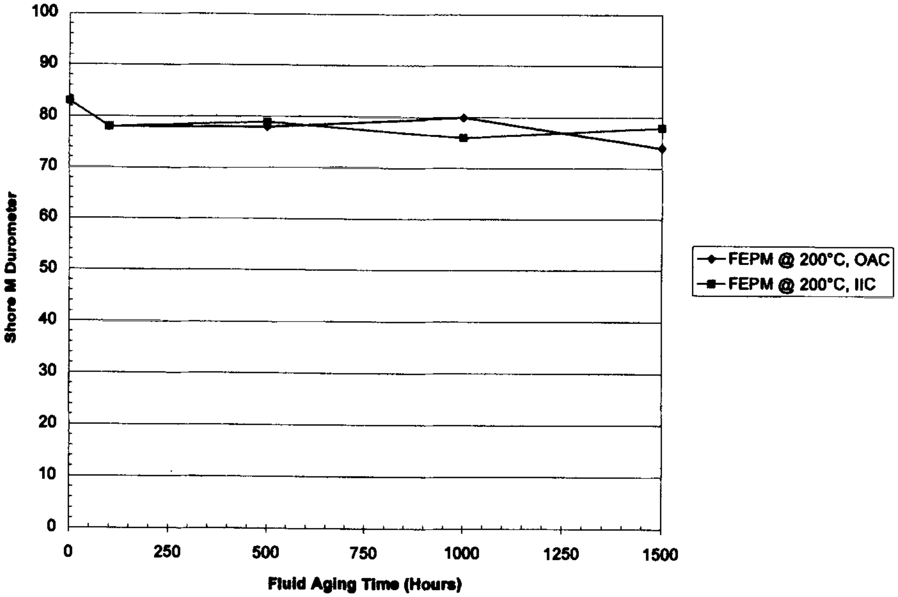

FIG. 22—*Shore M durometer for FEPM at 200°C.*

TABLE 1—*Dry aging of EPDM at 150°C.*

	Dry Aging Time, h				
Property	Original	100	500	1000	1500
Maximum stress, MPa	19.7	7.5	14.8	12.1	failed
Maximum strain, %	152	35	62	41	failed
Shore A durometer	82	89	88	89	failed

Dry Aged Dumbbells

A chart or table of maximum stress, maximum strain, and Shore A hardness versus dry heat aging time are presented for each of the candidate elastomers. These tests were performed in accordance with ASTM D 412 Method A.

Material failure is reported for brittle or completely degraded material. Tables were used to present data for EPDM and HNBR, since these materials failed 1000 h at 150°C and 500 h at 175°C, respectively.

The legend on each chart indicates the elastomer and test temperature used. For example, "FEPM @ 200°C" indicates FEPM aged at 200°C.

Tables 1 and 2 show dry aging of EPDM.

Tables 3 and 4 show dry aging of HNBR.

Figures 23 through 25 show dry aging of FEPM.

Tables 5 and 6 show strain energy density versus dry aging time for EPDM and HNBR.

Strain Energy Density at 20% Elongation

Charts of strain energy density at 20% elongation, $W(20\%)$, versus aging time are presented for fluid aged O-rings and dry aged dumbbells for each of the four candidate elastomers.

Figures 26 through 29 show strain energy density versus fluid aging time.

Fluoride Ion Concentration

Fluoride ion concentration in the test fluids was monitored for FEPM. A chart of the results is shown in Fig. 30.

Conclusions

Fluid Aged O-Rings

Clearly, NBR is not the material of choice for sealing in an environment with modern engine coolants. After only 500 h at 150°C, the NBR had chemically and physically broken down and

TABLE 2—*Dry aging of EPDM at 175°C.*

	Dry Aging Time, h			
Property	100	500	1000	1500
Maximum stress, MPa	12.8	failed	failed	failed
Maximum strain, %	62	failed	failed	failed
Shore A durometer	88	failed	failed	failed

TABLE 3—*Dry aging of HNBR at 150°C.*

Property	Dry Aging Time, h				
	Original	100	500	1000	1500
Maximum stress, MPa	26.1	18.7	26.7	25.3	15.2
Maximum strain, %	280	201	227	232	172
Shore A durometer	73	79	79	80	81

would not seal (for both dry heat aging and fluid aging). Thus graphs for this material were not included and the remainder of the discussion is limited to the remaining three candidate elastomers, namely FEPM, EPDM, and HNBR.

Compression set appears poor for HNBR at 175°C; the O-rings tested show over 100% compression set for both OAC and IIC fluids. FEPM is second best in compression set with nearly 55% set at 175°C and 65% set at 200°C (regardless of test fluid). EPDM exhibits the best compression set characteristics in fluid aging with 30 to 40% compression set in either fluid and temperatures of 150 or 175°C.

Shore M hardness remains virtually unchanged in FEPM and EPDM, while a significant amount of softening occurs in HNBR at 175°C; hardness decreases 17% after aging 1500 h in OAC fluid, and decreases 23% in IIC fluid.

Dry Aged Dumbbells

Dry heat aging more clearly defines FEPM as the superior compound. FEPM withstands 1500 h at 200°C while maintaining reasonable physical properties, while test specimens of EPDM and HNBR show failure after 500 and 1000 h, respectively at only 175°C. NBR fails after 500 h at 150°C.

Strain Energy Density

Integration of the stress versus strain curve gives a measure of energy per unit volume of elastomer, or external work performed on the system (the O-ring). The work done on the system can also be expressed as a product of shear modulus and a function of extension ratio, λ. Shear modulus, G, for an incompressible material (such as an elastomer) can be defined by the relation

$$E = 3G \tag{11}$$

where E is Young's modulus. Extension ratio, λ, is given in terms of the engineering strain, ε, by the relation:

$$\lambda = 1 + \varepsilon \tag{12}$$

TABLE 4—*Dry aging of HNBR at 175°C.*

Property	Dry Aging Time, h			
	100	500	1000	1500
Maximum stress, MPa	21.8	13.7	failed	failed
Maximum strain, %	202	107	failed	failed
Shore A durometer	79	86	failed	failed

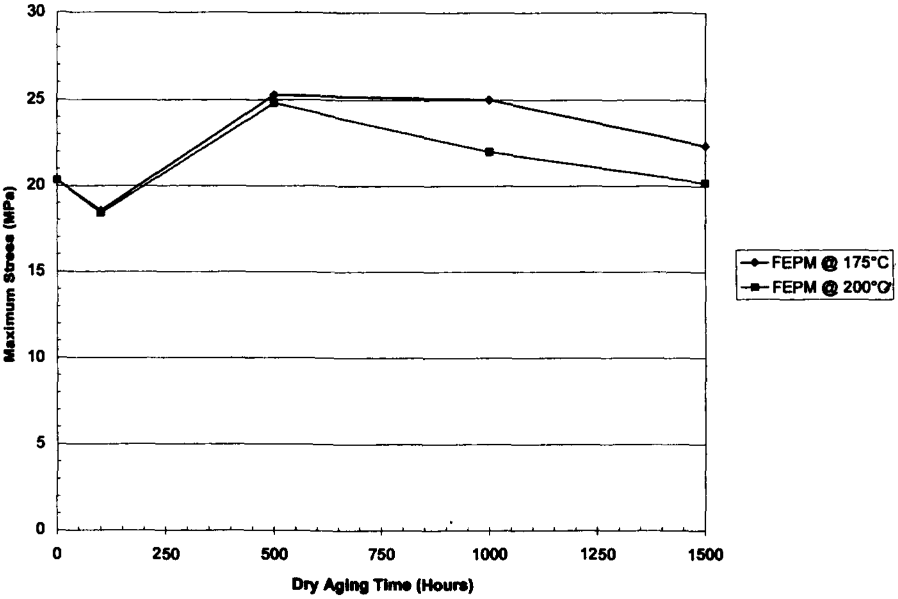

FIG. 23—*Maximum stress versus dry aging time for FEPM.*

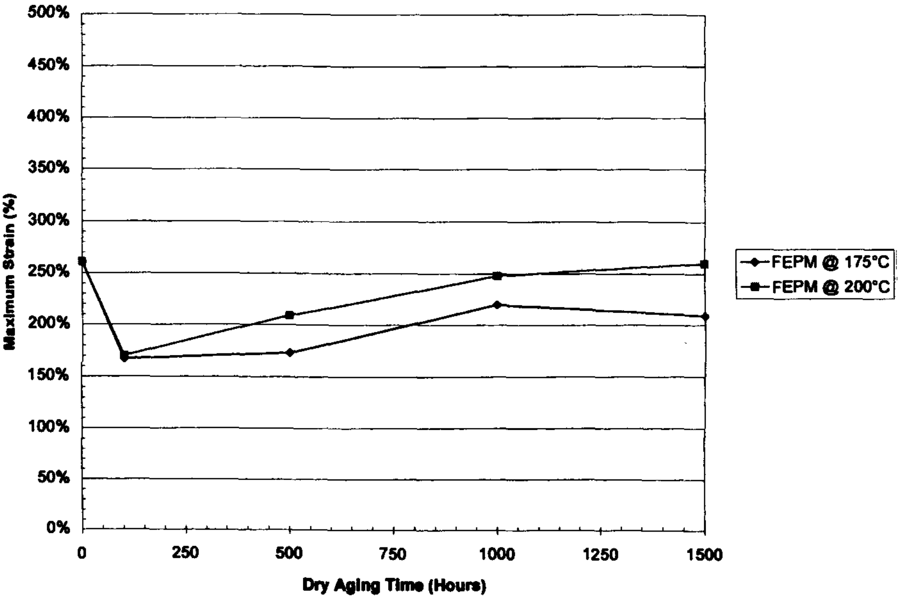

FIG. 24—*Maximum strain versus dry aging time for FEPM.*

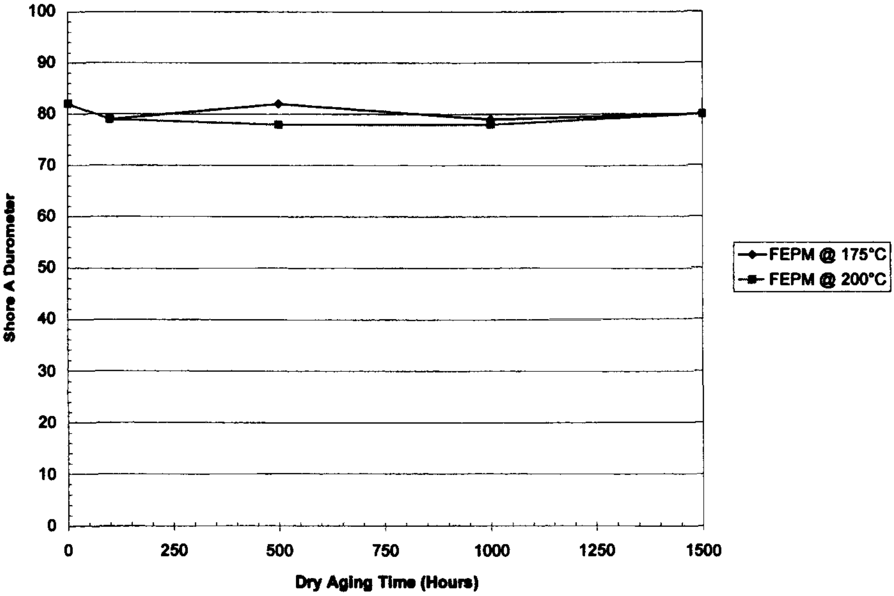

FIG. 25—*Shore A durometer versus dry aging time for FEPM.*

The relation between extension ratio and shear modulus [*6*] defining work density, *W*, is

$$W = \frac{G}{2}\left(\lambda^2 + \frac{2}{\lambda} - 3\right) \tag{13}$$

Another accepted definition [*2*] for shear modulus of an unfilled elastomer is:

$$G = \frac{\rho RT}{M_c} \tag{14}$$

where

ρ = density,
R = universal gas constant,
T = temperature in Kelvin, and
M_c = the molecular weight between crosslinks (a somewhat controversial term).

TABLE 5—*Strain energy density at 20% elongation versus dry aging time for EPDM.*

Strain Energy Density at 20% Elongation, kPa					
	Dry Aging Time, h				
Temperature	Original	100	500	1000	1500
150°C	379.7	600.5	515.5	790.4	failed
175°C		525.4	failed	failed	failed

TABLE 6—*Strain energy density at 20% elongation versus dry aging time for HNBR.*

	Strain Energy Density at 20% Elongation (kPa)				
	Aging Time				
Temperature	Original	100	500	1000	1500
150°C	188.1	240.0	238.7	275.8	221.3
175°C		265.7	328.6	failed	failed

Since M_c is the only variable in Eq 14, it must be considered as the variable reflecting chemical changes that occur during the aging process. That is, to observe a change in W at given values of extension ratio and temperature, the value of G must have changed. Furthermore, since ρ and R are constant values, variation in M_c is responsible for the change in W. Thus there is a direct correlation between strain energy density, W, and molecular weight, M_c.

Strain energy density measurement is by no means used in industry on a routine basis, but certainly should be. Recalling that chemical changes ultimately manifest themselves in changes in physical properties, strain energy density at 20% elongation can be used as early indicator of elastomer degradation.

Fluoride Ion Concentration

Fluoride ion concentration is an indication of the extent of de-hydrofluorination of a fluoropolymer. Thus this test was only performed on FEPM. The results show that the fluoride ion

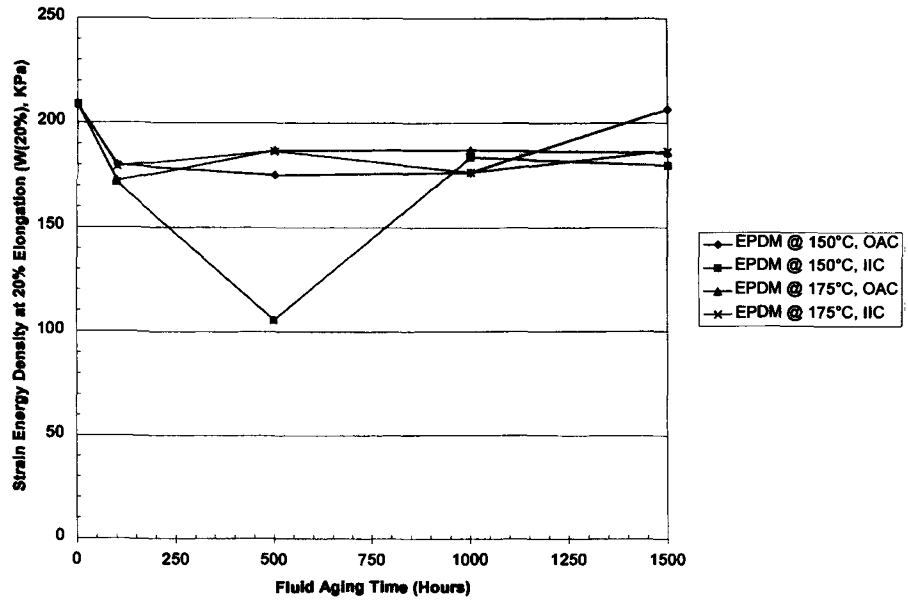

FIG. 26—*Strain energy density at 20% elongation versus fluid aging time for EPDM.*

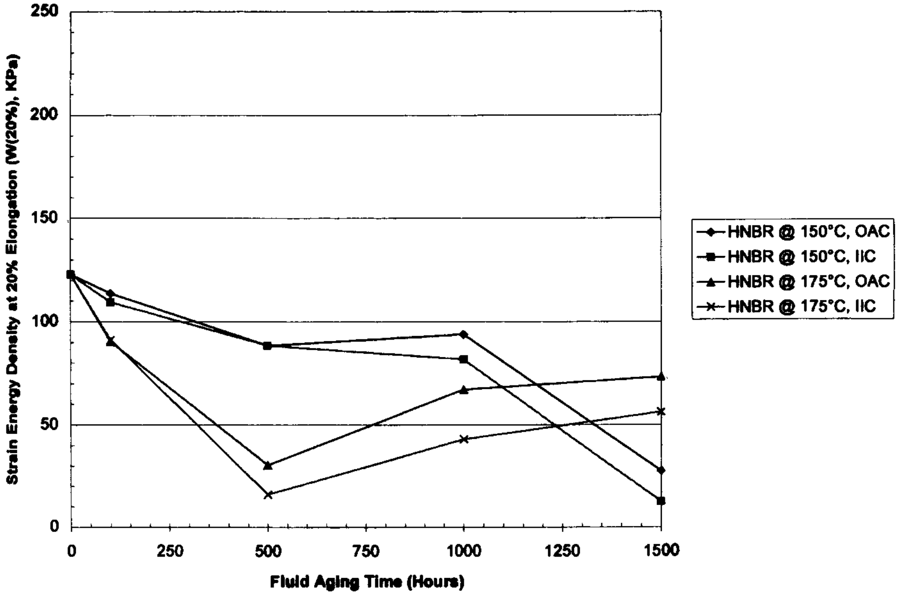

FIG. 27—*Strain energy density at 20% elongation versus fluid aging time for HNBR.*

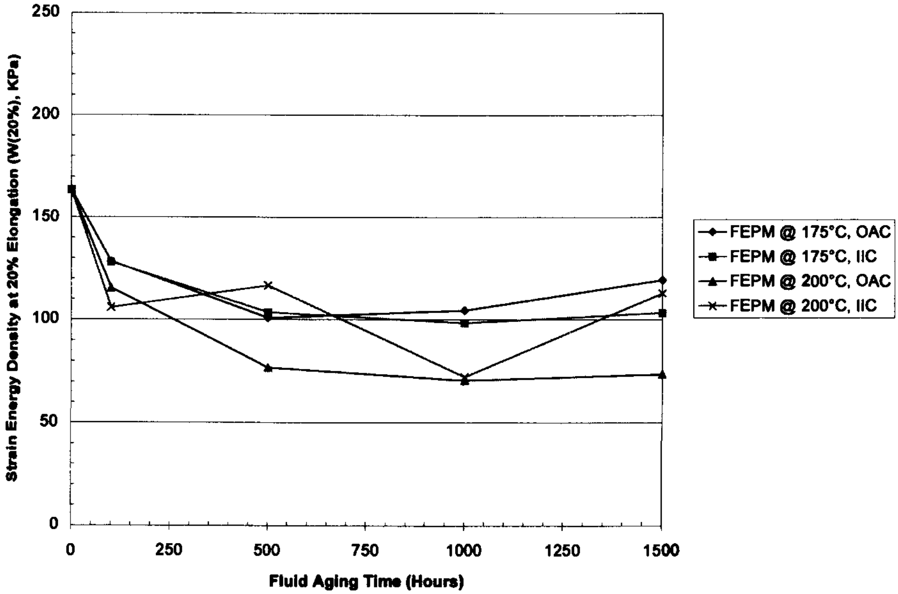

FIG. 28—*Strain energy density at 20% elongation versus fluid aging time for FEPM.*

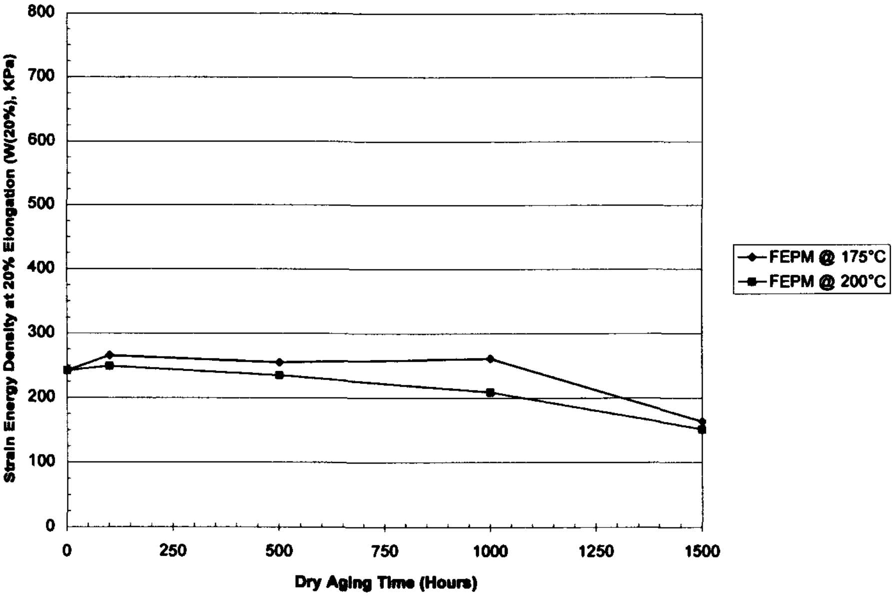

FIG. 29—*Strain energy density at 20% elongation versus dry aging time for FEPM.*

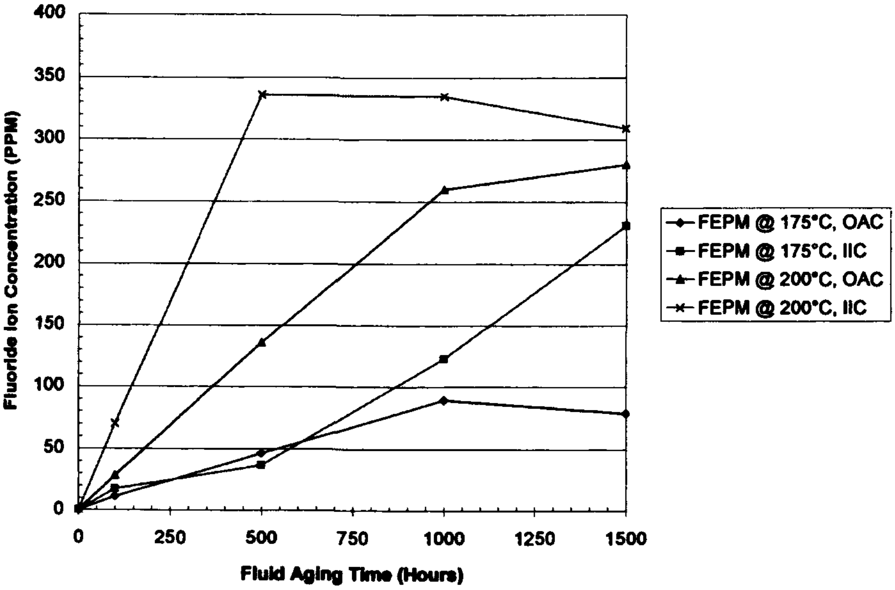

FIG. 30—*Fluoride ion concentration versus fluid aging time.*

concentration reaches a maximum of approximately 340 ppm after 1000 h aging time in IIC fluid at 200°C. This indicates that FEPM is extremely stable and is not likely to degrade further after additional time.

Summary

The results presented shed a new light on the high temperature capabilities of the four elastomer types tested. Specifications for the suitability of these materials in severe service environments should be carefully examined. For example, NBR is recommended routinely for service environments up to 120°C (275°F); it has been shown here to degrade quickly. Also, EPDM has been specified as suitable for service in 275°C (550°F) environments [*8*]; it has been shown to fail after 100 h of dry heat aging at 175°C (350°F). Finally, HNBR has been described as a viable substitute for fluoroelastomers in 175°C (350°F) service environments, while FEPM has been wrongly scorned as a high compression set material that is difficult to mold. The results show that FEPM is the material of choice for applications demanding long service life in harsh environments such as modern engine coolants.

APPENDIX

Compound Formulations

The EPDM is formulated using DuPont-Dow Nordel,[7] compounded in accordance with DuPont bulletin IF-ND-519.0683 listed in Ref *8*.

The HNBR compound used for this experiment is mixed as listed in Table 7.

The NBR compound used for this experiment is mixed as shown in Table 8.

The FEPM is formulated using a proprietary Seals Eastern formulation (7182X) with Asahi Glass, AFLAS[8] 100H base polymer.

Test Fixture Specifications

Figure 31 shows the test fixture specifications.

Tensile versus O-Ring Tests

There appears to be a discrepancy between the measured values of strain energy density for each material depending on the test method used. For example, the original values of strain energy density for FEPM are as shown in Table 9.

This difference is easily explained. The ASTM D 1414 standard specifies that the gage length of an O-ring sample is based on twice the initial grip separation plus the circumference of one spool (Fig. 32). However, the standard does not specify that the sample be taut as in Fig. 32*B*. Thus, there is a small amount of displacement the grips must undergo before the O-ring actually experiences any amount of strain. Since the strain is overestimated, the O-ring sample appears to have a lower value for strain energy density than a dumbbell of the same material. However, since all O-rings were tested using the same standard, no correction was made to the values of strain or strain energy density to allow comparison between the two test methods.

[7] Registered trademark of the DuPont Dow Company.

[8] AFLAS is a registered trademark of Asahi Glass Co., Ltd.

TABLE 7—*HNBR formulation.*

Ingredient	phr
Zetpol 2000	100.00
Carplex 1120	30.00
Maglite D	3.00
Silane A-172	1.50
Naugard 445	1.50
Vanox MTI	1.00
HVA #2	2.00
Sartomer SR-350	6.00
Vul-Cup 40KE	9.00
Total	154.00

TABLE 8—*NBR formulation.*

Ingredient	phr
KRYNAC 34.80	100.00
Sulfasan R	1.00
M.E.T. Powder Blend	3.00
MBTS	1.00
Stearic Acid-Triple Pressed	1.00
Zik-Stick 85	5.00
Aminox Powder	1.50
N550 Sterling-50	50.00
Total	112.50

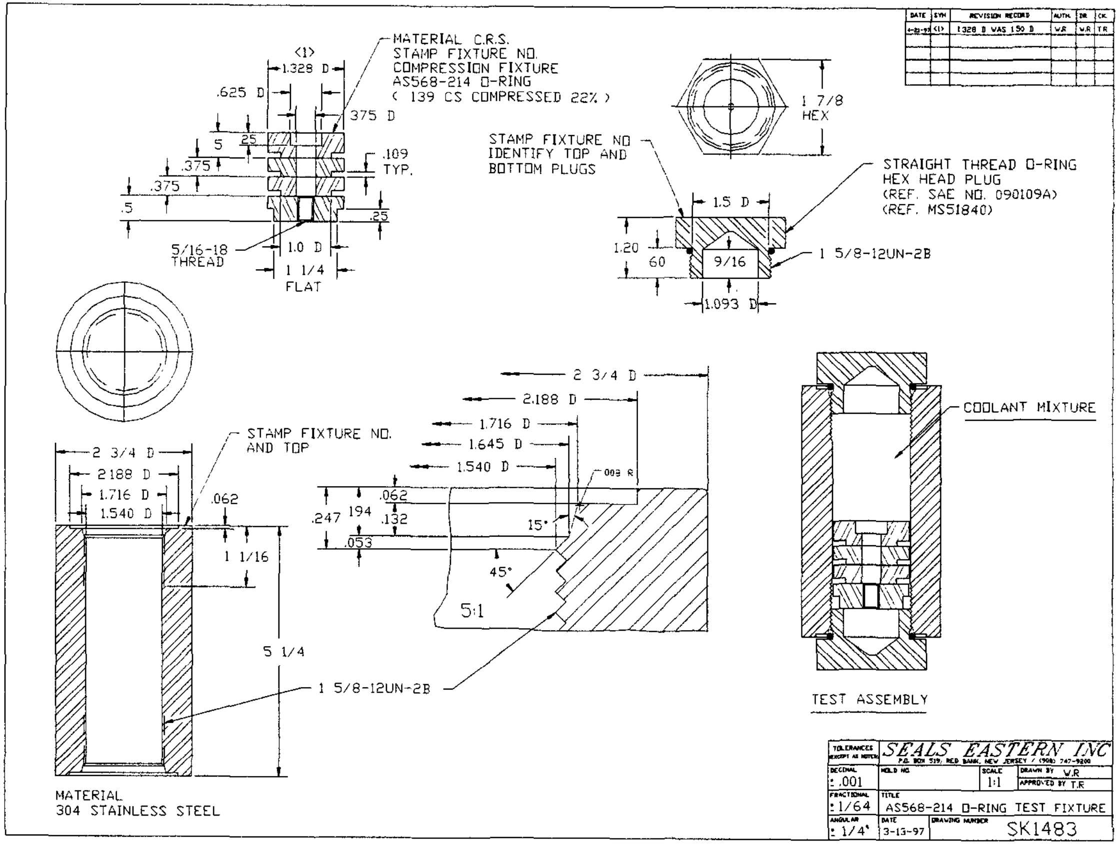

FIG. 31—*SK 1483 test fixture dimensions.*

TABLE 9—*Strain energy density example.*

Test Method	Unaged FEPM Strain Energy Density at 20% Elongation, kPa
Tensile	242
O-ring	164

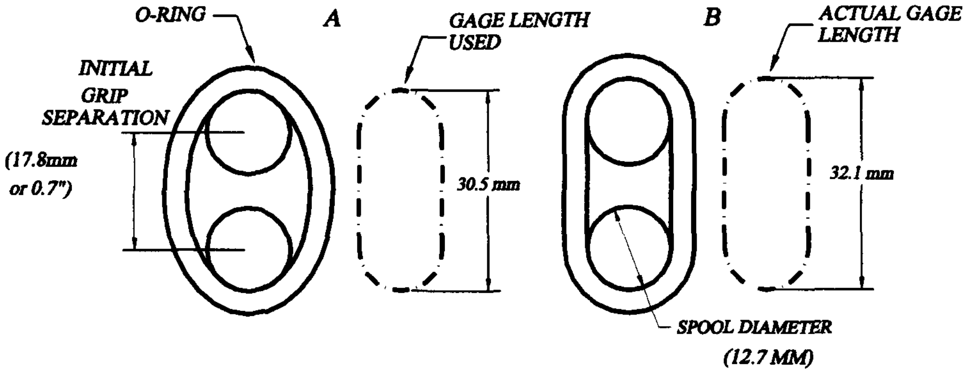

FIG. 32—*O-ring gage length discrepancy.*

Measurement of Compression Set

Scatter in compression set data is a major concern since even a small error in measurement can cause a large error in compression set results. Measurement tools in this experiment had a precision of ±0.013 mm (or ±0.0005 in.) for measuring original, final and compressed wall thickness of the O-rings used in this test. Even with this precision, a compression set measurement may be in error by as much as ±15% due to tolerance stackup alone.

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James P. Greaney[1] *and Robert A. Smith*[1]

Engine Coolant Compatibility with the Nonmetals Found in Automotive Cooling Systems

REFERENCE: Greaney, J. P. and Smith, R. A., "**Engine Coolant Compatibility with the Nonmetals Found in Automotive Cooling Systems,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 168–181.

ABSTRACT: High temperature, short term immersion testing was used to determine the impact of propylene and ethylene glycol base coolants on the physical properties of a variety of elastomeric and thermoplastic materials found in automotive cooling systems. The materials tested are typically used in cooling system hoses, radiator end tanks, and water pump seals. Traditional phosphate or borate-buffered silicated coolants as well as extended-life organic acid formulations were included. A modified ASTM protocol was used to carry out the testing both in our labora-tory and at an independent testing facility. Post-test fluid chemistry including an analysis of any solids which may have formed is also reported. Coolant impact on elastomer integrity as well as elastomer-induced changes in fluid chemistry were found to be independent of the coolant's glycol base.

KEYWORDS: compatibility, cooling system, elastomer, engine coolant, organic acid, physical properties, rubber compounds, silicate

The primary focus in engine coolant development and testing is on the ability of the fluid to prevent metal corrosion. A host of performance tests which measure this parameter have been developed and are used typically throughout the coolant industry. Boil-over and freeze protection, although more critical from an acute standpoint, are taken for granted since these properties will be ensured as long as the appropriate ratio of coolant to water is used. Nearly as important as corrosion protection, though examined less frequently, is the impact that the coolant has on nonmetals. These include the elastomers and thermoplastics which are commonly found in hoses, water pump seals, gaskets, radiator end tanks, and coolant overflow bottles. Significant degradation of any of these materials can also result in cooling system failure.

A test program was designed and undertaken to study the effects of coolant contact with a variety of these nonmetallic materials at elevated temperature. The test protocol was based on a modification of an ASTM Standard Test Method for Rubber Property—Effect of Liquids (D 471). The materials tested included ethylene-propylene (EPDM), silicone, and nitrile (NBR, HNBR) rubber compounds, fluoroelastomeric polymers (Viton[2]), and nylon. High density polyethylene (HDPE), used to manufacture coolant overflow bottles, was tested individually using a different procedure. Test plaques were provided by either the raw material manufacturers or the cooling system component suppliers. All of the test samples were original equipment man-

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[2] Viton is a registered trademark of E. I. Dupont, Wilmington, DE.

TABLE 1—*Coolants in test program.*

Coolant	Base Glycol	Inhibitor Package
A	ethylene	Two organic acids with azole; no borates, phosphates, nitrates, nitrites, or silicates.
B	propylene	Two organic acids (same as A) with azole; no borates, phosphates, nitrates, nitrites, or silicates.
C	propylene	Experimental formula with four organic acids, azole, and nitrate; no borates, phosphates, nitrites or silicates.
D	propylene	Experimental formula with two organic acids and azole; no borates, phosphates, nitrates, nitrites, or silicates.
E	propylene	Experimental "hybrid" formula with two organic acids, azole, borate, nitrate, and silicate.
F	ethylene	"Conventional" with high silicate; phosphate buffer.
G	propylene	"Conventional" with high silicate; borate buffer.
H	propylene	Low silicate "heavy duty" formula intended for use with supplemental coolant additives.

ufacturer (OEM) grade material. Commercially available propylene and ethylene glycol base coolants were used in addition to several experimental formulations. Both traditional (borate or phosphate buffered with silicate) and organic acid inhibitor technologies were included. Adverse effects of exposure to coolant were expected to be concentration dependent so coolant concentrates as well as dilutions were tested. Concentrate effects were determined at an independent testing facility [*1*] while mixtures (50/50 dilutions of coolant with water) were examined in our laboratories. In addition to pre- and post-immersion physical property measurements for each of the test specimens, a number of the post-test fluids were analyzed and, where feasible, solids which may have formed during the testing were also examined. The overall intent of the testing was to generate comparative rather than absolute data, focusing on the effects of different inhibitor technologies and different base glycols.

Experimental Details

Immersion Testing with Coolant Concentrates

Eight coolant concentrates were used in the immersion testing of nine elastomeric materials and one sample of nylon. The coolants (Table 1) are representative of traditional (silicated), organic acid, and hybrid (silicate + organic acid) inhibitor technology. Both propylene and ethylene glycol base fluids were included. The elastomers tested (Table 2) consisted of four types of EPDM rubber, silicone rubber, two types of Viton®, nitrile rubber (NBR), and hydrogenated nitrile rubber (HNBR). A sample of reinforced nylon-6,6′ used to fabricate radiator end tanks was also tested.

Pre-immersion tensile strength, elongation, volume, and Shore A hardness (Shore D for nylon) were determined for each material (Table 3). Test specimens (dog bones) for Instron testing were cut according to ASTM Standard Test Methods for Vulcanized Rubber and Thermoplastic Rubbers and Thermoplastic Elastomers-Tension (D 412) and 50 by 25 mm coupons were used for determining changes in volume and hardness. The test fluids were analyzed and the pre-test pH was measured. Three dog bones and three coupons were submerged in 200 mL of coolant in a large test tube equipped with a reflux condenser. Each tube was immersed in an oil bath and held at 100°C for 70 h. Post-test physical properties were determined for each

TABLE 2—*Test materials.*

Material	Description
Viton A	Fluoroelastomeric polymer; biphenol cured.
Viton B	Fluoroelastomeric polymer; peroxide cured.
EPDM A	Ethylene-propylene rubber; sulfur cure; ECR.[a]
EPDM B	Ethylene-propylene rubber; sulfur cure; non-ECR.[a]
EPDM C	Ethylene-propylene rubber; peroxide cure; non-ECR.[a]
EPDM D	Ethylene-propylene rubber; sulfur cure; semi-ECR.[a]
NBR	Butadiene-acrylonitrile rubber.
HNBR	Hydrogenated NBR.
Silicone rubber	Peroxide cure; primarily used in heavy duty applications.
Nylon-6'6	Polyamide salt of adipic acid and hexamethylenediamine; glass reinforced.

[a] Electrochemical resistant.

specimen as was the pH for each coolant. Any changes in color or appearance of the fluid were also noted. Selected post-test fluids were analyzed using inductively coupled plasma (ICP) spectroscopy and liquid chromatography (LC) techniques and the corresponding solids which may have formed during the immersion were examined using wavelength dispersive X-ray fluorescence spectroscopy. No attempt was made to identify organic constituents in the solids.

Immersion Testing with Coolant Dilutions

Actual vehicle conditions were more closely simulated by using coolant dilutions. The same materials were tested in our laboratory using five of the coolants diluted 50/50 by volume with distilled water. The experiments were run using round-bottom, thick wall, glass pressure vessels equipped with a pressure gage, an adjustable relief valve, and a silicone rubber sealing gasket. Each glass vessel contained three 50 by 25 mm coupons which were allowed to settle on the bottom of the tube completely submerged in the coolant mixture. Small holes were bored through each of the three tensile bars so that they could be suspended in the solution using

TABLE 3—*Pre-immersion physical properties.*

Material	Tensile Strength, psi	Elongation at Break, %	Hardness Shore A Units
Viton A	2145	192	76
Viton B	2870	238	76
EPDM A	2071	575	64
EPDM B	1752	401	68
EPDM C	1616	391	70
EPDM D	1431	418	66
NBR	2190	539	63
HNBR	2869	352	68
Silicone	1141	200	71
Nylon	1989	3.5	89

NOTE: Nylon hardness in Shore D units.

Teflon[3] tape which was threaded into one of the fittings on the underside of the stainless steel sealing flange. Teflon spacers prevented the bars from contacting one another. Each tube was pressurized with air to approximately 10 psig and was placed in an oil bath controlled at 125°C; pressure was adjusted as needed to maintain ~20 psig and thereby prevented boiling. After 168 h, the tubes were removed from the oil bath and the specimens were handled as required by D 471. Coolant mixtures were analyzed and any solids which were observed were collected and characterized.

Overflow Bottle Testing

A slightly different testing program was used to evaluate the effects of long term contact between engine coolants and the high density polyethylene (HDPE) used to produce coolant overflow bottles. This testing was both longer term and also contained temperature cycling. HDPE tensile bars were immersed in beakers containing solutions of the test coolant and distilled water. Coolant concentration was adjusted such that the freezing point of the mixture was approximately −44°C (~55 volume% for EG base and ~57 volume% for PG base). The beakers were fitted with condensers and held at mild reflux conditions in a temperature controlled oil bath. Bars were evaluated visually and changes in tensile strength and elongation were determined after 168, 504, and 1008 h of exposure to the refluxing coolant solutions. Heat was maintained uninterrupted for the first 168 h. After the first three bars were removed, intermittent cool-down periods (for example, weekend shutdowns) were employed. The temperature cycling was used in an attempt to mimic under-the-hood exposure conditions, for example, a repeating sequence of contact with hot coolant followed by a slow cool down to ambient temperature. Again, traditional silicate-containing products were used as were organic acid formulations. Pre- and post-test analytical characterization of fluids and solids (if observed) was also conducted.

Results and Discussion

Concentrates

After 70 h of contact with the test specimens, many of the coolant concentrates exhibited varying amounts of precipitate. This was true for organic, hybrid, and conventional inhibitor technologies, and for both base glycols. The post-test pH behavior depended on the type of additive package: the organic acid and hybrid formulations generally showed a slight pH increase, while the pH of the conventional coolants containing silicate and other inorganic inhibitors decreased (Table 4).

Clear and consistent physical property changes as a result of exposure were not evident. There was a general increase in elongation and hardness, little or no change in volume, and mixed results for changes in tensile strength. Figures 1 and 2 are presented to allow a somewhat closer examination of the effect of different additive packages and different base glycols. The tensile strength data in Fig. 1 are grouped by inhibitor type and the elongation data in Fig. 2 by base glycol. Virtually no differences in tensile strength were seen due to inhibitor type or base glycol for either of the Viton samples, EPDM B and D, or for HNBR, where immersion resulted in no change in tensile strength in any of the four coolants. The data for the other elastomers were less consistent. Although an inhibitor effect might exist for EPDM C and NBR, and a glycol effect for silicone rubber (Fig. 1), the magnitude of the differences observed makes such a conclusion tenuous, at best. What appears to be a glycol related effect for EPDM

[3] Teflon is a registered trademark of E. I. Dupont, Wilmington, DE.

TABLE 4—*Post-test pH and appearance of coolant concentrates after contact with test specimens for 70 h at 100°C.*

Coolant	Initial pH	Viton A	Viton B	EPDM A	EPDM B	EPDM C	EPDM D	NBR	HNBR	Silcone	Nylon
A	7.8	7.9 clear	. . .	7.7 solids	8.3 solids	7.9 cloudy[a]	8.2 solids	9.7 cloudy[a]	8.2 cloudy[a]	8.2 clear	7.6 clear
B	7.7	7.6 clear	7.6 clear	7.5 solids	7.9 solids	7.5 cloudy[a]	7.8 solids	7.5 cloudy[a]	7.5 cloudy[a]	7.8 clear	7.8 clear
C	8.0	8.5 clear	8.4 clear	8.4 solids	8.7 solids	8.5 clear[a]	8.6 solids	8.1 solids	8.6 clear[a]	8.5 clear	8.4 clear
D	7.5	8.2 clear	8.2 clear	8.1 solids	8.5 solids	8.1 clear[a]	8.5 solids	8.3 solids	8.2 clear	8.2 clear	8.0 clear
E	6.2	6.4 clear	6.3 gel	6.3 solids	6.5 solids	6.2 gel	6.6 clear[a]	6.5 cloudy[a]	6.2 cloudy[a]	6.5 solids	6.3 clear
F	11.1	10.6 solids	10.5 solids	10.7 clear	10.7 clear	10.7 solids	10.6 solids	9.2 solids	10.8 solids	10.7 solids	10.6 solids
G	11.0	10.0 clear	9.7 clear	9.2 clear	9.5 clear	9.6 clear	9.2 clear	8.3 solids	9.7 clear	9.9 clear	10.0 clear
H	10.7	9.4 solids	9.4 solids	9.8 solids	9.7 solids	9.8 solids	10.0 solids	9.6 solids	9.5 solids	10.0 solids	9.8 solids

[a] Fluid was initially clear or cloudy while at elevated temperature but solids formed during cooldown.

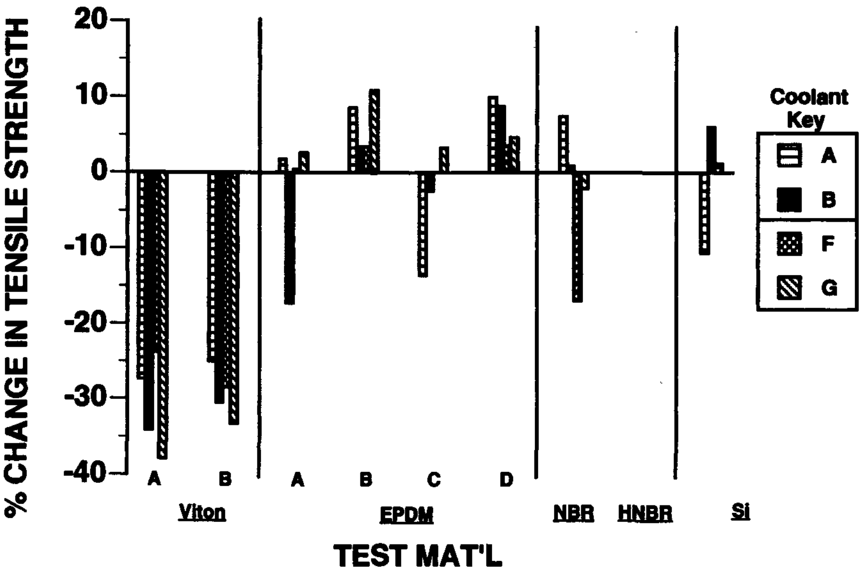

FIG. 1—*Change in tensile strength after immersion in concentrates for 70 h at 100°C.*

A in coolant B was not observed for the same elastomer in the other propylene glycol coolants. The elongation data (Fig. 2) present a more uniform picture. No inhibitor or base glycol trends are apparent for any of the test materials. What might be argued as a difference between silicate and organic acid inhibitors for HNBR is again clouded by the relatively small differences in magnitude observed.

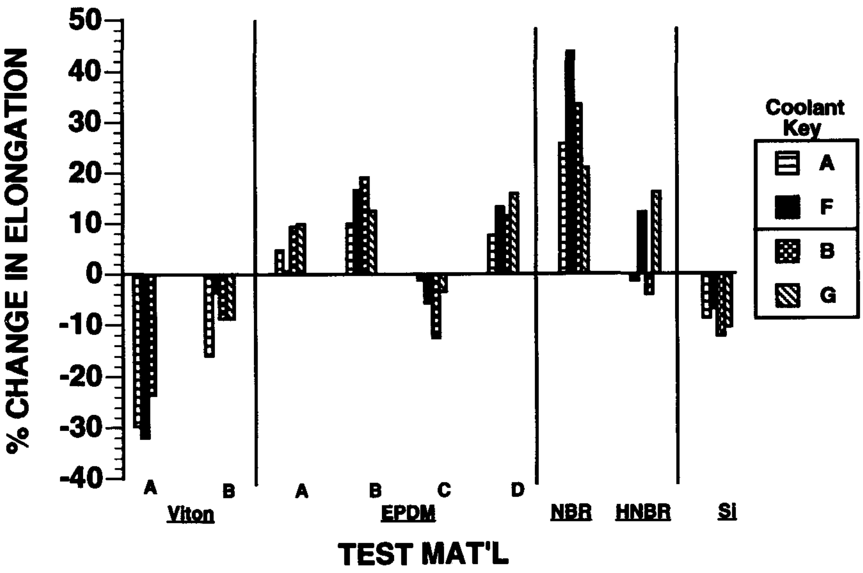

FIG. 2—*Change in elongation after immersion in concentrates for 70 h at 100°C.*

TABLE 5—*Total silicon (ppm) in post-test fluid concentrates after 70 h at 100°C.*

		Viton		EPDM					
Coolant	Base Fluid	A	B	A	B	C	NBR	HNBR	Silicone
E	340	300	300	300	400	400	400	400	500
F	670	500	400	400	400	400	400	400	500
G	700	600	500	500	500	700	500	500	1000
H	120	...	98	...	...	...	200	100	100

NOTE: No silicon was detected in the organic acid coolants except those exposed to silicone rubber; levels of 75, 600, and 200 ppm were detected in coolants A, B, and C, respectively.

Determining whether any of the physical changes which were observed are statistically significant would require a more exhaustive examination of the data which was beyond the scope of this paper. In addition, it is unclear whether the data generated in the concentrates should be extrapolated to working antifreeze solutions. Overall, the data do not support that changes in elastomer physical properties were dependent on the type of base glycol or the type of additive package contained in the coolants tested.

Selected post-test fluids and any corresponding solids which had formed were analyzed in an attempt to determine whether exposure had altered the inhibitor content of the coolants or whether any materials had been leached from the test specimens. Particular attention was paid to inhibitor depletion (primarily silicon and organic acid levels) in the liquids and whether the solids contained sulfur, zinc, or inhibitor components. Representative data for the fluids are shown in Tables 5 through 8 and for selected solids in Tables 9 and 10.

Inhibitor levels, both inorganic and organic, remained essentially intact for all of the samples although certain inhibitor components were detected in a number of the solids, indicating some level of destabilization. Many of the fluids also contained low levels of sulfur and zinc, apparently extracted from the test specimens. Little or no evidence for the buildup of glycol degradation acids (for example, formic, acetic, etc.) was observed. Although the amount of solids collected from each coolant was not quantified, the intensity of the responses (X-ray) for the inorganic constituents in a weighed amount of sample which was analyzed led to a rough approximation of composition. All of the solids were primarily composed of organic material but the estimated level of total organic components depended on the elastomer tested. The solids from the silicated coolants typically contained appreciable amounts of sodium, potassium, silicon, and phosphorous with lower amounts of sulfur and zinc. The organic acid coolants, with much lower levels of inorganic inhibitors to begin with, generally yielded solids which were primarily composed of sulfur and zinc, with lesser amounts of sodium. Since no attempt

TABLE 6—*Total organic acid inhibitor content (wt. %) in post-test fluid concentrates after 70 h at 100°C.*

		Viton		EPDM					
Coolant	Base Fluid	A	B	A	B	C	NBR	HNBR	Silicone
A	3.0	2.8	...	...	2.8	2.7	2.8	2.7	2.8
B	3.0	2.8	2.8	2.6	2.8	2.8	2.8	2.8	2.8
C	4.0	3.9	3.7	3.5	3.6	3.7	3.5	3.7	3.8
E	2.0	1.8	1.8	1.7	1.7	1.8	1.8	1.7	1.7

TABLE 7—*Zinc content (ppm) in post-test fluid concentrates after 70 h at 100°C.*

		Viton		EPDM					
Coolant	Base Fluid	A	B	A	B	C	NBR	HNBR	Silicone
A	<0.5	<0.5	...	<0.5	<0.5	<0.5	<0.5	1.4	<0.5
B	<0.5	<0.5	0.6	2.4	2.6	1.8	11	1.6	1.8
C	<0.5	<0.5	<0.5	18	9.7	26	12	23	0.6
E	<0.5	<0.5	0.8	52	13	62	36	68	1.2
F	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
G	<0.5	<0.5	<0.5	100	1.2	86	55	3	<0.5
H	<0.5	...	<0.5	...	...	...	<0.5	<0.5	<0.5

was made to identify any of the organic components in the solids, the only conclusion that can be drawn from the data is that all of the coolants suffered at least some loss of inhibitor integrity. In addition, sulfur and zinc, presumably artifacts of the elastomer manufacturing process, were leached from each of the test materials. This is not unusual [*2*,*3*] as a result of this type of coolant contact and would be expected to have little impact on the ultimate performance of the elastomers in hose applications. The observed effects were found to be independent of base glycol or inhibitor type.

Dilutions

Two of the conventional (coolants F and G) and three of the organic acid (coolants A, C, and D) concentrates were diluted with distilled water (50%, by volume) and used for the second phase of the test program. After 168 h of exposure at 125°C, physical properties of the raw materials were determined and compared to pre-test data. It is again useful to review the data with a focus on whether the inhibitor technology or the base glycol contained in the coolants had any discernible impact on the properties of the test specimens. The data are presented using this type of format in Figs. 3 through 6. Coolant D is not included in these charts since it had essentially the same impact on the test materials as Coolant C.

No inhibitor or glycol effects are apparent in the tensile, elongation, or hardness for any of the materials. However, a clear inhibitor package impact can be seen for the change in volume of the NBR (Fig. 5). The organic acid coolants caused a decrease in volume while the silicated products caused swelling. The same trend was not observed for the concentrates and the cause for the difference with the diluted samples is unclear.

A General Motors specification for Striation-Resistant Engine Coolant Hose (GM6278M) governs coolant hose made from EPDM, but when compounded and reinforced with Aramid

TABLE 8—*Sulfur content (ppm) in post-test fluid concentrates after 70 h at 100°C.*

		Viton		EPDM					
Coolant	Base Fluid	A	B	A	B	C	NBR	HNBR	Silicone
A	<20	<20	...	100	<20	100	200	40	<20
B	<20	<20	<20	100	<20	200	400	52	<20
C	<20	<20	<20	200	<20	200	300	50	<20
E	<20	24	33	100	56	200	400	88	33

TABLE 9—*Composition of selected solids samples after immersion in organic acid concentrates for 70 h at 100°C (weight%).*

	Coolant A					Coolant B				
Component	EPDM A	EPDM B	EPDM C	NBR	HNBR	EPDM A	EPDM B	EPDM C	NBR	HNBR
Sodium	0.61	0.36	0.02	0.38	0.08	0.50	0.20	0.35	0.38	0.08
Silicon	0.03	0.02	0.02	0.01	0.16	0.03	0.05	0.03	0.01	0.05
Sulfur	4.0	...	...	3.0	0.06	3.70	0.01	0.06	4.50	0.01
Zinc	3.0	1.30	0.03	3.50	1.50	2.50	0.90	1.90	4.80	0.40
Total organics (estimate)	90	96	99	92	96	90	96	95	87	98

TABLE 10—*Composition of selected solid samples after immersion in conventional concentrates for 70 h at 100°C (weight%).*

	Coolant F[a]			Coolant G[a]		Coolant H[a]			
Component	Viton A	Viton B	Silicone	HNBR	NBR	Viton B	Silicone	NBR	HNBR
Sodium	1.10	1.60	13	21	0.79	6.30	3.60	6.10	3.10
Silicon	0.32	0.17	3.1	0.44	5.10	0.05	...	0.06	0.09
Phosphorous	0.41	0.64	...	11	0.04	7.50	4.30	7.40	3.40
Sulfur	...	...	0.15	0.01	4.70	0.11	0.03	...	0.05
Zinc	...	0.01	0.10	0.02	5.70	...	...	0.02	0.01
Total organics (estimate)	97	96	58	45	75	62	79	63	82

[a] Solids which formed as a result of immersion of EPDM C and D, NBR, and nylon were not analyzed; no solids resulted after immersion of EPDM A and B.

[b] No solids were observed as a result of immersion of any of the test specimens except NBR.

[c] Solids were observed in all test solutions; only the ones listed were analyzed.

yarn, so it is not directly applicable to the raw materials used in this program. However, since it does provide the maximum physical property changes allowed for coolant hose after immersion under similar conditions, it was still useful as a guide in gauging whether any notable degradation of properties had occurred. The maximum changes allowed by the specification after immersion in boiling coolant solution for 168 h are as follows:

• Tensile strength change, %, maximum	−15
• Volume change, %, maximum	+20
• Hardness change, durometer, Shore A	−15 to +10
• Elongation change, %, maximum	−30

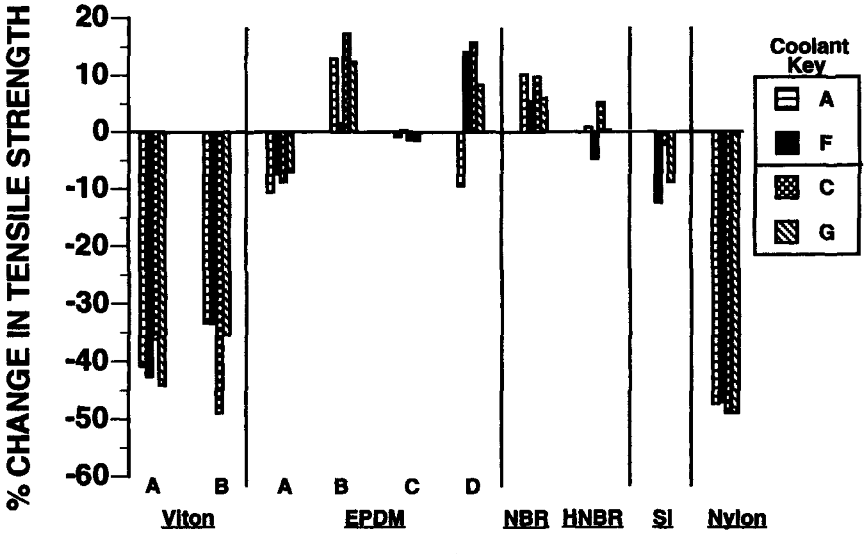

FIG. 3—*Change in tensile strength after 168 h at 125°C.*

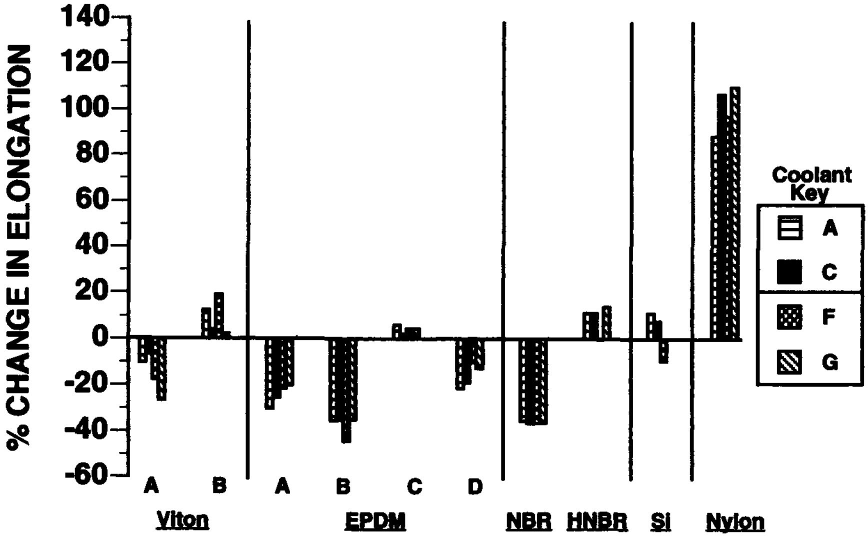

FIG. 4—*Change in elongation after 168 h at 125°C.*

Tensile strength (Fig. 3) for both samples of Viton and the nylon decreased by more than 15% but neither of these materials would typically be found in a cooling hose application. Similarly, using the −30% limit for elongation, the EPDM B and the NBR (Fig. 4) could be termed marginal. Of the four EPDM samples, the nonelectrochemically resistant, peroxide cured sample (C) fared the best, showing virtually no changes except for a minimal amount of

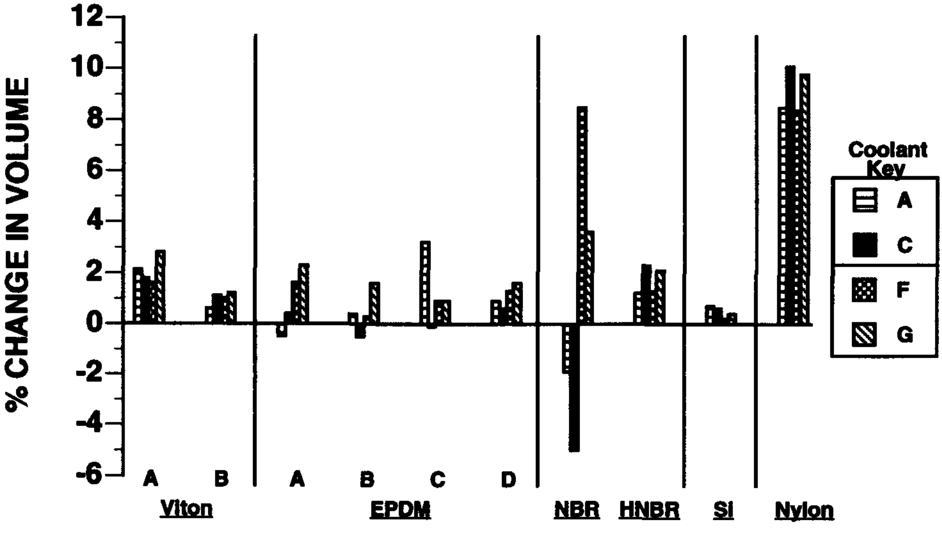

FIG. 5—*Change in volume after 168 h at 125°C.*

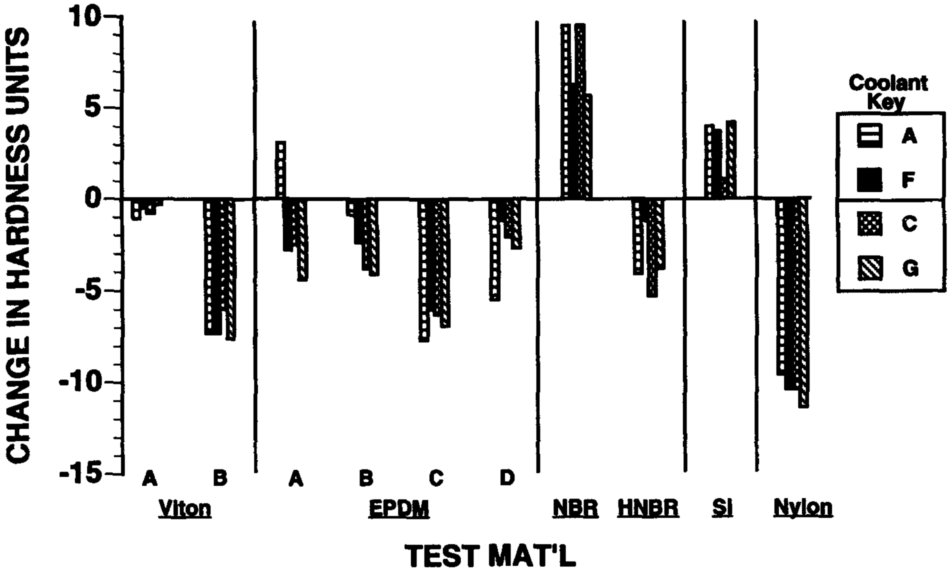

FIG. 6—*Change in Shore A hardness units after 168 h at 125°C (Shore D units for nylon).*

softening (Fig. 6). The other EPDM samples all showed slight decreases in elongation, perhaps due to embrittlement. The silicone rubber also showed fairly good resistance in all of the fluids with slightly greater increases in elongation (possible softening) observed in the organic acid coolants. Analysis of the nylon data was difficult since the D 471 protocol is not designed for use with this type of material. There was a general softening in all of the coolants which could have caused the decrease in tensile strength. Nylon has a tendency to absorb water which subsequently could have caused the increases in elongation observed.

For the diluted fluids, the magnitude and the direction of the changes observed for some of the elastomers were considerably different than the changes seen for the concentrates. The lower coolant concentration was likely offset by the higher test temperature and duration. However, as in the results observed for the concentrates, except for the NBR anomaly mentioned earlier, coolant inhibitor composition was not a factor. Any degradation in properties observed was observed "across the board" in all of the coolants tested.

Perhaps more meaningful than the changes in the physical properties of the elastomers were the changes observed in the coolant solutions. A number of the coolants extracted sulfur from several of the elastomers (Table 11), most notably the sulfur cured EPDM samples (A, B, and

TABLE 11—*Sulfur content (ppm) in post-test dilutions after 168 h at 125°C.*

Coolant	Base Fluid	Viton		EPDM				NBR	HNBR	Silicone	Nylon
		A	B	A	B	C	D				
A	<20	<20	<20	130	32	130	200	220	63	<20	<20
C	<20	<20	<20	130	150	29	140	230	71	<20	<20
D	<20	<20	<20	...	...	34	100	280	98	...	<20
F	<20	<20	39	110	250	<20	140	320	72	<20	<20
G	<20	25	<20	150	240	42	160	330	86	<20	<20

TABLE 12—*Total silicon content (ppm) in post-test dilutions after 168 h at 125°C.*

Coolant	Base Fluid	Viton A	Viton B	EPDM A	EPDM B	EPDM C	EPDM D	NBR	HNBR	Silicone	Nylon
A	23	43	240	51	32	59	92	9	26	160	<20
C	<1	<20	<20	44	11	18	27	19	23	200	<20
F	300	140	150	260	260	220	120	120	230	500	<20
G	350	180	160	180	190	190	150	250	240	560	<20

D) and the nitrile rubbers; the highest levels were observed in the samples which had been in contact with NBR. In addition to a small amount of silicon apparently leached from the glass pressure vessels, some attack of silicone rubber also occurred in all of the coolants as evidenced by the increase in silicon in solution (Table 12). This was also observed for this elastomer when tested in the concentrates (Table 5). There was little evidence of an appreciable decrease in inhibitor content in the organic acid fluids (Table 13), but at least some degree of silicate destabilization was observed for the conventional and hybrid coolants, where significant quantities of gel formed. Further evidence for polymer formation was the decrease in total silicon in these post-test solutions (Table 12). Little or no zinc was detected in any of the post-test coolant liquids. Changes in the pH of the test fluids followed the same general trends established with coolant concentrates: slight increases for organic acid coolants and decreases for the conventional products.

Solids were also evident in all of the post-test fluids. The conventional coolants typically contained considerably more solids than their organic acid counterparts, presumably due to the silicate polymerization mentioned above. The major components in the solids which were analyzed using qualitative X-ray analysis were silicon, sulfur, and zinc, with lesser amounts of sodium and potassium. Again, no attempt was made to identify the organic constituents in the solids and efforts to accurately quantify the total amount of solids formed in each tube were hindered by the repeated plugging of the filtering apparatus. A blank, consisting of distilled water only, yielded solids which contained predominantly silicon, assumed to have been leached from the glass tube. Trace amounts of sodium, iron, and aluminum were also detected. Coolant blanks (50/50 mixtures of coolant and water without tension bars) for several of the formulations were also run and, although significantly lower levels of solids were generated, analysis did reveal the presence of many of the same components. Taken as a whole, the data would seem to indicate that the cause of solids formation during this phase of the testing consisted of three elements: elastomer deterioration, coolant breakdown, and the test conditions and equipment used.

TABLE 13—*Total organic acid inhibitor content (weight%) in post-test dilutions after 168 h at 125°C.*

Coolant	Base Fluid	Viton A	Viton B	EPDM A	EPDM B	EPDM C	EPDM D	NBR	HNBR	Silicone	Nylon
A	1.7	1.9	1.9	1.9	1.8	1.8	1.9	1.6	1.8	1.9	1.8
C	2.1	2.2	2.1	...	...	2.2	2.0	2.0	2.0	1.9	2.0
D	2.9	...	...	3.3	...	3.0	2.8	2.5	2.7	3.2	2.9

TABLE 14—*Change in tensile strength (psi) of HDPE during immersion in refluxing coolant solution for 1008 h.*

Coolant	Initial	168 h	504 h	1008 h
A	3792	3905	3928	4058
B	3792	3873	3877	3995
C	3792	3791	3909	3840
D	3792	3835	3874	3913
F	3792	3905	3813	3856
G	3792	3896	3810	3873

HDPE Overflow Bottle Testing

The high density ethylene-hexene copolymer samples were evaluated in the four organic acid coolants (A through D) and in the two conventional products (F and G). Changes in tensile strength, elongation, and hardness are shown in Tables 14 through 16. Little or no significant change in tensile strength or hardness was observed. There was a general decrease in elongation (Table 15) indicating some degree of hardening or loss of pliability of the test plaques. However, the fact that actual overflow bottles would not be subjected to elongation of this type, coupled with the minimal changes seen in tensile strength, indicate that the elongation losses observed are not an issue.

Two of the coolant mixtures, B and G, discolored the tension bars slightly. Subsequent experiments indicated that this was a dye issue rather than being glycol or inhibitor related. No staining was observed after 4 to 6 weeks of immersion in uninhibited, aqueous solutions of each base glycol. Similarly, no discoloration was seen after a 5 week test in Coolant G which had been formulated with a replacement dye package.

Conclusions

The test program was primarily designed to determine whether propylene glycol base coolants affect the nonmetallic materials typically found in automotive cooling systems any differently than their ethylene glycol base counterparts. Despite the short duration and somewhat mild conditions, the testing was rigorous enough to impact the physical properties of a number of the test materials. Although none of the observed changes were thought to be significant, this is a judgment more appropriately made by component and vehicle manufacturers. However, several other conclusions can be drawn.

All of the test materials suffered at least some degree of deterioration after exposure to coolant concentrates and dilutions, as evidenced by the presence of zinc or sulfur in the post-

TABLE 15—*Change in elongation at break (%) of HDPE during immersion in refluxing coolant solution for 1008 h.*

Coolant	Initial	168 h	504 h	1008 h
A	388	348	219	188
B	388	370	337	311
C	388	184	237	231
D	388	240	276	312
F	388	187	303	248
G	388	276	295	253

TABLE 16—*Change in hardness (Shore D) of HDPE during immersion in refluxing coolant solution for 1008 h.*

Coolant	Initial	168 h	504 h	1008 h
A	69.6	68.4	69	69.8
B	69.6	68.8	68.8	69.8
C	69.6	69	69.6	69
D	69.6	68.8	69.4	69.6
F	69.6	68.4	69.4	69.8
G	69.6	69	69.2	68.8

test liquids or solids. However, a correlation between the presence of these components in the test fluids and the ultimate performance "under the hood" of products made from the test materials (for example, hoses, seals, etc.) cannot be made.

Conventional, hybrid, and organic acid coolants affected the elastomers similarly. The coolants were also influenced by exposure to the elastomers. Qualitative analysis confirmed the presence of inhibitor components in the solids which developed in many of the fluids. The impact was greater in the conventional silicated formulations where significant destabilization and subsequent gel formation was noted. This resulted in a decrease in the level of silicate in these products but no appreciable depletion of any other inhibitors in any of the other coolants was observed. There was no evidence that any of the changes in elastomer or coolant integrity were dependent on the identity of the glycol base which was used.

Acknowledgments

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G. L. M. Vroomen,[1] *S. S. Lievens,*[2] *and J. P. Maes*[3]

Influence of Engine Coolant Composition on the Electrochemical Degradation Behavior of EPDM Radiator Hoses

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REFERENCE: Vroomen, G. L. M., Lievens, S. S., and Maes, J. P., "**Influence of Engine Coolant Composition on the Electrochemical Degradation Behavior of EPDM Radiator Hoses,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335,* R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 183–195.

ABSTRACT: EPDM (ethylene-propylene rubber) has been used for more than 25 years as the main elastomer in radiator hoses because it offers a well-balanced price/performance ratio in this field of application. Some years ago the automotive and rubber industry became aware of a problem called electrochemical degradation and cracking. Cooling systems broke down due to a typical cracking failure of some radiator hoses. Different test methods were developed to simulate and solve the problem on laboratory scale. The influence of different variables with respect to the electrochemical degradation process has been investigated, but until recently the influence of the engine coolant was ignored. Using a test method developed by DSM elastomers, the influence of the composition of the engine coolant as well as of the EPDM composition has now been evaluated. This paper gives an overview of test results with different coolant technologies and offers a plausible explanation of the degradation mechanisms as a function of the elastomer composition.

KEYWORDS: elastomers, electrochemical degradation, EPDM, inhibitors, nitrite, carboxylates, organic acids, hoses, seals, propylene glycol

The reduction of the overall mass of vehicles to improve fuel economy entailed extensive use of light materials such as aluminum and plastics for the construction of engine and cooling system parts. Modern engines are smaller and more powerful which means they dissipate more heat and require a coolant that is stable at high heat fluxes and temperatures. The introduction of more efficient engines operating at higher temperatures with less coolant volume has prompted an increased awareness of the importance of the engine coolant quality. Coolants are ethylene glycol (or propylene glycol) based. However, the most important additive constituents of engine coolants are corrosion inhibitors [*1*]. The inhibitor packages of these coolants have changed in the last few decades. Nowadays, conventional inhibitor technologies are increasingly being replaced by organic acid inhibitors. The organic acid based systems used in extended life coolants are buffered at a low, near neutral, pH and generally provide improved corrosion protection. However, the effect of these new inhibitors on the elastomer materials currently used in engine cooling systems has been questioned.

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FIG. 1—*Crack formation in the tube, detailed representation.*

EPDM has for a long time been regarded as the ideal material for rubber parts of automotive cooling systems. Apart from its use in sealing rings/membranes of cooling systems, EPDM is used especially in coolant hoses.

For a variety of reasons the European automotive industry uses both sulfur-cured and peroxide-cured coolant hoses. Both types amply meet the automotive requirements.

EPDM apparently has the right qualifications, including an optimum price/performance ratio, for these applications in the automotive industry. Nevertheless, the European automotive industry has drawn attention to a rather strange type of damage, which was first reported a few years ago [*2*]. The failure consists in leakage of the cooling system due to cracks formed in EPDM radiator hoses.

The cracking process starts in the inner hose, with the cracks running mainly perpendicular to the direction of mechanical stress (axial direction, Fig. 1). Once a crack has been initiated, it deepens until the reinforcement material (usually aramid) is exposed to the water/glycol mixture. Because aramid as well as polyester cannot withstand this medium, especially at high temperatures, the polymer degrades and fiber strength is dramatically reduced (as was found during the investigation).

The nature of the problem and the type of cracks were found to be very similar to a problem observed several years ago in the United States [*3,4*]. The phenomenon as such is referred to as electrochemical cracking of EPDM (Fig. 2) and has been the subject of study for many years.

Theoretical Considerations

The Galvanic Cell

The major components of coolants used in car engines are water and ethylene glycol, the latter providing antifreeze protection. Depending on the application and the severity of operation, different corrosion inhibitors are added to the coolant (usually combinations or selections of inhibitors such as borax, benzoates, nitrites, silicates, phosphates, triazoles and carboxylates).

FIG. 2—*Dendrite or so-called striae structures in cracked radiator hose.*

By choosing the right inhibitor package one can suppress corrosion in the cooling system, thus assuring long engine life.

The cooling system problems, however, do not always originate in the metal components but can also find their origin in the rubber. The carbon in the EPDM rubber and the metal of engine components may form a galvanic couple, giving rise to galvanic corrosion (Fig. 3).

The engine (parts) or other metal alloys or both in the cooling system in combination with the radiator hose are the electrodes of the galvanic cell. Theoretically, an electrical current cannot flow if no electrolyte is available. The electrolyte is responsible for the transportation of the electrons from one electrode (for example, anode) to the opposite electrode (cathode). A coolant is such a suitable electrolyte. It contains, besides water, monoethylene glycol or

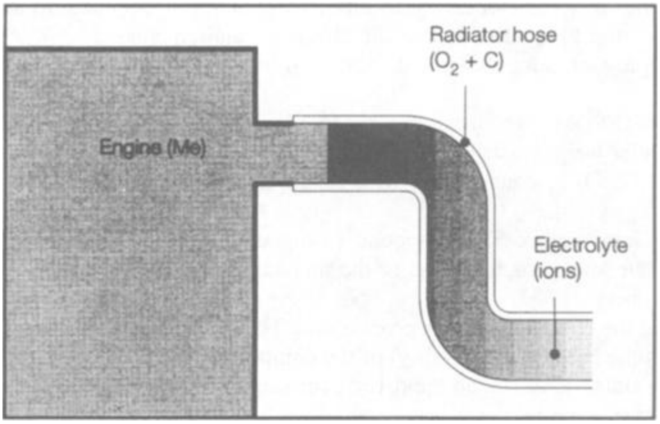

FIG. 3—*Principle of galvanic cell in the cooling system.*

monopropylene glycol and a substantial amount of inhibitors to protect the engine, or generally all metal parts, in the cooling system from corrosion.

Coolant

Coolant requirements and specifications are changing rapidly. These requirements are met by the development of multicomponent coolants that provide a low freezing point, high thermal conductivity and specific heat, good fluidity, elevated boiling point, low toxicity, and a proper balance of additives. Additives may include corrosion inhibitors to give protection against uniform as well as localized corrosion. Other additives, present in lower concentrations, are:

- stabilizing agents to improve the hard water stability.
- sequestering agents to inhibit deposit formation.
- antifoam agents to suppress foam formation.
- dye to characterize the product.
- sodium hydroxide (NaOH) or potassium hydroxide (KOH) to optimize the pH.

Coolant Hoses

As already mentioned, sulfur and peroxide cured EPDM hoses are commercially used. The type of curing system to be used is primarily determined by the requirements imposed by the OEM. If a high service temperature or relatively slow aging (above 125°C) is requested, a peroxide-curing system is necessary due to the better aging properties/heat resistance compared to sulfur-cured EPDM (high retention of physical properties). Besides the aging properties some car manufacturers demand an extremely low deposit formation in their cooling system. This is to prevent blocking of the radiator or other cooling system parts like the water pump, which will negatively affect the cooling capacity of the system (lower heat transfer at higher engine temperatures). Extremely low or no deposit formation is much easier to achieve with a peroxide-cured hose than with a sulfur-cured hose (the tube). Sulfur cured EPDM hoses contain a relatively high amount of accelerators that are less soluble in the rubber matrix and are consequently leached out by the ethylene glycol/water mixture. The leached substances can sediment in the system at cooler spots or can react with chemicals from the inhibition package of the antifreeze to create insoluble substances.

Besides the type of curing system used, the filling degree (amount of additives added to the rubber compound) of a radiator hose can differ from one hose producer to another and from one car manufacturer to another (due to the different requirements).

But in principle each hose compound contains more or less the same basic ingredients:

- the polymer (EPDM), which can differ in Ethylene/Propylene (E/P) ratio, molecular weight and molecular weight distribution, type and amount of unsaturation.
- zinc oxide (ZnO) in combination with stearic acid, which are necessary to activate the sulfur curing system.
- carbon black to reinforce the compound. Compounds can differ in the type of carbon black used (particle size, structure) and in the amount added (expressed in parts per hundred parts of rubber).
- oil to make the compound better processable. The oil/carbon black ratio to a large extent determines the hardness (flexibility) of the compound.
- processing aid(s), to obtain an improved extrusion behavior without affecting the hardness or other physical properties.
- an anti-oxidant, to protect the polymer against thermo-oxidative degradation.

TABLE 1—*Volume resistivity of some rubber ingredients.*

Type of Ingredient	Volume Resistivity, Ω cm
EPDM	10^{14} to 10^{16}
Paraffinic oil	10^{12} to 10^{14}
Carbon black	10^{-2} to 1
Mineral fillers	10^{12} to 10^{15}

Carbon black has a significantly higher electrical conductivity than the other ingredients used (an overview of the conductivities of the different ingredients is listed in Table 1). Therefore, carbon black is the ingredient which contributes most to electrochemical degradation. Over the years, a lot of information has been collected about factors affecting the conductivity of compounds or composites. It appears that many physical processes can be involved and that the dominant process depends upon the composition of the composite and the conditions of the measurement. At low loads of carbon black the conductivity of the composite is essentially that of the dielectric medium. As the loading increases, a critical point is reached (percolation threshold) where the conductivity starts to increase rapidly (or resistivity decreases) as a function of loading (Fig. 4). The entire region of conductivity increase (region B) is called the percolation region. In this region, conductivity is limited by the potential barrier (V_0) which the charge carriers (electrons) must surmount to move from one carbon black aggregate to another which is close but not touching (tunneling effect). The gap distance may be of the order of 15 to 100 Å.

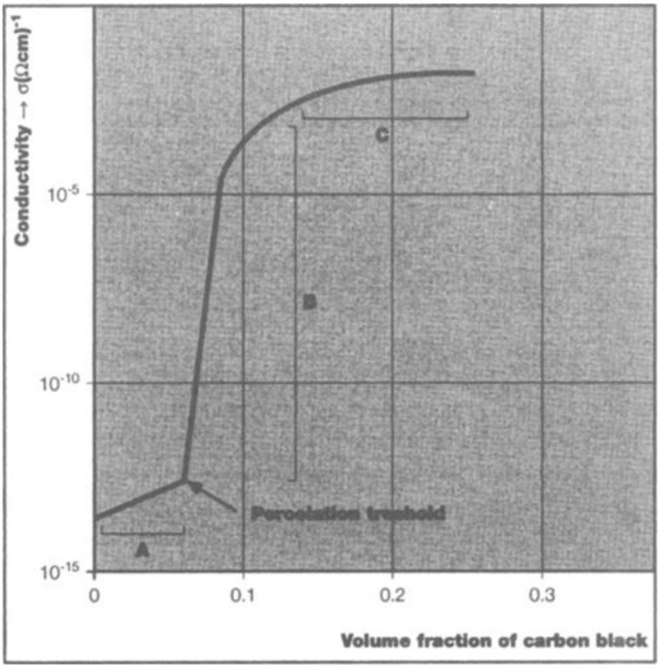

FIG. 4—*Conductivity versus volume fraction of carbon black.*

The polymer and paraffinic oil are in principle electrically neutral due their organic structure and the absence of free electron pairs. The influence of the ZnO, stearic acid or the processing aid are negligible due to their very low volume fraction in the compound.

Volumewise, the contribution of the carbon black in the compound is the most significant. The presence of free electrons, especially at the surface of the carbon black particle, makes the carbon black an interesting object of study. Within DSM elastomers an extensive study into the contribution/influence of the carbon black type and amount has recently finalized. This part of the investigation will be reported and published separately.

Experiments

The Test Method

In the literature several test methods are described [*2*,*3*,*4*,*9*]: the Brabolyser test, the U-tube test and the DSM test to determine the electrochemical degradation behavior of rubber compounds.

The Brabolyser and U-tube tests are less suitable for development purposes, the mechanical stress in the material being undefined. In addition, in both cases the electrochemical aging takes place under "static conditions," with stagnant coolant, while in practice it is flowing. Further, the connection of the rubber electrode to a metal electrode which is connected to the voltage source plays an important role. In principle, polymers are electrical insulators relative to metals.

For the DSM laboratory test (Fig. 5) a better defined setup was chosen, essentially consisting of a stainless steel holder in which a specimen can be tested under mechanical strain. The specimens used were S2 dumbbells according to ISO 37.

The specimen is elongated under defined conditions after which it is exposed for a certain time. The test setup is designed (Fig. 6) so that the dumbbell is galvanically isolated from the holder, allowing the latter to serve as a cathode while the dumbbell serves as the anode. The current from the anode through the dumbbell can be measured. In the present setup a 100 ohm measurement resistor is used; at this value of the resistor the reduction in cell voltage at the current measured is negligible.

FIG. 5—*The DSM ECD-test kit.*

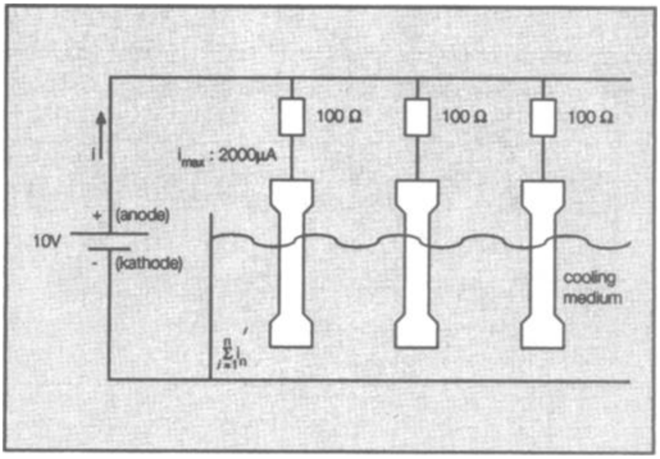

FIG. 6—*Principle of the DSM ECD-test kit.*

Test Conditions

As test medium a solution of commercially available coolant is used (50 volume% coolant and 50 volume% demineralized water) at a temperature of 80 to 95°C. The test duration can be varied. After the test, the dumbbells are inspected microscopically. The cracking behavior is qualified/quantified according to several reference pictures of cracked dumbbells surfaces (Fig. 7).

Besides the microscopic examination, the retention of specifically tensile strength and elongation at break is used to characterize the electrochemical degradation behavior of the tested samples.

Test Samples (EPDM Compounds)

To study the influence of the type of coolant with respect to its contribution to the electrochemical degradation behavior, different EPDM compounds were exposed to various coolants.

The tested EPDM compounds were more or less representative of the radiator hose formulations that are used nowadays (in the different markets).

Besides the examination of the influence of the type of curing system, the loading level (especially the carbon black level) was investigated as an additional parameter. To obtain more or less the same hardness level, which is again representative of the radiator hose market, the carbon black level was varied in combination with the oil level. Consequently the carbon black level was varied from approximately 16 to 27 vol. % (detailed information see Table 2).

A basic difference between compounds is the type of vulcanization system used: sulfur or peroxide. Additionally, the peroxide cured compounds are free from zinc-oxide (because it makes no contribution to the curing) but contain stearic acid to improve the processing behavior (mixing and milling).

Tested Coolants

Simultaneously with the changes in engine design, the inhibitor technology has been altered and upgraded to comply with new requirements. Depending on the application, ecological

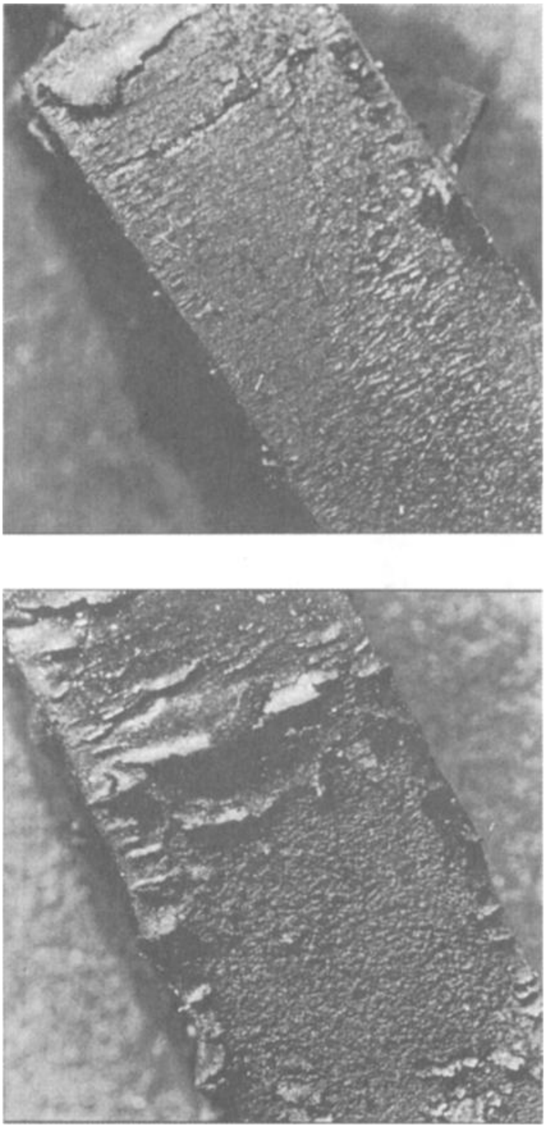

FIG. 7—*Surface deterioration of some exposed samples.*

TABLE 2—*Tested EPDM formulations.*

Ingredient	I	II	III	IV	V
Polymer	100	100	100	100	100
ZnO	3	3	3	3	3
Stearic acid	1.5	1.5	1.5	1.5	1.5
N-550	100	130	100	80	60
N-660	50	. . .	. . .	. . .	. . .
Paraffinic oil	85	75	60	50	40
Vulcanization system[a]	7.3	7.3	7.3	7.3	7.3
Polymer	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5
N-550	100	130	100	80	60
N-660	50	. . .	. . .	. . .	. . .
Paraffinic oil	70	65	50	45	35
Peroxide	8	8	8	8	8
Co-agent	1.5	1.5	1.5	1.5	1.5

[a] Sulfur/sulfur-donor system.

aspects, toxicological aspects, and availability, different inhibitors are used worldwide. Most of the inhibitors are normally ionic, resulting in an increased electrical conductivity of the coolant. The tested coolant formulations are representative of modern as well as traditional coolant inhibitor packages. Table 3 gives an overview of the inhibitor compositions of the tested coolants.

Results and Discussion

Tension Tests

Figures 8 and 9 show the retention of tensile strength in sulfur-cured and peroxide-cured compounds after an exposure time of 7 days. The carbon black content has a significant influence on the retention of the tensile strength (calculated as tensile strength after exposure divided by the original tensile strength) of the rubbers. When less than 19 volume% carbon black is used in the sulfur-cured EPDM rubber, a negligible influence on tensile strength is observed.

TABLE 3—*Engine coolant inhibitor formulation.*

	Coolant					
Inhibitor	A	B	C	D	E[a]	F
SiO_3^{2-}		x	x	x		
NO_3^-	x	x	x	x		
NO_2^-		x				
$B_4O_7^{2-}$		x				
PO_4^{3-}						
MoO_3^-	x					
Triazol		x	x	x	x	x
Benzoate	x	x		x		
Mono acid	x		x	x	x	x
Dibasic acid	x		x		x	x
Organic buffer						x

[a] Formulation in propylene glycol.

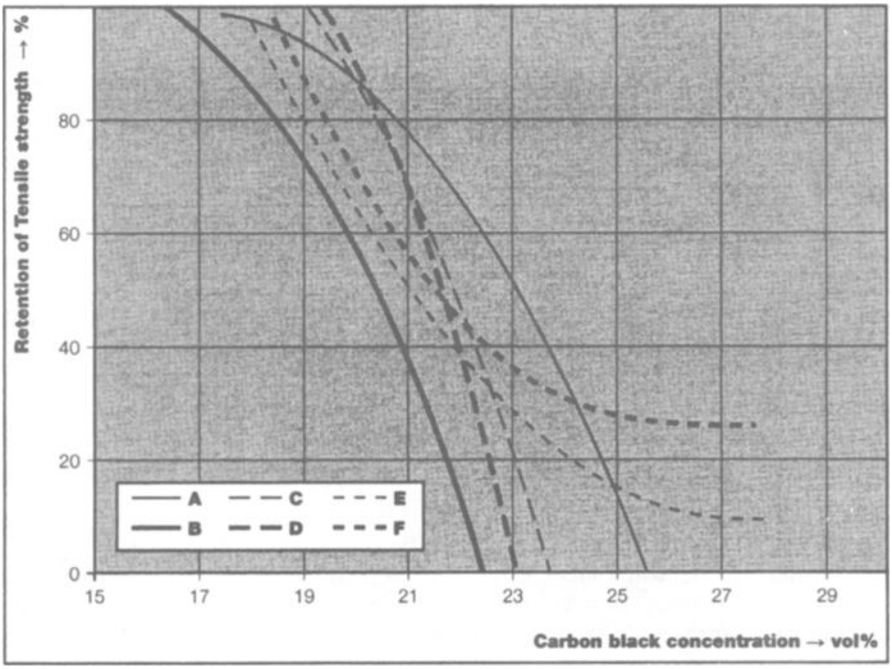

FIG. 8—*Retention of tensile strength as function of volume% carbon black and type of coolant (sulfur-cured EPDM).*

This is in line with the results of the microscopic examination: no surface deterioration is observed. A rapid change in tensile strength properties can be observed in rubbers having a carbon black content of between 20 and 23 volume%.

Many test specimens made of sulfur-cured EPDMs (see Fig. 8) with a relatively high carbon black content broke during the test period. In the same figure we can observe that coolant inhibitor formulations consisting only of organic inhibitors initially show a less good performance (curves E and F). However, when increasing the amount of carbon black in the rubber compounds these formulations perform better than others (curves C and D) and are able to complete the whole test duration without breaking. Some compounds showed surface deterioration. This same figure shows that the inhibitor package tends to perform when dissolved in ethylene glycol better than when dissolved in propylene glycol (re: curves E and F). An interesting observation is that the coolant formulation B, containing nitrite and borate, gives a worse overall result than the other formulations. This is probably mainly due to the presence of nitrite. Nitrite is a reactive chemical component with an oxidizing tendency. The potential (negative value) indicates that the reaction with water, which is present in the system, will happen spontaneously.

$$HNO_2 + H_2O \leftrightarrow NO_3^{2-} + 3H^+ + 2e$$

$$E_0 = -0.94\ \text{V}$$

In coolant, the nitrite is consumed quite rapidly [*10*] because of its reactive nature. Although electrochemical reactions may occur with components of the coolant, the changes in concen-

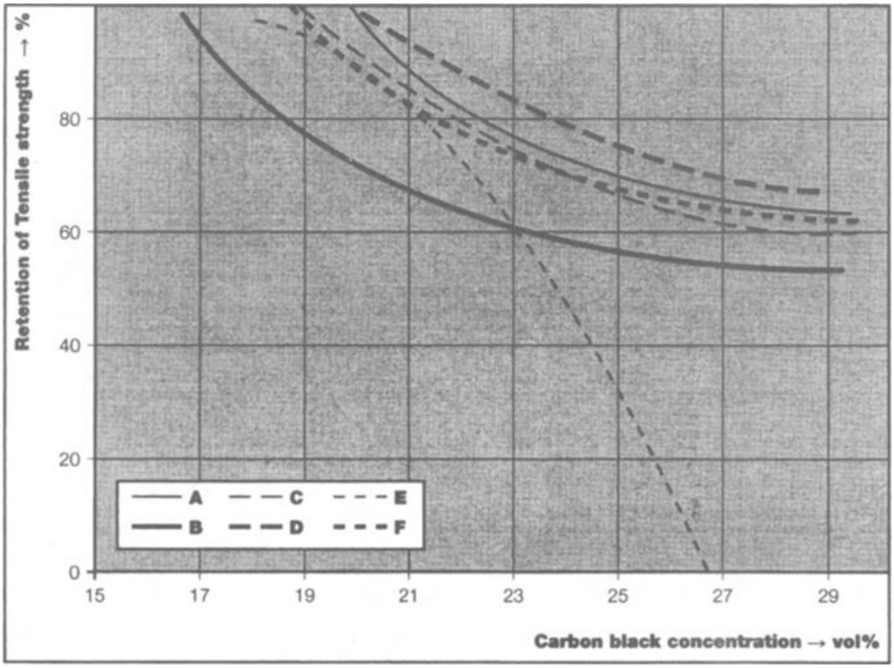

FIG. 9—*Retention of tensile strength as function of vol. % carbon black and type of coolant (peroxide-cured EPDM).*

tration of these components were too low to be detected with the normal (HPLC/EAF/IC) analytical instrumentation techniques. No significant change in inhibitor concentration: nitrite, organic acids, or silicates, could be observed during the test period. A possible explanation is that the amount of reaction is too limited certainly if the dumbbell/coolant volume ratio is considered.

In general, the observation can be made that the same coolant technology performs similarly (for example, curves C and D and curves E and F). Between different technologies a slight difference could be observed, with the performance of the coolant depending on the amount of carbon black in the hose material. Only coolant formulations containing nitrite give clearly more electrochemical cracking than the ones without nitrite.

Similar observations can be made for the peroxide cured rubbers. Again, the nitrite-containing formulation performs worse than the other inhibitor packages. The other formulations (curves A, C, D, and F) show almost equal performances during the test and even after the critical range of 20 volume% carbon black in the rubber compound a relatively high tensile strength is left. The overall higher retention of tensile strengths indicates that the peroxide cured rubbers are to a lesser extent attacked by electrochemical cracking.

A strange phenomenon that is not fully understood could be observed when comparing the same inhibitor package (curves E and F) in different fluids. In propylene glycol a rapid decrease in retention of tensile strength could be observed; from a certain point the rubber was no longer able to survive the test conditions. In these experiments too, no changes in inhibitor concentrations could be observed with the normal analytical test methods.

The effect of the inhibitor package on the electrochemical cracking is almost negligible compared with the influence of the carbon black level. It is even more negligible in the case

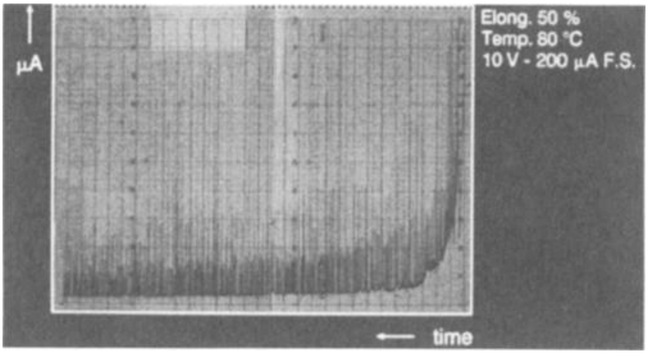

FIG. 10—*Electrical current as a function of exposure time for sulfur-cured EPDM.*

of peroxide cured rubbers. This can be understood from the fact that carbon-carbon crosslinks formed in the peroxide cured system are expected to be much more resistant to chemical as well as to electrochemical reactions.

Electrical Current as a Function of Compositions of Compound and Coolant

The observations from the tensile strength measurements are in agreement with the current measurements. The higher the current in the experimental electric circuit is, the more electrochemical cracking is observed. The observation that electrochemical cracking increases with carbon black content is not unexpected because it is well known that the conductivity results from the presence of carbon black in the compound. The lack of conductivity of compounds with low carbon black loading is attributed to the inability of electrons to jump from one carbon black aggregate to the other aggregate.

The measured current density is not much influenced by the change in inhibitor package of the coolant. This is not surprising either, because most of the coolants have similar conductivities. The aqueous electrolyte (coolant) has a much higher dielectric constant and current will easily flow through it. A slight change in the most conducting part of the electrical circuit considered (the aqueous electrolite) will not have the same impact as the drastic change in conductivity that is observed when the carbon black content in the rubber component is changed.

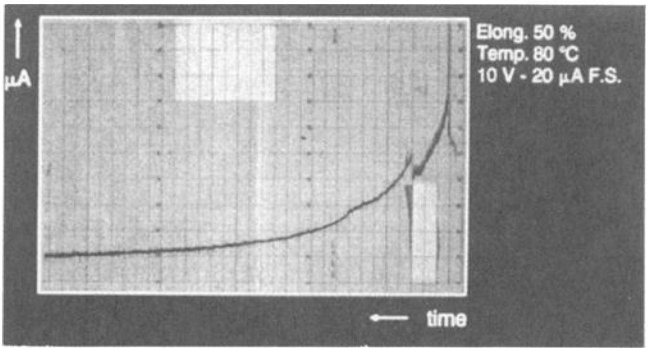

FIG. 11—*Electrical current as a function of exposure time for peroxide-cured EPDM.*

Figures 10 and 11 represent the current as a function of the exposure time, both for the sulfur-cured and peroxide-cured compounds. Peak currents were recorded on the baseline. These peak currents are much higher for sulfur-cured EPDM than for peroxide-cured EPDM.

The peak currents are probably caused by discharge phenomena when a certain amount of electrons are transferred from one group of carbon black aggregates to another group.

Besides the difference in the peak currents, the absolute level of the base line differs significantly between a sulfur and peroxide-cured EPDM compound. Both tested compounds differ only in the vulcanization system (carbon black levels are the same).

This observation confirms that sulfur-cured EPDM is more vulnerable to electrochemical cracking than peroxide-cured EPDM.

Conclusion

The phenomenon of corrosion in a radiator hose is an electrochemical process. Such hoses are usually carbon filled and attached to metal parts. The setup causes the hoses to act, accidentally, as a conductor in a galvanic system. The current that is produced can force destructive reactions in such a way that the rubber is damaged. Because a S-S bond is much more easily broken than a C-C bond, the sulfur-cured hoses are more subject to electrochemical cracking than peroxide-cured hoses. The influence of the coolant is limited. Different inhibitor packages give almost similar results. Carbon black contents in the rubber compound can be reduced so that they no longer sustain electrochemical activity at the coolant interface and further damage is prevented. A strange observation was made when propylene glycol was used as medium for the inhibitor package. In such coolants an increase in electrochemical cracking was observed especially in peroxide-cured EPDM rubbers. This observation is not yet completely understood; further experiments will have to be performed to obtain an explanation.

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Heavy-Duty Coolant Technology

Richard P. Carr[1]

Assessment of the Validity of Conductivity as an Estimate of Total Dissolved Solids in Heavy-Duty Coolants

REFERENCE: Carr, R. P., "**Assessment of the Validity of Conductivity as an Estimate of Total Dissolved Solids in Heavy-Duty Coolants,**" *Engine Coolant Testing, Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 199–209.

ABSTRACT: Conductivity is widely used in the analysis of heavy-duty coolants to estimate total dissolved solids. TDS is of concern in heavy-duty coolants because the practice of adding supplemental coolant additives (SCAs) to the coolant can lead to overloading and to subsequent water pump seal weepage and failure. Conductivity has the advantage of being quick and easy to measure and the equipment is inexpensive. However, questions are continually raised as to whether conductivity truly is a valid method of estimating TDS and, if so, over what concentration range. The introduction of new chemistries in heavy-duty coolants and new extended service interval (ESI) technologies prompts a critical assessment. Conductivity and TDS measurements for all of the coolants and SCAs used in heavy-duty engines in North America will be presented. The effects of glycol concentration on conductivity will also be examined.

KEYWORDS: conductivity, total dissolved solids, heavy duty, engine coolant, supplemental coolant additive (SCA), extended service coolant, fully formulated coolant

Total dissolved solids (TDS) are of concern in heavy-duty coolants because the practice of adding supplemental coolant additives to the coolant can lead to overloading of inhibitors in the coolant and to subsequent water pump seal weepage and failure. Conductivity has been used as a field test to estimate total dissolved solids for many years. Conductivity has the advantage of being quick and easy to measure and the equipment is inexpensive. So much so that many laboratory TDS values are probably extrapolations of conductivity measurements. Figure 1 is a photograph of a laboratory conductivity meter. Note that the switch has a TDS/ppm setting. However, the reading obtained is merely the specific conductance multiplied by a factor that is certainly not applicable to engine coolants.

On the other hand, the true measurement of TDS by, for example, (Modified) Federal Method 2540C is a lengthy process requiring a high-temperature drying oven and an analytical balance. Thus the correlation of conductivity measurements to TDS would be useful.

Both pure water and pure glycol are essentially nonconducting. The conductivity of coolants is caused by the motion of ionic species in solution, that is, the dissolved inhibitor ions, under the influence of an electric field. The magnitude of the conductivity of the coolant is a function of the concentration of ions, the type of ions and the dielectric constant of the solvent mixture.

Lange's Handbook of Chemistry[2] contains a table of Limiting Equivalent Ionic Conductances. Unfortunately, the list is incomplete from the point of view of ions commonly found

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[1] Vice-president, Research and Development, The Penray Companies, Inc. Wheeling, IL

[2] *Lange's Handbook of Chemistry*, Editor: John A. Dean, Twelfth Edition, McGraw-Hill Book Company.

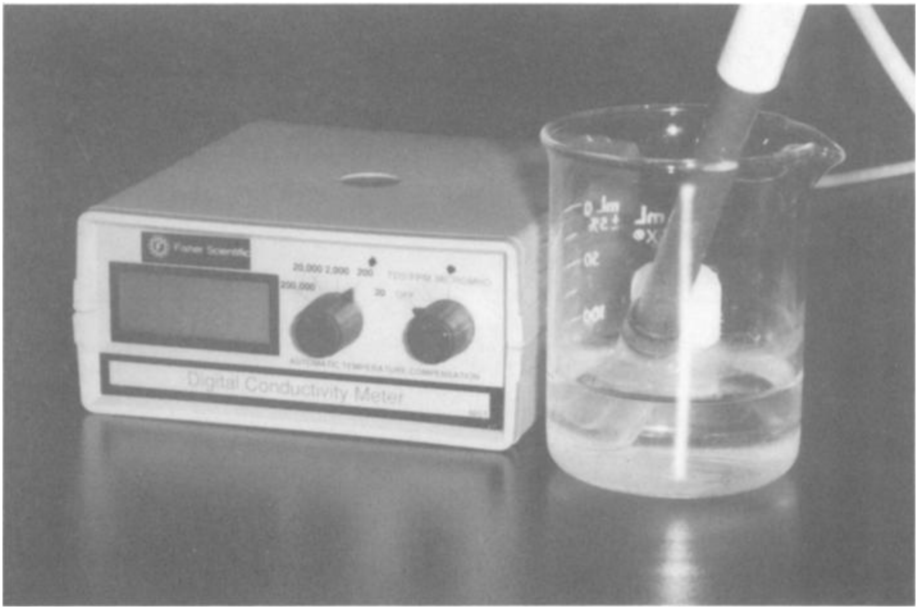

FIG. 1—*Photograph of a laboratory conductivity meter.*

in coolants; however, the ions of interest that are there are listed in Table 1. Essentially, limiting equivalent ionic conductance is a measure of the contribution that each ion makes to the total conductance of the solution. Note that the values for the inorganic ions fall in a fairly narrow range. Thus, one might expect the conductivity of conventional coolants to be fairly independent of formulation.

Azelate is listed because it contains just one less carbon atom in its molecular structure than sebacate. Butyrate is fairly close in structure to octanoate. Thus, these ions are analogous to sebacate and octanoate that are used in organic acid-inhibited coolants. Note that their values are lower than those for the inorganic ions.

TABLE 1—*Limiting equivalent ionic conductances in aqueous solutions at 25°C (mho-cm^2/equivalent).*

INORGANIC CATIONS	
Na^+	50.1
K^+	73.5
INORGANIC ANIONS	
HPO_4^{2-}	57
NO_2^-	71.8
NO_3	71.4
ORGANIC ANIONS	
Azelate^{2-}	40.6
Benzoate$^-$	32.4
n-Butyrate	32.6

As the concentration of ions in solution increases and the ions are in closer proximity, their interactions increase and thus reduce conductivity. Thus one would expect, at some level, that incremental increases in TDS would result in progressively smaller increases in conductivity.

As might be expected, temperature influences conductivity. If the temperature of the solution being measured has not stabilized, significant drifting of the conductivity measurement can occur.

Finally, conductivity is greatly affected by the dielectric constant of the solution. Water has a high dielectric constant, ethylene glycol's value is approximately half that of water. Propylene glycol's is about 15% less than ethylene glycol's. Thus, one would expect the glycol content of the solution to have a significant effect on its conductivity. The higher the glycol content, the lower the conductivity.

Experimental Results and Discussion

All of the solutions measured in this paper were prepared by dissolving solid supplemental coolant additives in the various coolant solutions. Solids were used to avoid varying the percent glycol content of the solutions. Conductivity measurements were made with a Fisher portable conductivity meter on solutions that had stabilized at room temperature. TDS values were determined by evaporating solutions to constant weight in accordance with (Modified) Federal Method 2540C.

Figure 2 shows graphs which plot conductivity as a function of TDS for solutions of Pencool 3000 and Fleetguard DCA-4, separately, in water. Note that the graphs are essentially linear. Thus, in this range of concentrations, inter-ionic interactions have little effect on conductivity. However, more importantly, the graphs may almost be superimposed.

There are significant differences in the formulations of the two products. Pencool 3000 contains sodium salts of borate, nitrite, nitrate, and silicate, Fleetguard DCA-4 contains both

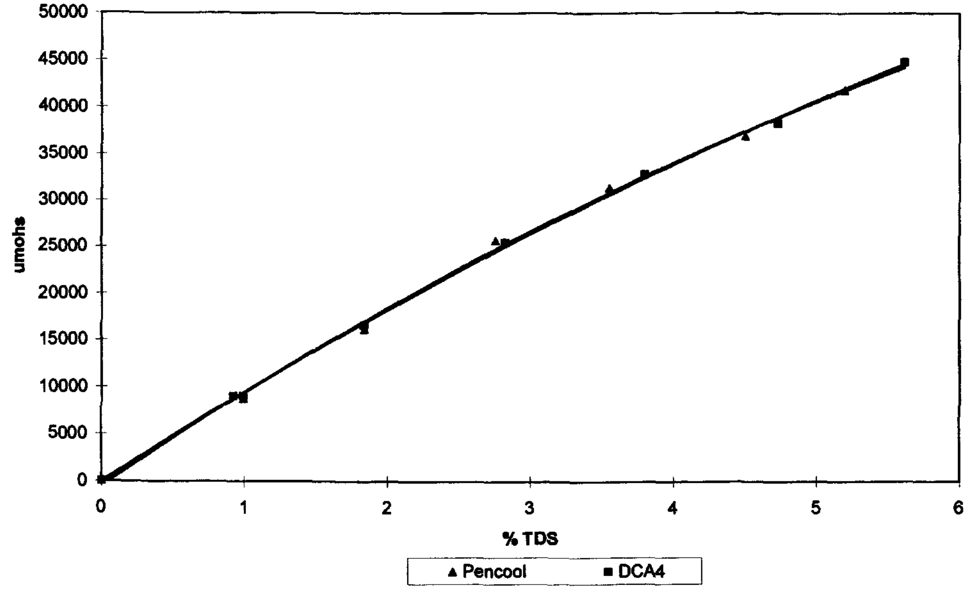

FIG. 2—*TDS versus conductivity in water.*

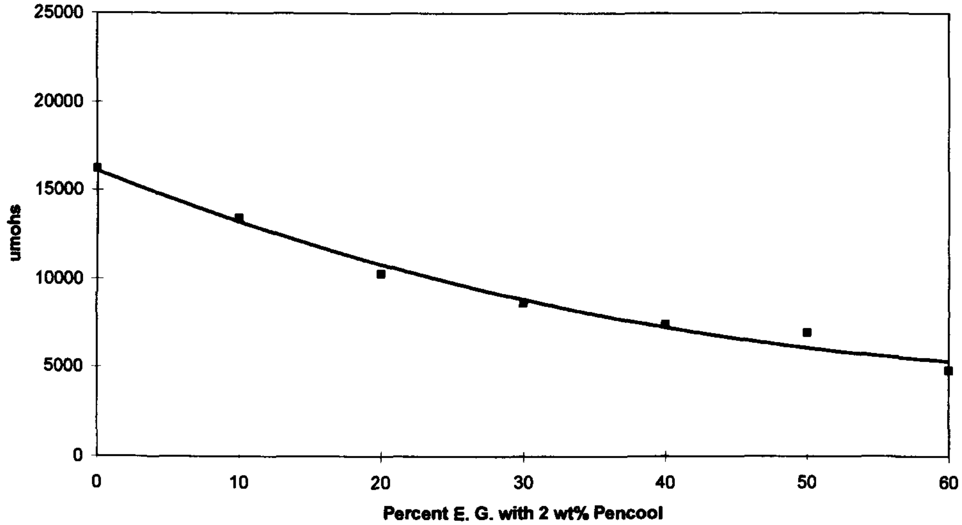

FIG. 3—*Glycol concentration and conductivity.*

potassium and sodium salts of phosphate, molybdate, nitrate, nitrite and silicate. Thus, the mobilities of the various ions appear to be similar enough that conductivity is essentially independent of formulation for conventional inorganic inhibitors.

These graphs are for water-only solutions, but most heavy-duty coolants also contain glycol. Figure 3 shows the conductivities of 2% solutions of Pencool 3000 containing varying concentrations of ethylene glycol. Note that the conductivity of the 60% glycol solution is about one quarter that of the water-only solution. Thus, glycol content has a major effect on conductivity.

Figure 4 shows Pencool 3000 and Fleetguard DCA-4 dissolved in 50% GM 6038M coolant. Again, the graphs may essentially be superimposed.

However, coolants are not always 50% glycol. Figure 5 shows Pencool 3000 solutions in 40 and 60% GM 6038M coolant. The graphs have significantly different slopes. In order to convert a conductivity measurement into a TDS value the glycol concentration would have to be known, and a series of conversion factors would be needed for different glycol concentrations. This would obviously be unwieldy.

However, the effect of the glycol can be minimized by dilution. Note how the 60 and 40% graphs converge when conductivities of samples diluted to 10% by volume with deionized water are plotted.

Figure 6 shows Fleetguard DCA-4 in 40 and 60% GM 6038M coolant. Again, the graphs are very similar; they converge when the conductivities at 10% dilution are plotted.

The use of ASTM D 4985-type coolants, exemplified by GM 6038M, is being superseded by the use of "fully-formulated," TMC RP-329 specification coolants. These coolants, together with their SCAs, are shown in Fig. 7.

Figure 7 compares coolants mixed with:

1. Caterpillar Diesel Engine Antifreeze/Coolant and Caterpillar coolant additive.
2. Fleetguard Compleat and DCA-4.
3. Fleetcharge and Pencool 3000.

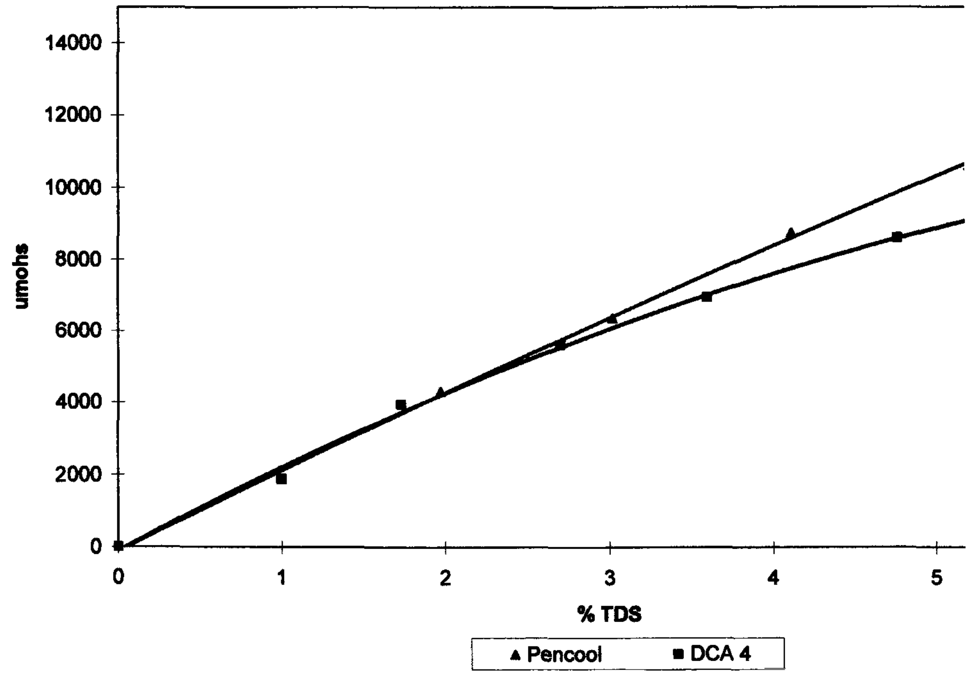

FIG. 4—*Conductivity in 50% GM 6038M.*

All are 50% glycol solutions diluted 9:1 with deionized water for the conductivity measurement. With this graph a rule of thumb becomes apparent, note that 1000 micromhos (umhos) conductivity roughly corresponds to 1% TDS when the conductivity is measured on the solution diluted to 10%.

Figure 8 shows plots of the most recent practice in heavy-duty diesel coolant service, namely, extended service interval (ESI) coolants. The graph compares conductivities of 10% dilutions of Fleetcharge/Need-Release and the Fleetguard ES System. Again, the rule of thumb of 1000 umhos per 1% TDS appears to fit.

All of the products discussed so far use inorganic inhibitors almost exclusively. Thus we have been measuring conductivities of solutions of inorganic ions.

Some coolants directed at the heavy-duty market make use of organic inhibitors. As stated earlier, from the limiting equivalent ionic conductance of these and analogous organic ions, these solutions are expected to exhibit lower conductivities per TDS value than inorganic solutions. Figure 9 shows conductivity of 10% dilutions versus %TDS for Deere coolant. Deere coolant is a hybrid organic/inorganic coolant containing sodium benzoate together with sodium nitrite and other inorganic inhibitors. The SCA recommended for this coolant is Fleetguard DCA-4. Note that the graph is less linear than previous graphs and that the rule of thumb of 1000 micromhos per 1% TDS no longer appears to apply. Perhaps the graph should be regarded as having two slopes. Up to about 2.5% TDS, the graph reflects the hybrid Deere coolant with a lower slope. Above 2.5%, the higher slope of the inorganic DCA-4 SCA applies.

Other coolants containing exclusively or predominantly organic inhibitors are Dex-Cool, which is nonnitrated and Caterpillar Extended Service Coolant, which is nitrited. Dex-Cool requires no addition of SCAs; thus, the TDS does not vary except perhaps by dilution. A 50%

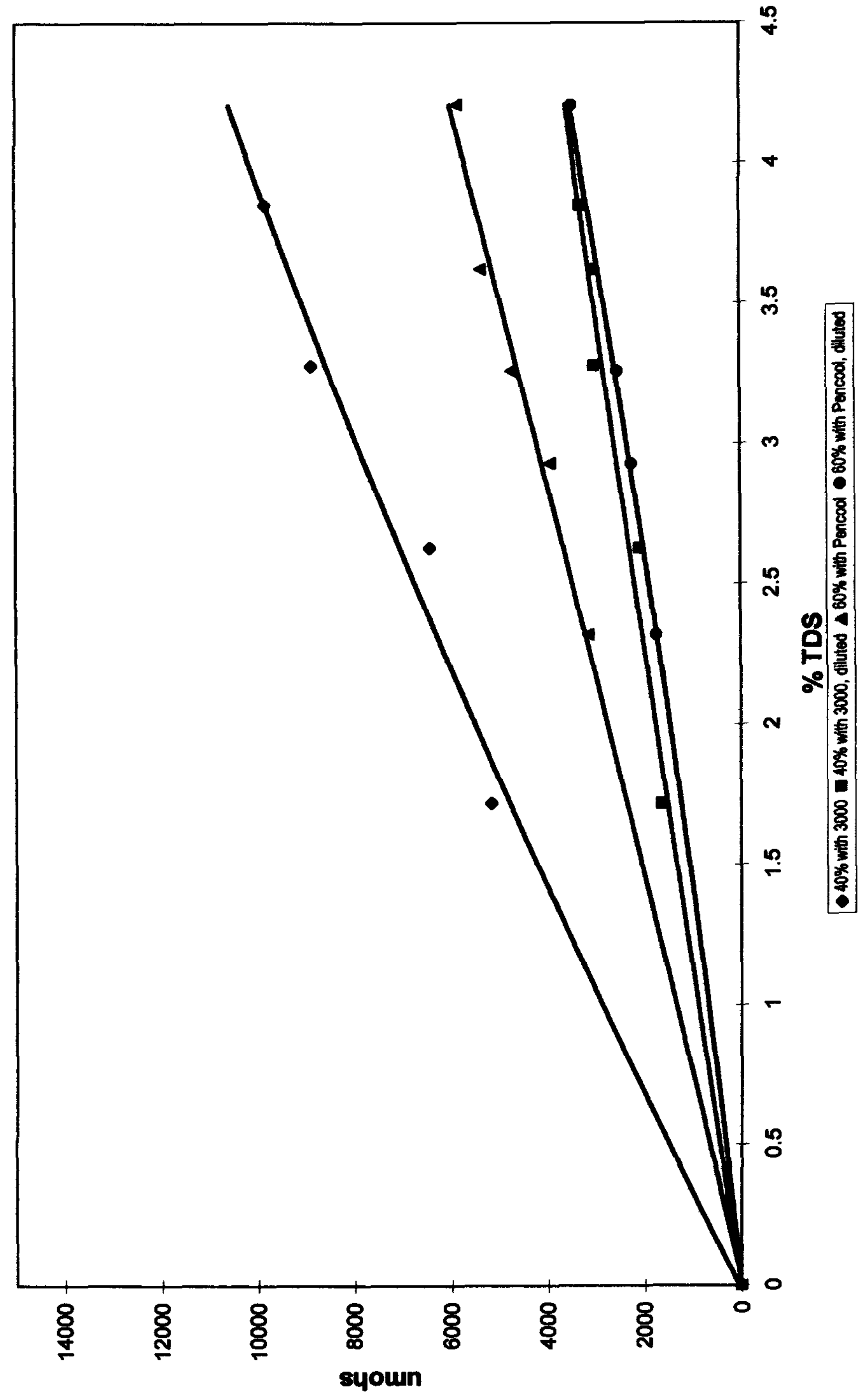

FIG. 5—*Conductivity of Pencool in 6038M coolant.*

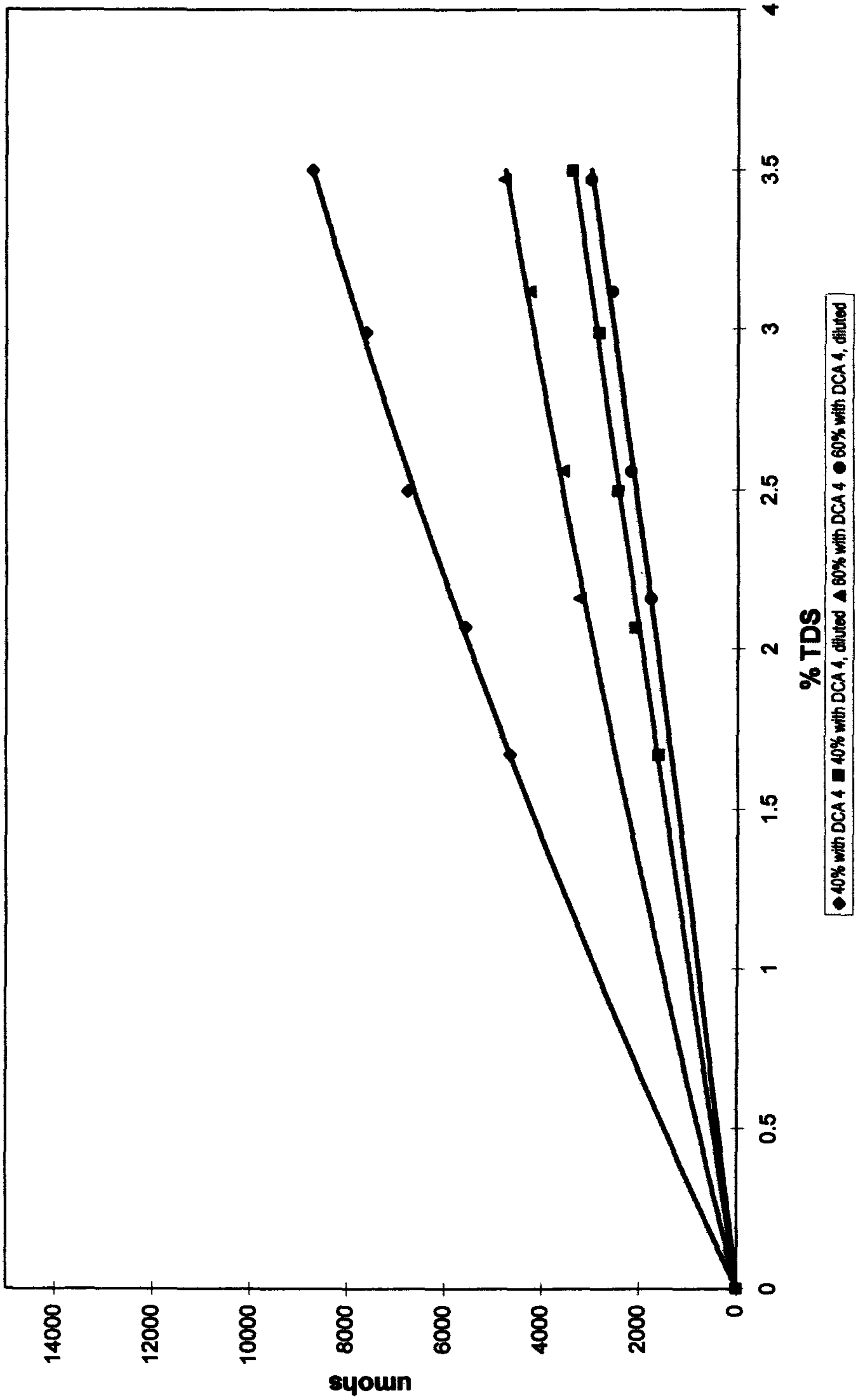

FIG. 6—*Conductivity of DCA-4 in 6038M coolant.*

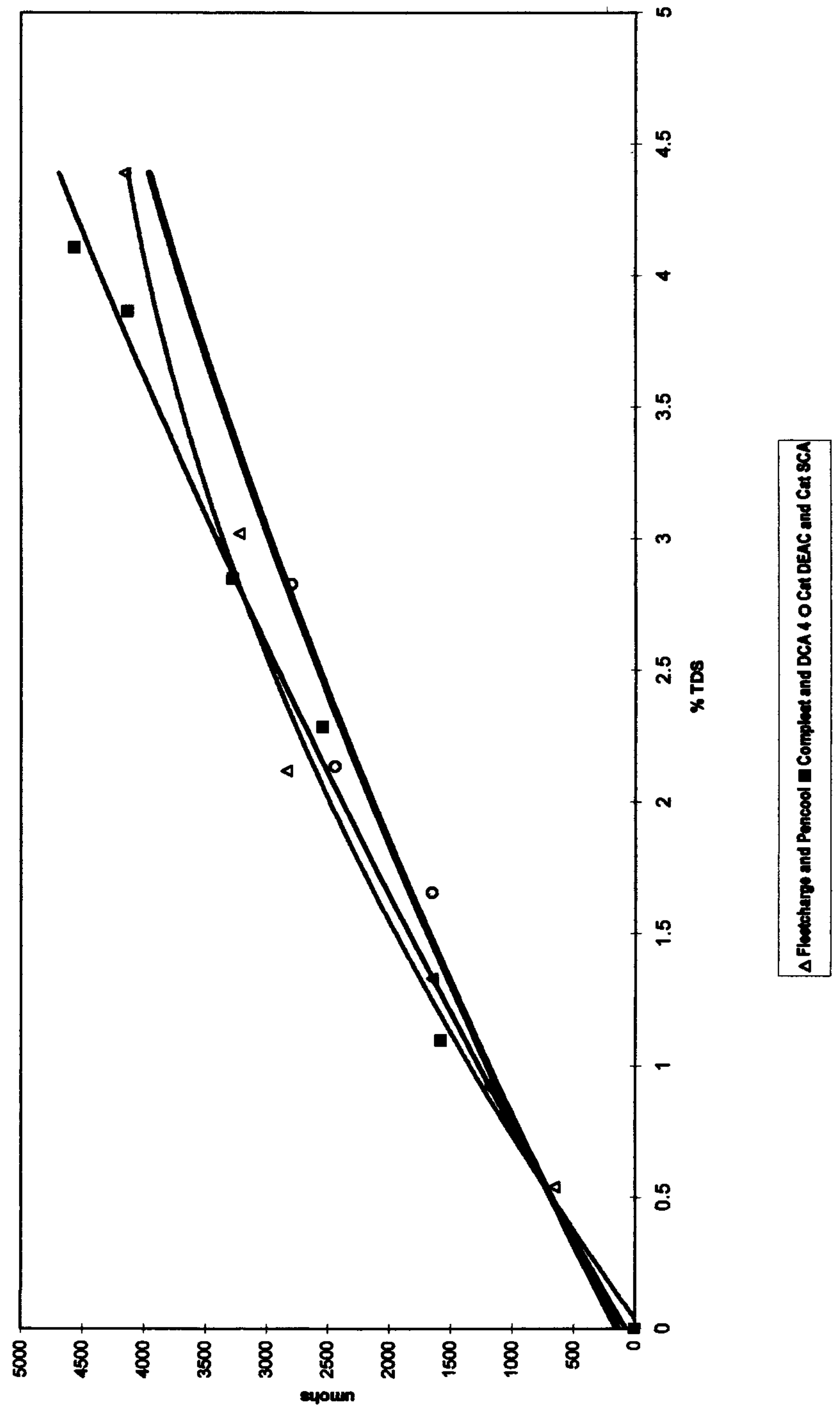

FIG. 7—*Conductivity of fully formulated coolants diluted to 10%.*

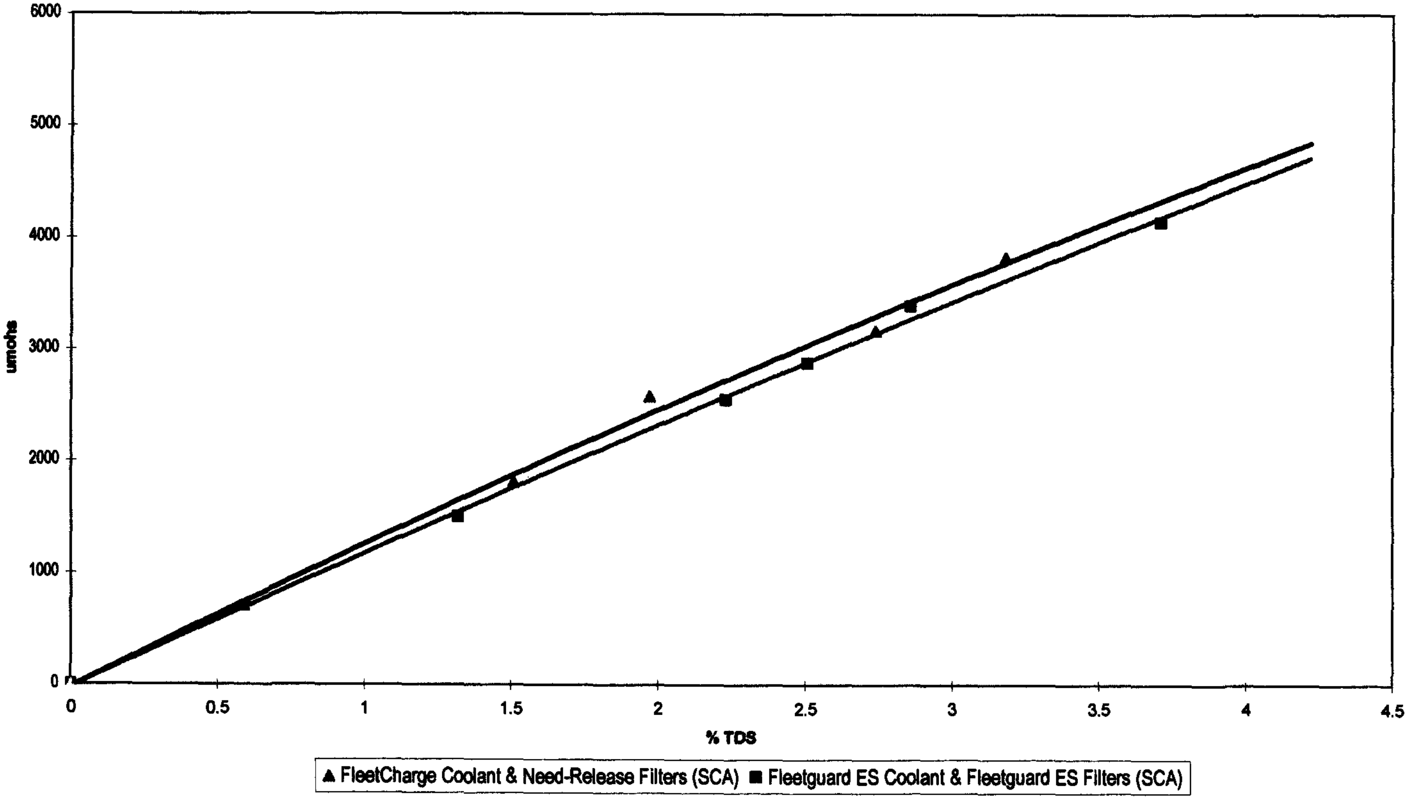

FIG. 8—*Conductivity of extended service coolants diluted to 10%.*

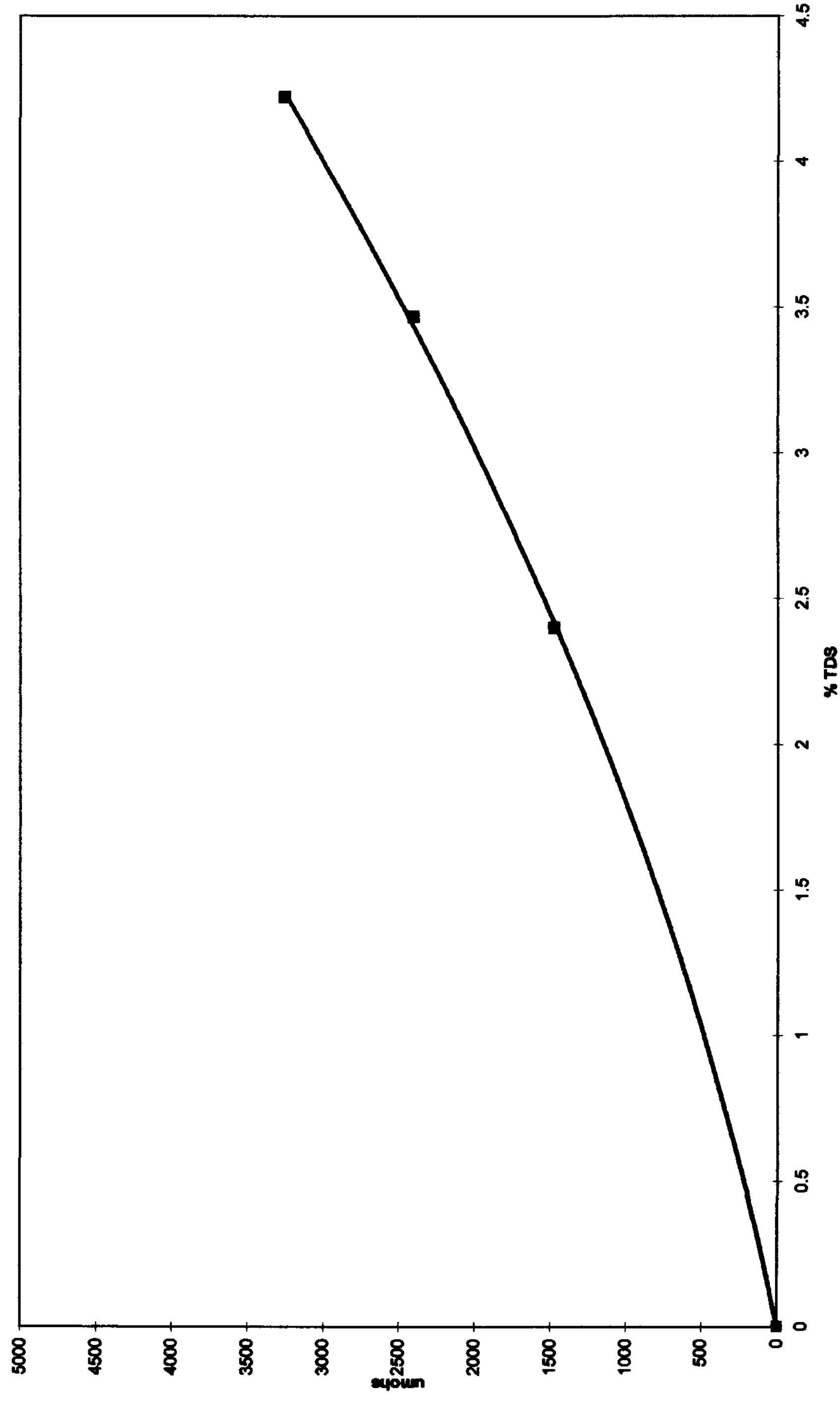

FIG. 9—*Conductivity of Deere coolant and DCA-4 diluted to 10%.*

solution of Dex-Cool has a TDS of 2.3%. The conductivity after tenfold dilution is 1260 umhos, less than half that would be expected for inorganic inhibitors.

The corresponding values for the Caterpillar product are 2.6% and 1630 umhos. The Caterpillar product requires the addition of an extender after 150 000 miles (241 395 km). The values after the addition of the extender are 2.8% and 1810 umhos. Obviously, the rule of thumb does not apply to either of these products.

Conclusions

1. For conventional North American coolants using mainly inorganic inhibitors, conductivity is essentially independent of formulation.
2. The conductivity of coolants is greatly affected by glycol concentration.
3. The effect of glycol concentration can be eliminated by dilution with deionized water. The conductivity of coolants diluted to ten times volume with deionized water are directly proportional to coolant total dissolved solids. Each 1% TDS results in a conductivity of approximately 1000 umhos in the diluted coolant.
4. A rule of thumb of 1000 micromhos per 1% TDS, applicable to inorganic-inhibited coolants, does not apply to organic acid inhibited coolants.

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Scale and Deposits in High-Heat-Rejection Engines

REFERENCE: Chen, Y.-S., Kershisnik, E. I., Hudgens, R. D., Corbeels, C. L., and Zehr, R. L., "**Scale and Deposits in High-Heat-Rejection Engines,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335,* R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 210–228.

ABSTRACT: Scaling under conditions very similar to those of a heavy-duty diesel engine cooling system was investigated using a newly designed, versatile test stand. The parameters included flow rate, heat flux, hardness, along with bulk fluid temperatures. The hot surface temperature, a critical parameter, was also measured. Results were interpreted in terms of the conditions in the boundary layer at the hot surface. Critical values of flow rate and heat flux existed for scaling under experimental conditions. A quantitative relationship of scale with heat flux and hardness was observed. Deposits produced from testing of different types of commercial coolants, including phosphate based and nonphosphate based, were measured and compared with results from simple beaker tests.

KEYWORDS: scale, deposits, inverse solubility, cooling systems, heavy duty, beaker tests, hot surface, heat transfer, heat flux, flow rate, hardness, bulk fluid temperature, surface temperature, boundary layer, supplemental coolant additive, water-soluble polymer, phosphate

Scaling and deposits in truck and automobile cooling systems have been a concern for over 40 years. The issue grows in importance especially for heavy-duty diesel engines as horsepower density continues to increase along with durability expectations. For instance, the power output of the Cummins 14 L engine has doubled from 275 to 550 hp in the past 30 years, while life overhaul has gone from 400/500 K miles to 800/1000 K miles.

To effectively manage this problem, the effect of coolant chemistry and cooling system dynamics (flow rate and heat rejection rate) need to be better understood. Further improved test methods are required. Simple beaker tests, which focus on precipitant formed with an antifreeze coolant/hard water mixture under static conditions in the absence of hot surface, may not correlate with scaling and deposits formed under actual engine conditions.

The purpose of the present work was to investigate scaling under conditions very similar to those of a heavy-duty diesel cooling system, to compare scale control in industrial water treatments with engine coolant systems, to study effects of coolant chemistry on scale formation, and to compare the beaker test results with the scaling bench test.

General Background

Water used for engine coolant often has high levels of hardness, that is, >300 ppm of calcium and magnesium carbonates. This is particularly true of well water since wells are often drilled

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[1] Dober Group, Dober of Glenwood Division, Glenwood, IL 60425.
[2] Fleetguard, Inc., Cookeville, TN 38502.
[3] Cummins Engine Company, Inc., Columbus, IN 47201.

into limestone or dolminite rock formations. The solubility of these materials, as well as other scale-forming compounds such as calcium phosphate and calcium sulfate, changes inversely with temperature. As an example, the solubility curve of various forms of calcium sulfate (CaSO4) from 0 to 100°C is shown in Fig. 1 [1].

Because of their inverse solubility—lower at higher temperature—these salts can form deposits directly on hot surfaces. These include the head, upper half of the cylinder liner, oil cooler, and aftercooler, where the high temperatures result in precipitation.

At hot surfaces, the temperature increase in the heat-transfer boundary layer causes supersaturation. The increased temperature is the result of natural convection or nucleate boiling. It is not necessary to have boiling to form scale provided that the concentration of hard water ions is sufficiently high. As these scale-forming compounds begin to approach the threshold level of insolubility, submicroscopic crystals begin to form on the surface through the process of nucleation. Over time, scaling increases through the growth of the crystals at the nucleation site [1].

The other source of deposits is coolant insolubles or debris. This includes coolant additives precipitated by hard water (primarily calcium/magnesium silicate and phosphate), silica gel, corrosion products, dirt/dust, and lube oil sludge. Unlike the scaling process, insolubles can cling to both a heat rejecting hot surface and a heat accepting cold surface. An example of a cold surface would be the tubes in the radiator.

Scale and deposits dramatically reduce heat transfer from a metal surface to the coolant. Nordall in his book, *Water Treatment*, makes the point that scale and deposits have a thermal conductivity similar to that of fire brick [2]. The table below compares the thermal conductivity of scale/deposits to fire brick and common cooling system metals.

Materials	Conductivity, Btu/ft^2/h/°F/ft
Deposits/porous scale	0.20
Fire brick	0.75
Nonporous scale	0.60 to 2.0
Cast iron	30
Brass (70/30)	60
Aluminum	120
Copper	220

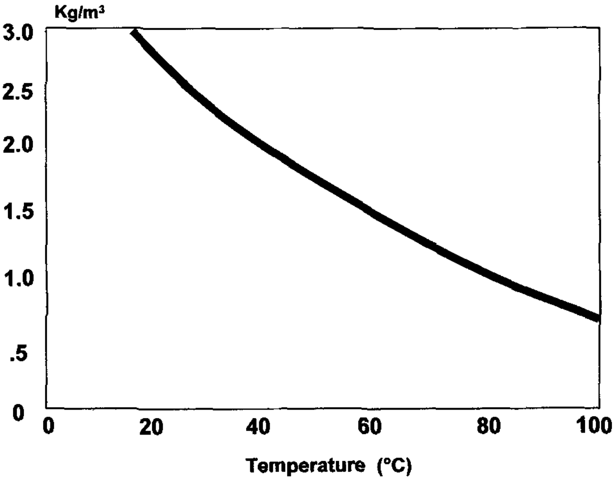

FIG. 1—*Solubility curve for calcium sulfate in water (Landolt-Bernstein 1965).*

Scale layers in the range of 0.010 to 0.050 in. (0.0254 to 0.127 cm) (about 1⁄32) on a metal surface can significantly retard heat transfer and increase metal surface temperatures. The magnitude of the temperature increase at the head or upper part of the cylinder liner will be at least 100°F (38°C) to more than 200°F (93°C) depending on such conditions as heat flux and coolant flow. Head surface temperatures can increase from the 600/700°F (315/370°C) range to 800/900°F (427/482°C) [*3*]. The increased metal temperatures or reduced heat transfer can cause the following problems:

- Head cracking.
- Ring wear which in turn causes high oil consumption and blow-by.
- Oil overheating which in turn causes breakdown, which then contributes to lube system deposits and corrosion.

The fact that these problems have their origin in the cooling system often is not recognized.

Scaling of the head and liners can actually result in a decrease in coolant temperature as waste heat is trapped within the engine. In some cases a vehicle operator can monitor coolant temperature and never suspect a severe problem developing within the cooling system.

A final issue is that two-stroke cylinder diesel engines are more sensitive to scale buildup and head cracking compared with four-stroke cycle engines. The reason for this is that two-stroke cycle engines usually have four exhaust valves per cylinder with no inlet valves. Air inlet is accomplished through the use of charge air ports in the lower cylinder wall when the piston is at bottom dead center. This means that these engines have hotter cylinder heads and corresponding coolant temperatures versus a four-stroke design. In a four-stroke cycle engine, there are typically two inlet and two exhaust valves in each cylinder head. The inlet valves serve a dual purpose of providing air for the next combustion cycle plus helping to cool the cylinder head. Thus, the cylinder heads of four-stroke cycle engines run cooler and are less sensitive to scale formation.

Experimental Procedures

The Scale Tester

The HS-300 hot surface scale deposit test stand built by Amalgamated Technologies was used in this study. It is constructed of stainless steel (SS304 and SS316) in order to avoid complications involving corrosion and corrosion products. It uses a centrifugal pump to circulate test fluids, such as engine coolant, within a stainless steel plumbing circuit (see Fig. 2). Scale test fluid is drawn by the pump from the main tank, and is pumped past the electrically heated scale deposit tube. The heater is on continuously, which raises the temperature of the test fluid. Then the heated fluid travels back to the main tank, where the fluid temperature controller regulates water flow through the cooling coil to remove heat and maintain a uniform temperature, from 100°F (38°C) to 200°F (93°C), in the bulk volume of test fluid.

The test stand has a flow capacity from 2.00 to 10.00 gal/min (7.5 to 37.8 L/min) [flow speed 1.584 to 7.920 ft/s (0.482 to 2.414 m/s)]. A valve and flowmeter adjust the flow rate through the scale cell. It has a 4000 W heater and the heater power is infinitely adjustable through regulation of the voltage applied to the heater. The HSR also has a heater temperature monitor to read the heater internal temperature.

The Scale Cell and the Heater Rod

The scale cell is a 1-in. (2.54 cm) stainless tube. The ½-in. (1.27 cm) 316 stainless steel heater rod of 23.5 in. (59.7 cm) total length fits through the center of the tube. The scale cell

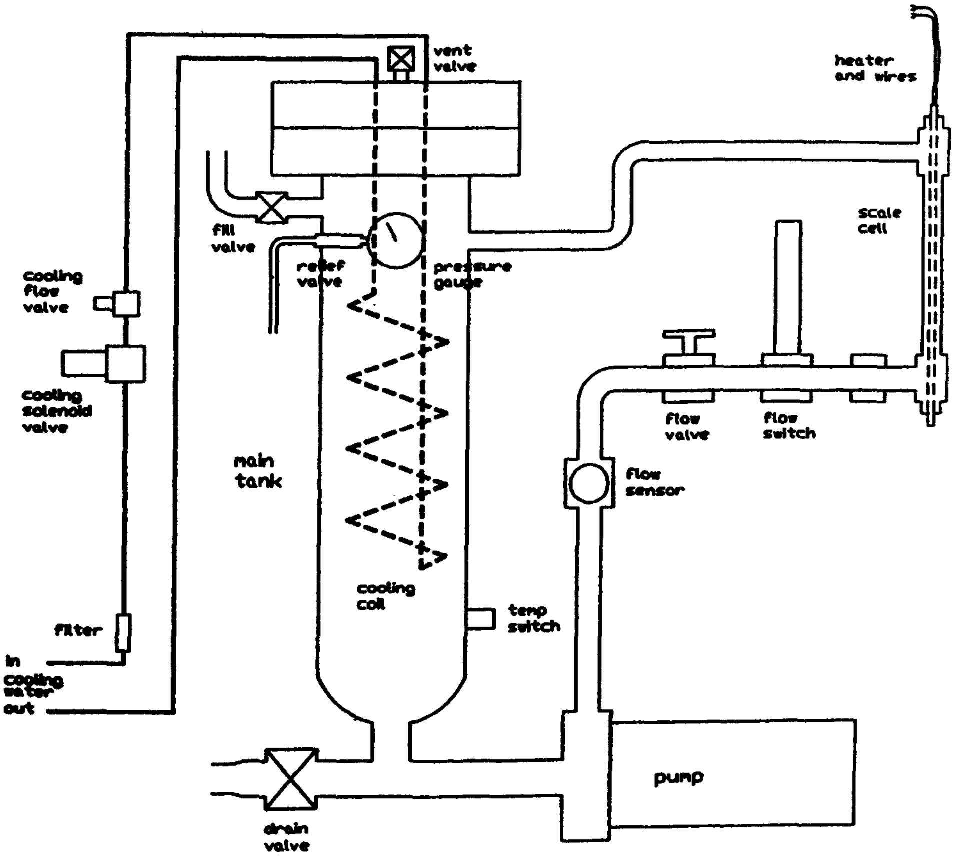

FIG. 2—*Diagram of HS300 scale test stand.*

consists of 1-in. (2.54 cm) Swagelock tees with 1 to ½-in. (2.54 to 1.27 cm) reducers. The reducers are fitted with trifluoroethylene Telfon ferrules to seal against the scale surface without permanently damaging the scale tube.

For higher heat flux, the HS-300 test stand was designed to eliminate the standard ½-in. stainless tube with its ⅜-in. (0.375 cm), 1600 W cartridge heater. The heating element and thermocouple were embedded inside the rod and scale was formed directly on the outside surface of the ½-in. (1.27 cm) 4000 W heater rod, which contained a heated section of 14-in. (35.5 cm) length. The test stand allows variable heat flux from 0 to 281.9 kW/m^2 (or 89 380 btu/ft^2/h, at the maximum of 208 V.

The Test Procedure

Before the test, firstly, the heater rod needs to be prepared and the test stand cleaned following the procedures as described in Appendices 1 and 2. The matrix conditions included: heat flux 125 and 250 kW/m^2 (39 630 and 79 270 btu/ft^2/h); total hardness 300 and 450 mg/L as $CaCO_3$; flow rate 2.15, 5.00, and 10.00 gal/min (8.1, 18.9, and 37.8 L/min) (1.70, 3.96, and 7.92 ft/s [0.5, 1.2, and 2.4 m/s]). Specific parameters were changed or added for investigation of different conditions outside the matrix set. GM 6038-M coolant was used for the study. Additional phosphate was added to give a total phosphate concentration of 400 mg/L as Na_2HPO4 in the test solution. For testing commercial products, the GM 6038-M coolant was replaced with the specific coolant, without addition of the $Na_2PO4 \cdot 12H_2O$ solution.

A typical test procedure for the matrix conditions involving GM 6038-M coolant follows. To begin, 6 L of deionized water was added to the tester. Subsequently, solutions of $CaCl_2 \cdot 6H_2O$, $MgSO4 \cdot 7H_2O$ and $NaHCO_3$, 1 L each, were added stepwisely to provide the desired hardness for the test. (See Test Solutions in Appendix 3.)

Then the pump was turned on and it remained on until the end of experiment. A one-liter solution of $Na_3PO4 \cdot 12H_2O$ (7.365 g/L) was added. A small amount of precipitate formed. Afterwards, 1.300 L of GM 6038-M EG concentrate coolant (see Appendix 3) was added. Many more precipitates formed. It was followed by the addition of 1.700 L of deionized water, making a total of 13 L of test solution. The pH of the solution mixture was typically 9.2 to 9.5 and it remained basically unchanged in the course of test.

After the tester had run for 30 min, with the pump on, a 500 mL sample was collected by opening the drain. To bleed the test cell of air, the small top nut of the cell was loosened to allow air to escape the test cell and the nut was tightened up as liquid started to escape the system. The fluid temperature controller was set at 190°F (88°C) and the heater was turned on. See Table 1 for the voltages applied and the corresponding watts and heat flux values. The test officially began at this point. The normal operating pressure was 9 to 13 psi (62 to 89.6 kPa), depending on the fluid flow rate.

The test was run for 4 days (96 h). To stop the test, first the heater was shut off. The fluid temperature was lowered in 20°F (6.6°C) increments until the heater temperature was less than 90°F (32°C) and a sample was collected. The pump was turned off and the whole system was shut down. Subsequently, the fluid was drained off and the heater rod was removed. The rod was dried in an oven at 212°F (100°C) until it reached a constant weight, typically, overnight. The appearance of scale was recorded and the weight of the heater rod was measured. The difference in the weights before and after the test gave the weight of scale. The test solution, before and after the test, was analyzed chemically.

The thickness of scale was measured using a PosiTector 6000N-FN1 gage from DeFelsko Corp., Ogdensburg, New York. It was measured in micrometers at three different locations on the heater rod from top to the bottom. Then, the average thickness was calculated. It should be used only for relative, and not absolute, comparison. However, the data correlated reasonably well with that of scale weights.

Initially in this study, the effect of test duration on the formation of scale was investigated for one set of the matrix conditions: heat flux 125 kW/m^2 (39 630 $btu/ft^2/h$), total hardness 450 mg/L as $CaCO_3$, fluid flow rate 5.00 gal/min (18.9 L/min) (flow speed 3.96 ft/s [1.2 m/s]). The data from 2, 4 and 7-day tests are shown in Fig. 3 for the weight and thickness of scale. The results indicated that more scale formed with longer test time.

TABLE 1—*Voltages used for investigation and the corresponding watts and heat flux.*

Voltage	Watt	kW/m^2	$btu/ft^2/h$
208.0	4000.0	281.9	89 380
195.9	3550	250	79 270
138.5	1770	125	39 630
117.5	1280	90	28 540
103.7	980.0	70	22 200
87.6	709.5	50	15 850

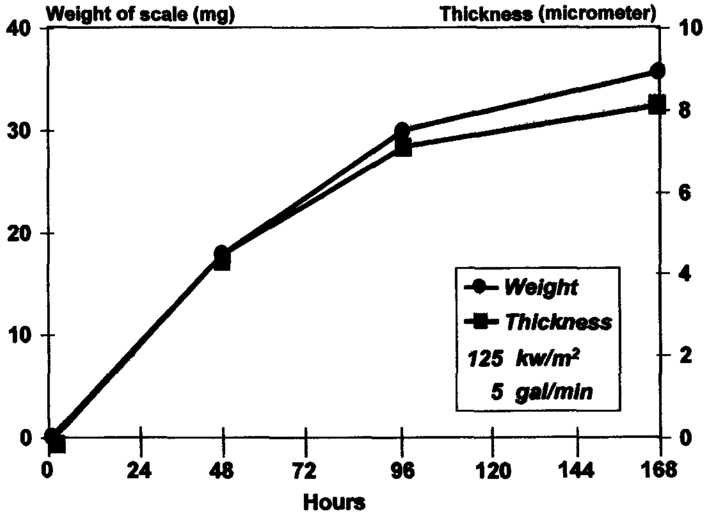

FIG. 3—*Test duration effect.*

To measure the reproducibility, the 4-day test was run three times. The weight of scale was 0.026, 0.030, and 0.035 g, respectively, with an average of 0.030 g. As the data indicate, the reproducibility was reasonably good. From the effect of test duration and the reproducibility results, the test duration of 4 days was chosen for all subsequent tests, unless otherwise specified. As it turned out, the 4-day test duration produced reliable and consistent data for this work. In his previous study Little showed that short-term testing (1 to 2 days) gave erratic results in the absence of scale inhibitors [*4*]. He selected the test duration of seven days as the length for reasons of convenience and to give ample time for equilibrium to become established.

Effect of Coolant System Variables

A general review of the literature showed that scale formation increases with

—decreased coolant flow or velocity
—increased heat flux
—increased hardness
—increased coolant bulk temperature
—increased pH

The point was made by several authors that flow and heat transfer at the fluid/surface boundary layer are very important, not just overall system temperatures and flow. However, bulk fluid properties do have an effect. Literature results show that more scale is produced from warmer fluids [*5*].

The large majority of the data in the literature were generated with boiler water, cooling water, and other industrial heat exchanger applications. We wanted to focus on testing under conditions that more nearly simulate those found in a heavy-duty diesel cooling system, and determine how coolant flow, heat flux and hardness levels affected scaling along with different bulk coolant temperatures. The HS-300 unit allows us to study these parameters together.

The matrix conditions investigated in this work included three different flow rates (2.15, 5.00, 10.00 gal/min [8.1, 18.9, 37.8 L/min] or 1.70, 3.96 and 7.92 ft/s [0.51, 1.2 and 2.41 m/s]) and two different heat fluxes (125 and 250 kW/m^2, or, 39 640 and 79 280 btu/ft^2/h) along with two different total hardness (300 and 450 mg/L as $CaCO_3$). The fluid temperature was kept at 190°F for all tests with matrix conditions. Specific parameters were changed or added for tests outside the matrix set. The system pressure ranged from 9.0 to 13.0 psi (62 to 89.6 kPa). The coolant GM 6038-M was chosen because of its wide use in heavy-duty diesel applications. To ensure good quality, this coolant was freshly prepared each month. The experimental results are listed in Appendix 4.

In 1988 Little reported his preliminary work on devising a bench scale hot surface deposit test [*4*]. The test conditions he studied included heat fluxes of 30 000 and 42 000 btu/ft^2/h, total hardness of 300 and 600 as mg/L $CaCO_3$, at a fixed flow rate of 3.00 gpm (11.3 L/min) (2.40 ft/s [0.73 m/s], Reynolds number 8050). In the present work, the dimensions of these parameters have been much expanded. Also, the rod surface temperatures were measured. They turned out to be very useful for understanding of scale formation and interpretation of data.

The tests as currently run in this work examine scale formation and/or deposition of solids formed in situ by the coolant and/or the SCA (supplemental coolant additive). No provision is currently made for the study of deposition of materials introduced into the cooling system from outside (such as oil or dirt).

The Effect of Flow Rates (Fluid Velocity)

The results demonstrated that the flow rate has a great effect on scaling. With constant heat flux and hardness, the weight of scale varied inversely with flow rates; that is, the higher the flow rate, the less the weight of scale. Thus, for example, as the flow rate increased from 2.15 to 5.00 and 10.00 gal/min (8.1, 18.9, and 37.8 L/min) at a heat flux of 250 kW/m^2 and total hardness of 450 mg/L as $CaCO_3$, the weight of scale decreased from 335 to 92 and 31 mg, respectively (see Fig. 4).

As the flow rate reached 10 gal/min (37.8 L/min), the scaling became minimal for all the

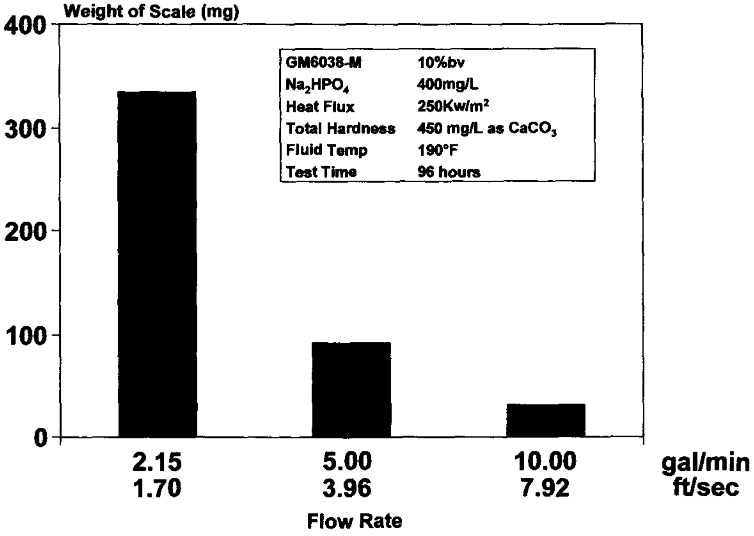

FIG. 4—*Flow rate effect.*

TABLE 2—*The difference of the weight of scale between flow rates 2.15 and 5.00 gpm under different heat flux and hardness conditions.*

Run	Heat Flux	Total Hardness	Weight of Scale, mg		Weight Difference, mg
			2.15 gpm[a]	5.00 gpm	
11, 12	250	300	171	87	84
14, 15	250	450	335	92	243
4, 5	125	450	160	30	130

[a] 1 gal/min = 3.785 L/min.

matrix conditions studied. Practically, under this condition, all other parameters became insignificant.

The effect of flow rates appeared to be more pronounced at higher hardness and higher heat flux as demonstrated in Table 2 for the difference of scale weight between 2.15 and 5.00 gal/min (8.1 and 18.9 L/min) flow rates. It was 84 mg versus 130 mg, at 250 kW/m^2 heat flux and 300 mg/L hardness, and at 125 kW/m^2 heat flux and 450 mg/L hardness, respectively. When the hardness was increased to 450 mg/L in the first case, or, the heat flux was increased to 250 kW/m^2 in the second case, the difference increased to 243 mg.

As the flow rates were changed, two other important parameters were varied: the temperature on the heater rod surface and the removal rate in the boundary layer. The observed data should be a result of these two effects working together.

At higher flow rates, conceivably the fluid is more efficient in removing heat from the hot surface. Therefore, the rod surface temperatures would be lower. This is what was observed experimentally, as demonstrated in Fig. 5 for 250 kW/m^2 heat flux and 450 mg/L hardness. When the flow rate varied from 2.15 to 5.00 and 10.00 gal/min (8.1 to 18.9, and 37.8 L/min), the heater rod surface temperature decreased from 407 to 363 and 343°F (208 to 184 and 173°C), respectively. The lower heater rod surface temperatures would render less scale formation on the rod surface.

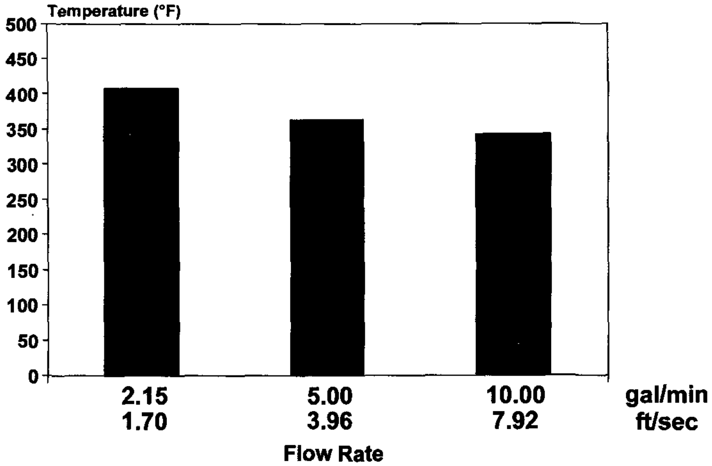

FIG. 5—*Flow rate effect on heater rod surface temperature.*

TABLE 3—*The "true" flow rate effect.*

Run	Heat Flux, kW/m^2	Hardness, mg/L	Flow Rate, gal/min	Surface Temp., °F	Weight of Scale, mg	Weight Difference, mg
5A	191	450	5.00	325	46	
4	125	450	2.15	325	160	114

The change of flow rate also affects the fluid turbulence. Theoretical calculation for the scale test rig gave a Reynolds number of 5748 for 2.15 gal/min (8.1 L/min) flow rate. It increases to 26 740 at 10.00 gal/min (37.8 L/min). See Appendix 5. Because these numbers are higher than 2300, all the examined flow rates in this work should produce turbulent flow structures in the boundary layer which is critical in the removal process. The higher flow rates led to an increase of fluid velocity and turbulence and, therefore, a higher removal rate. As a result, the particles became more difficult to settle on the surface and a lower rate of scale formation was observed. Similar results have been reported in other scaling models [*6,7*].

The true flow rate effect was demonstrated in experiments #4 and #5A which had flow rates of 2.15 and 5.00 gal/min (8.1 and 18.9 L/min), respectively (see Table 3). The heat flux for #5A was set at 125 kW/m^2 initially. However, as the heater rod surface temperature reached constant value of 281°F (138°C) (in <2 h in the test procedure), the heat flux was increased gradually to 191 kW/m^2 to give the heater rod surface a temperature of 325°F (163°C). Both experiments then had the same hardness and surface temperature. Therefore, the difference of 114 mg stemmed from only the effect of flow rate.

The Effect of Hardness

The hardness showed a positive effect on scale. With higher hardness, more scale was produced. Hence, as shown in Fig. 6 for 250 kW/m^2 heat flux and 2.15 gal/min (8.1 L/min) flow

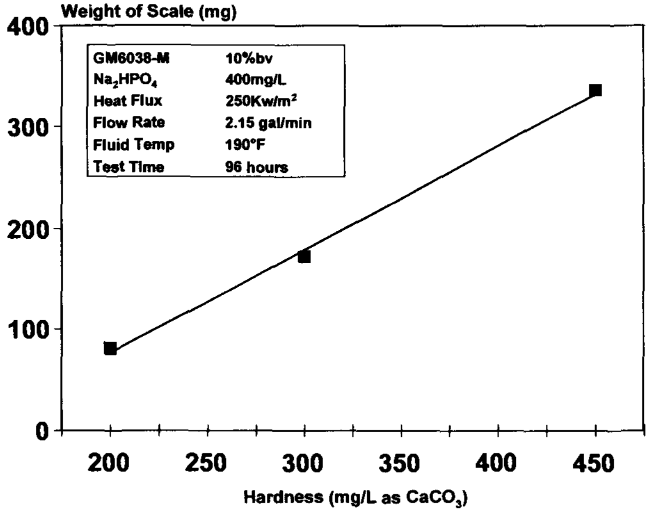

FIG. 6—*Hardness effect.*

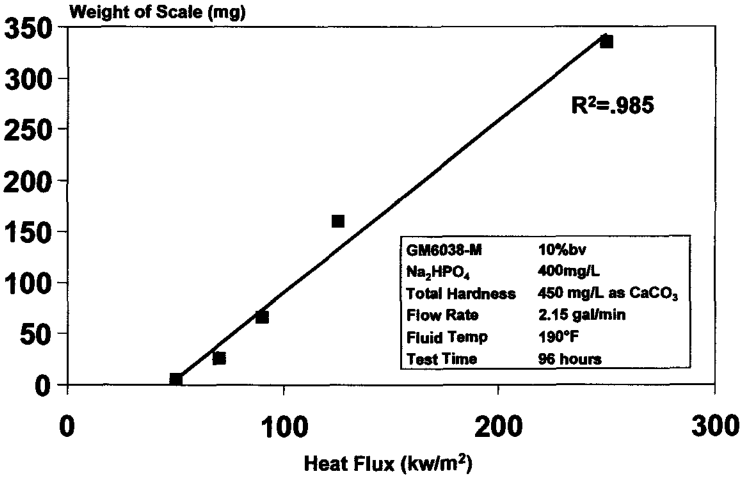

FIG. 7—*Effect of heat flux.*

rate, the weight of scale increased from 81 to 171 and 335 mg when the hardness was increased from 200 to 300 and 450 mg/L. As a baseline, at 0 hardness, 10 mg of scale was produced.

It appeared that a quantitative relationship existed between hardness and the weight of scale under experimental conditions. But, undoubtedly, more data are needed for further establishment.

The effect of hardness was studied by Little at a fixed flow rate of 3.00 gal/min (11.3 L/min) (2.40 ft/s [0.73 m/s], Reynolds number 8051) and a fixed heat flux of 30 000 btu/ft^2/h [*4*], and by others [*8*]. They reported similar results—scale formation rate increases with hardness.

The Effect of Heat Flux

The heat flux was studied for 50, 70, 90, 125 and 250 kW/m^2. It showed a great effect as the higher heat flux led to more scale. The results are shown in Fig. 7 for 2.15 gal/min (8.1 L/min) flow rate and 450 mg/L hardness. As data demonstrates, a very good linear relationship ($r^2 = 0.985$) exists between the weight of scale and heat flux under experimental conditions.

The corresponding heater rod surface temperatures are shown in Table 4. They increased progressively with increase of heat flux. Because increasing the surface temperature increases the fluid temperature in the thermal boundary layer, the amount of precipitation and scale was increased due to the inverse solubility of the scale-forming compounds.

Similar results were obtained for 2.15 gal/min (8.1 L/min) flow rate and 300 mg/L hardness.

TABLE 4—*Effect of heat flux on heater rod surface temperatures.*

Heat Flux, kW/m^2	Surface Temperature, °F
250	407
125	325
90	272
70	251
50	234

As the heat flux was doubled from 125 to 250 kW/m^2, the weight of scale increased by two times, from 86 to 171 mg. The corresponding heater rod surface temperatures increased from 312 to 408°F (155 to 209°C).

The results of Little, and the data of Muller-Steinhagen, Knudsen and others, have also shown that the scaling rate increases with increased heat flux under the models they studied [*1*,*4*,*8*].

As demonstrated in Fig. 7, when the heat flux decreased to 90 kW/m^2, the scale became moderate (66 mg). At 70 kW/m^2 it became insignificant (26 mg). As heat flux reached 50 kW/m^2, essentially no scaling occurred (6 mg).

This means that a limiting heat flux value exists for scaling under a specific set of conditions. It is 70 kW/m^2 (22 200 btu/ft^2/h) for the matrix conditions under the present experimental conditions. If the heat flux is lower than the limiting value, the scaling ceases even under very scaling-demanding conditions such as 2.15 gal/min (8.1 L/min) flow rate (1.70 ft/s [0.51 m/s]) and 450 mg/L hardness at pH 9.2 to 9.5 and fluid temperature of 190°F (88°C) in the present study.

The Effect of Bulk Fluid Temperatures

Three different bulk fluid temperatures 190, 180 and 170°F (88, 82 and 77°C) were investigated for 2.15 gal/min (8.1 L/min) flow rate, 450 mg/L hardness and 250 kW/m^2 heat flux. As the temperature decreased, the weight of scale increased. The results are shown in Fig. 8.

This effect is being studied further for a better understanding. At this time, the increase of scale at lower bulk fluid temperatures could be due to two reasons. Firstly, the concentration of scale forming compounds was different at different bulk fluid temperatures. The test solution was saturated with precipitates of scaling compounds before the test began. At lower fluid temperatures, due to the inverse solubility, the solution contained a higher concentration of these compounds. Because the heat flux remained the same, more precipitates and scale would form on the hot surface in the thermal boundary layer for lower bulk fluid temperatures. The surface temperatures were 407, 404 and 400°F (208, 207 and 204°C), respectively, for these three conditions. The relatively small difference among them should not account for the big difference of scale.

Secondly, the major driving force for scaling could be the degree of temperature difference

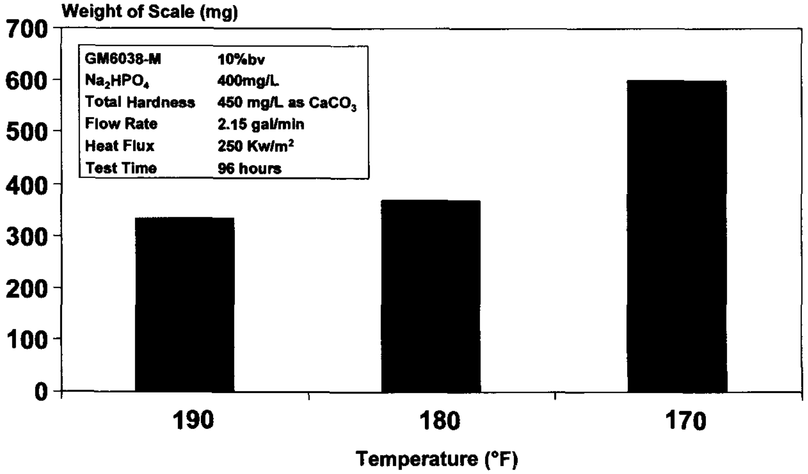

FIG. 8—*Effect of bulk fluid temperature.*

between the incoming fluid and the heater surface. A lower incoming fluid temperature would give a higher degree of temperature difference and therefore more scale.

This result is in disagreement with what was reported in the literature. The discrepancy is possibly because of different experimental models. In contrast to the conditions employed in the present study, the literature results dealt with conditions where unsaturated solution was used and scale was collected on unheated surfaces [*5*].

Coolant Chemistry and Test Method Issues

Since the middle 1950s, efforts have been made to modify coolant chemistry to control scaling and deposits on heat-transfer surfaces. The first heavy-duty supplemental coolant additives were chromate-based. These chromate-based SCAs were used along with a cation exchange resin (CER) to control scaling due to calcium/magnesium carbonate. The resin was either contained inside a spin-on coolant filter or placed inside a canvas bag that went into a housing through which coolant flowed. This approach worked well, particularly in water-only coolant because the hardness remained soluble long enough for the resin to remove it prior to any scale formation or precipitation.

In the mid to late 1960s, borate-nitrite SCAs started to replace chromate. With this change also came a dramatically new approach to scale and deposit prevention. CERs were replaced with low molecular weight, water-soluble polymers that had been developed for the boiler and cooling water industry. Resins did not work because the silicate in the additive package quickly reacted with the hardness to form a precipitate. This insoluble material would then adhere to heat transfer surfaces.

Further changes took place in the early to mid-1980s when Cummins and other OEMs switched to a phosphate-molybdate based SCAs.

Phosphate-based programs have long been used for industrial water treatments [*9*]. They include, for boiler water treatment, the phosphate and the coordinated phosphate programs [*10*], and, for cooling water treatment, the "soft" phosphate, the "stabilized" phosphate and the alkaline zinc programs [*9,11*]. Inorganic phosphate, typically orthophosphate, occasionally in combination with polyphosphates, was used.

In these programs the resultant deposition potential, mainly for calcium phosphate, is eliminated or controlled through the use of a variety of polymer materials. Beginning in the 1960s polyacrylates and later polymethacrylates and polymaleics were utilized. However, these polymers have given way to a variety of more efficient materials including acrylic and maleic acid-based copolymers, sulfonated copolymers and other types of copolymers.

Functioning as dispersants and antiscalants, these polymers effectively control deposition of not only calcium phosphate, but also calcium carbonate, calcium sulfate and barium sulfate in high temperature heat exchangers. Extremely low deposition rates were achieved in the water systems when programs were successfully implemented [*12–14*].

The scale/deposit control mechanisms by which polymers are known to function, although not well understood, include threshold inhibition, crystal distortion, dispersancy of precipitated particles (rendering precipitated solids soft and nonadherent), surface coating and altering the physical characteristic of scale [*15,16*]. The general adsorption of inhibitor molecules on all crystal faces reduce the rate of crystallization to zero, while the adsorption on selective faces leads to a change in morphology of the developing scale crystals [*13*].

Despite the success of "stabilized" phosphate programs in boiler and cooling water treatments, there has been significant resistance to phosphate containing SCAs and antifreeze coolants. This has been driven in large part by problems experienced at German OEMs, 30 to 40 years ago when phosphate-buffered coolants were used with hard water. These nonstabilized products allowed the formation of scale and deposits. The reaction was to prohibit the use of

TABLE 5—*Comparison of P-VW 1426 and Caterpillar EC-1 precipitation tests with scaling test.*

	P-VW1426 Test	Caterpillar EC-1 Test	Scaling Test
Full organic acid coolant	pass (rating t)	pass (<0.25 mL)	1972 mg
Benzoate/nitrite coolant	pass (rating n)	pass (<0.25 mL)	1175 mg
Long-life conventional coolant	pass (rating n)	pass (<0.25 mL)	35 mg
Light-duty low silicate	fail (rating s)	fail (2.8 mL)	111 mg

phosphate rather than require that phosphate containing coolants be formulated/stabilized to prevent the problem. What is often forgotten is that the carbonate present in the make-up water will form scale. Therefore, one needs to deal with this situation regardless of any phosphate or silicate that may be in the antifreeze coolant additive package.

Several beaker-type tests have been developed to evaluate the hard water compatibility of a coolant. The test usually involves diluting the antifreeze concentrate with hard water and heating the mixture for a prescribed length of time. At the conclusion of the test, the solution may be visually evaluated for precipitation or alternately centrifuged and the volume of solids measured. The thinking of many is that the coolant will not form scale and deposits on hot surfaces if there is little or no precipitation with hard water under static conditions. However, this is not necessarily the case. It should be obvious that beaker or glassware tests do not simulate the conditions of the boundary layer in contact with the 600 to 700°F (316 to 371°C) surface of a head or liner.

Table 5 compares results from the Volkswagen P-VW1426 and Caterpillar EC-1 hard water compatibility tests with the hot surface scaling test described earlier in this paper. An outline of the Volkswagen and Caterpillar tests are given in Appendix 6 and 7. As expected, the typical light duty phosphate buffered product fails both the beaker tests and allows a modest amount of scaling in this hot surface test. These results contrast to those of a heavy duty phosphate buffered product stabilized using polymer chemistry. The stabilized HD product not only passes the hard water compatibility tests but allows little scale to form on the hot surface. The benzoate-nitrite and full organic acid based coolants pass the compatibility tests. This is expected performance from the products that were developed in Europe. However, they allow heavy, unacceptable deposits in the hot surface tests. This shows that the beaker/glassware hard water compatibility tests are not adequate to determine the scale/deposit forming tendencies of a coolant under actual engine operating conditions.

The effectiveness of scale control by water-soluble polymers was also confirmed from engine dynomometer tests. Liners from engines run with hard water (300 ppm) and GM 6038-M antifreeze alone shows heavy, unacceptable scale deposits (see Fig. 9). This test was run again under similar conditions except that a phosphate-molybdate SCA was added to the coolant. The liner shows little solids buildup on the surface due to the polymers contained in the SCA (see Fig. 10).

Conclusions

1. Literature results or information based on boiler and cooling water treatments show that scale formation increases with

—decreased coolant flow or velocity
—increased heat flux
—increased water hardness
—increased coolant bulk temperatures
—increased pH

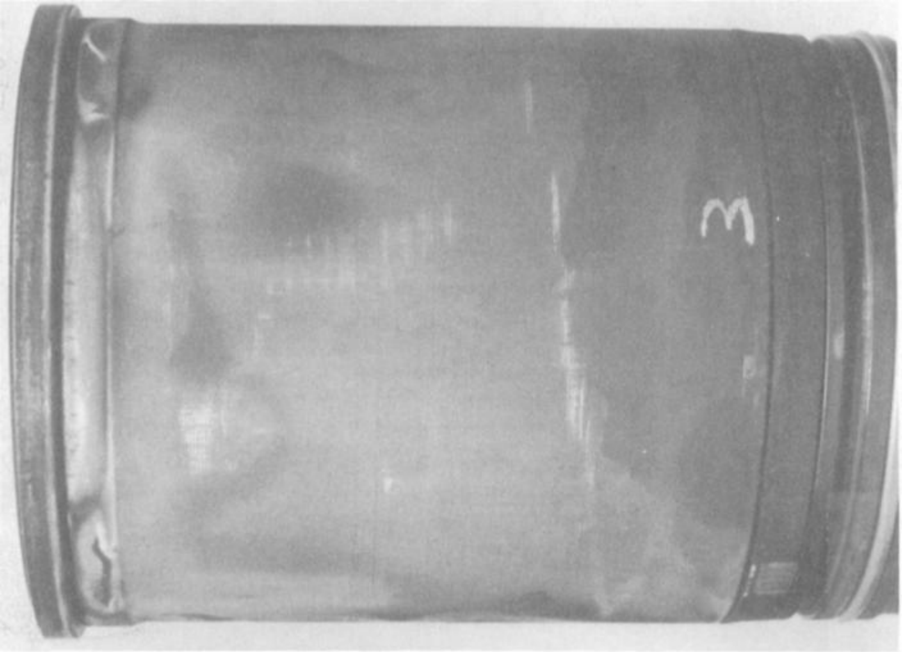

FIG. 10—*GM-6038 antifreeze plus phosphate-molybdate SCA.*

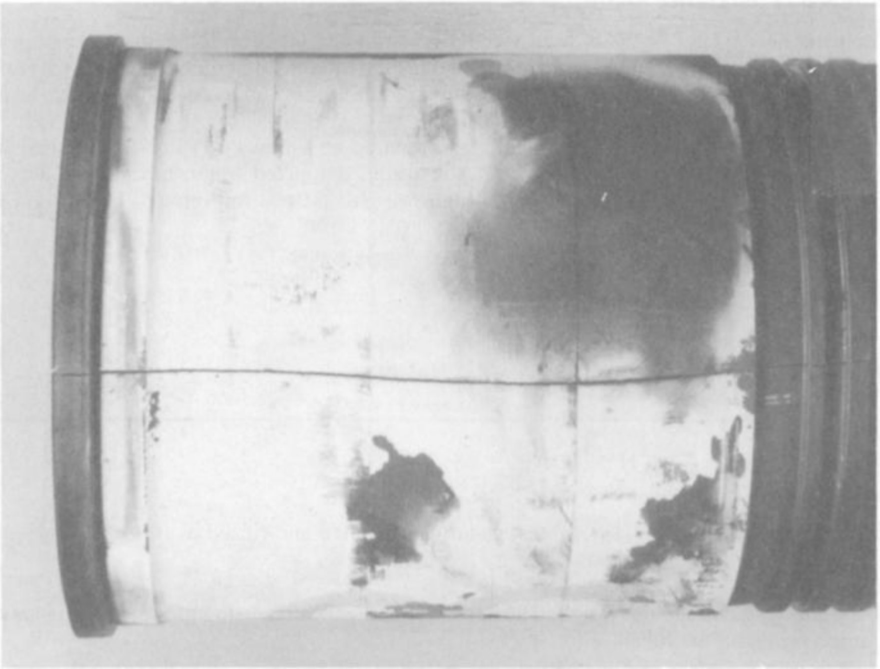

FIG. 9—*GM-6038 antifreeze only.*

2. Scaling/deposit formation at a hot surface is largely driven by the conditions in the thin or boundary layer at the hot surface more so than bulk coolant conditions.

3. Scaling tests run under conditions very similar to those of a heavy-duty diesel cooling system show the following:

—Scale formation is very sensitive to coolant flow rate. The increase of flow rate led to lowering of surface temperatures and increasing of the removal rate for particles in the boundary layer. Little scale forms at high flow/turbulence.

—Increasing water hardness resulted in a moderate increase in scale formation.

—A critical heat flux exists for scaling to occur. Under the matrix conditions in this study (450 ppm hardness, 1.70 ft/s (0.51 m/s) flow velocity, 190°F (88°C) bulk coolant temperature, pH 9.2 to 9.5), it was 70 kW/m^2 (22 200 $btu/ft^2/h$). Scaling ceases at heat flux lower than this critical value.

—Scale increased linearly with heat flux and hardness

4. Phosphate containing antifreeze coolants and SCAs can be well "stabilized" with low molecular weight, water soluble polymers such that they do not form scale or deposits with hard water.

5. Glassware-type hard water compatibility tests do not predict the tendency for an antifreeze coolant or SCA to form scale and deposits under actual engine operating conditions.

APPENDIX 1

Preparation of the Heater Rod

When the new heater rod was used for the first time, it was conditioned by cleaning and weighing as follows: (1) Degreased with hexane. (2) Polished with Scotch Brite pad. (3) Rinsed with deionized water and acetone. (4) Oven dried at 212°F (100°C) to constant weight (nearest milligram). This weight was recorded.

For the uses afterwards, the heater rod was prepared as follows: (1) It was scrubbed with Scotch Brite pad and soap. (2) Rinsed with soft water, deionized water, hexane and acetone. (3) Dried in an oven at 203°F (95°C) to constant weight (nearest milligram). The weight was recorded.

APPENDIX 2

Cleaning of the Test Stand

Before running a test, the HS-300 test stand was cleaned and rinsed as follows:

1. Carefully assembled the weighed heater rod in the scale cell, using gloves to avoid leaving fingerprints on the tube.

2. Filled with 13 L of cleaning solution. See Test Solutions.
3. Set fluid temperature controller to 140°F (60°C).
4. Set the heat power at 4000 W (208 V).
5. Ran rig with heater on for one hour.
6. Turned off heater and pump, drained completely.
7. Filled with 13 L of deionized water.
8. Ran pump for only 2 min.
9. Drained, refilled, ran pump twice more with deionized water.

APPENDIX 3

Test Solutions

1. Cleaning solution—13 L of deionized water containing 200 g of 38% Na4EDTA solution and 25 g of 50% NaOH solution.
2. To give 300 mg/L total hardness as $CaCO_3$ in the test solution—1 L of each of the following solutions was added: 7.114 g/L $CaCl_2 \cdot 6H_2O$, 1.603 g/L $MgSO4 \cdot 7H_2O$, 5.460 g/L $NaHCO_3$. The final concentrations in the test solution were: 547 mg/L $CaCl_2 \cdot 6H_2O$, 123 mg/L $MgSO4 \cdot 7H_2O$, 420 mg/L $NaHCO_3$.
3. To give 450 mg/L total hardness as $CaCO_3$ in the test solution—1 L of each of the following solutions was added: 10.670 g/L $CaCl_2 \cdot 6H_2O$, 2.401 g/L $MgSO4 \cdot 7H_2O$, 5.460 g/L $NaHCO_3$. The final concentrations in the test solution were: 821 mg/L $CaCl_2 \cdot 6H_2O$, 185 mg/L $MgSO4 \cdot 7H_2O$, 420 mg/L $NaHCO_3$.
4. The coolant solution: GM 6038-M EG Concentrate—The solution was prepared according to the procedure described by Little [*10*]. It was prepared fresh every month. It contained tetraborate, nitrate, phosphate, silicate and tolyltriazole, all as sodium salts, as well as defoamer and dye. It gave a pH of 10.6 to 10.7.

APPENDIX 4

Experimental Results

Key

Test length	days
Heat flux	kW/m^2
Hardness	total hardness as mg/L of $CaCO_3$
Flow rate	gallons per minute
Phosphate	as Na_2HPO4 in mg/L
Weight of deposit	mg
Thickness of deposit	micrometers
Temperatures	°F
*	commercial coolants

Run Number	Heater Rod	Test Length	Heat Flux	Hardness	Flow Rate	Phosphate	Weight of Deposit	Thickness of Deposit	Heater Rod Temperature	Bulk Fluid Temperature
1	1	4	125	300	2.15	400	86	8.0	312	190
2	1	4	125	300	5	400	13	1.6	277	190
3	2	4	125	300	10	400	14	2.7	268	190
4	2	4	125	450	2.15	400	160	8.2	325	190
5	2	4	125	450	5	400	30	7.3	281	190
5A	1	4	191	450	5	400	46	3.0	325	190
6	1	4	125	450	5	400	35	5.1	283	190
7	2	4	125	450	5	400	26	6.7	279	190
8	2	7	125	450	5	400	35	8.1	283	190
9	2	2	125	450	5	400	19	4.9	283	190
10	1	4	125	450	10	400	10	1.6	269	190
11	2	4	250	300	2.15	400	171	13.2	408	190
12	1	4	250	300	5	400	87	5.0	370	190
13	2	4	250	300	10	400	4	1.8	337	190
14	1	4	250	450	2.15	400	335	18.4	407	190
15	2	4	250	450	5	400	92	7.0	363	190
16	1	4	250	450	10	400	31	1.6	343	190
17	1	4	250	450	2.15	400	599	37.0	400	170
18	1	4	90	450	2.15	400	66	2.0	272	190
19	2	4	70	450	2.15	400	26	0.7	251	190
20	2	4	50	450	2.15	400	6	0.2	234	190
21	1	4	250	200	2.15	400	81	11.2	410	190
22	1	4	250	0	2.15	400	10	0	394	190
23	1	4	250	450	2.15	400	371	19.7	404	180
24*	2	4	250	450	2	0	1972		395	190
25*	1	4	250	450	2		35	1.7	401	190
26*	2	4	250	450	2	0	1175	(30.4)	408	190
27*	1	4	250	450	2		111	1.5	402	190

APPENDIX 5

Theoretical Analysis for the Scale Test System

A simple one-dimensional steady-state heat transfer analysis was completed using the physical dimensions of the scaling rig to study the variation of the thermocouple/heater rod temperature as a function of scale thickness. The theoretical analysis was based on the following assumptions: (1) Steady-state. (2) The temperature does not vary along the length of the heater rod. (3) The scale layer is a uniform thickness. (4) The coolant is at a fixed temperature of 190°F. (5) The heat flux is known and is distributed throughout the heater rod.

The results of the thermal circuit analysis for various flow rates, heat fluxes and scale thickness can be seen in Fig. 10. The results showed that, for a given flow rate, as the thickness of the scale layer increases the temperature of the heater core (thermocouple) increases. This is due to the additional thermal resistance to heat transfer of the scale layer. For a given heat flow rate between the thermocouple and the fluid, the increased thermal resistance drives the heater rod temperature up due to the "insulating" effect of the scale.

Also, for a given scale thickness, as the flow rate of the fluid past the heater rod increases, the temperature of the heater rod (thermocouple) decreases due to the convective heat transfer coefficient. As shown in the equation

$$Nu = 0.023\ \mathrm{Re}^{4/5}\ Pr^{0.4}$$

where Pr is Prandtl number (nondimensional) and Re is Reynolds number (nondimensional) which can be expressed as

$$\mathrm{Re} = p \cdot D_h \cdot v/u$$

where p is density of fluid, D_h is hydraulic diameter of the concentric annulus (= outer diameter—inner diameter), v is velocity of the fluid, and u is dynamic viscosity of the fluid.

The Nusselt number (thus convective heat transfer) increases nonlinearly with increasing flow rate. As the velocity of the fluid increases, the fluid has a greater potential to remove heat from the surface resulting in lower heater rod temperatures. This analysis is in agreement with the experimental results described in the text.

APPENDIX 6

Volkswagen P-VW 1426 Hard Water Stability Test Procedure

1. Volumetrically dilute antifreeze concentrate 1 : 1 with a synthetic hard water containing 275 mg/L $CaCl_2$ (equivalent to 248 mg/L $CaCO_3$), 148 mg/L Na_2SO4, 165 mg/L NaCl and 138 mg/L $NaHCO_3$.
2. Place the resulting solution in an oven at 80°C (176°F) for 10 days.
3. Record the precipitation for rating.

Rating

(s) if significant precipitation occurred.
(t) if the solution showed a trace or the barest perceptible solution opalescence.
(n) if the solution showed no precipitation or opalescence.

A rating assignment of (s) was deemed failing and ratings of (t) or (n) were passing.

APPENDIX 7

Caterpillar EC-1 Hard Water Stability Test Procedure

1. Measure and add 50 mL of the coolant concentrate to be tested to the 100 mL centrifuge tube using the graduated cylinder.
2. Measure and add 50 mL of the 600 mg/L hard water as $CaCO_3$ to the above mentioned centrifuge tube. Cover with a rubber stopper and agitate thoroughly.
3. Replace the rubber stopper with a clean air condenser prepared by inserting a short length (30 cm) of glass tubing through a properly sized one-hole stopper.
4. Immerse the tube to the level of the solution in a constant temperature bath at 88°C (190°F) for 24 h. Insert the Nichrome wire into the condenser to the bottom of the condenser tube.
5. At the end of the heating period, remove the centrifuge tube and solution from the bath and cool to ambient temperature (allow at least one hour).
6. Centrifuge for 30 min at 500 RCF.
7. After centrifuge, read the volume of solids in the bottom of the tube to the nearest tenth or hundredth of a mL as appropriate.

Rating

Pass, if no more than 0.25 mL of debris was collected in the centrifuge tube tip.
Fail, if 0.25 mL or more of debris was collected.

Note

1. 600 mg/L hard water—containing $CaCl_2 \cdot 6H_2O$ 1.093 g/L, $MgSO4 \cdot 7H_2O$ 246 mg/L, $NaHCO_3$ 420 mg/L.
2. Centrifuge tube, 100 mL capacity per ASTM D 1796.
3. Glass condenser tube, approximately 5 mm outside diameter × 3 mm inside diameter.

Acknowledgments

Yu-Sen Chen thanks Harold Martin of Fleetguard, Inc. for analyzing samples and Scott McCracken of Amalgamated Technologies for his useful suggestions on operation of the scale test stand.

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Engine Coolant Recycling Technology

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Overview of Used Antifreeze and Industrial Glycol Recycling by Vacuum Distillation

REFERENCE: Frye, D. K., Chan, K., and Pourhassanian, C., "**Overview of Used Antifreeze and Industrial Glycol Recycling by Vacuum Distillation,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 231–250.

ABSTRACT: A leading method of reclaiming ethylene glycol from both used automotive coolants and waste industrial glycol streams is vacuum distillation. Over 15 million gallons per year of total glycols are recovered by this technology, which are marketed for use in antifreeze and industrial chemicals. It is a robust technology, tolerant of many common feed contaminants, and producing minimum waste. This paper presents an overview of vacuum distillation as one part of a multistep process for recovering glycols from a wide variety of feedstreams. Described are industry practices for laboratory prescreening of feedstreams, process adjustments and pretreatments, distillation technologies and post-distillation polishing methods. In each section, information and data are presented from two independent facilities and for several streams processed at each facility. It is concluded that the facilities participating in this study can reliably produce ethylene glycol suitable for the production of ASTM specification engine coolants.

KEYWORDS: vacuum distillation, recycling, antifreeze, ethylene glycol, used antifreeze, engine coolant

Abbreviations

AA	atomic absorption spectrophotometer
BTEX	benzene, toluene, xylene, ethylbenzene
DEG	diethylene glycol
ECD	electron capture detector
EG	ethylene glycol
FID	flame ionization detector
GC	gas chromatograph
LC	liquid chromatograph
ICP	inductively coupled plasma spectrophotometer
PCB	polychlorinated biphenyl
PG	propylene glycol
TEG	triethylene glycol
UV/VIS	ultraviolet/visible spectrophotometer

The focus of this overview is to describe recycling by distillation as a process where laboratory prescreening, benchtop distillation, process adjustments, and a thorough understanding of each plant's operating characteristics are the elements required to produce consistent products. Vacuum distillation is not a "black box" process where mixed and unknown waste glycols

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are fed into a piece of equipment without this understanding. It is, however, a robust technology capable of processing many waste types. Data are presented from two distillation plants to illustrate typical feedstreams and the product that was made from each. Poor-quality distilled glycol and antifreeze seem to result only from poor equipment design and operation, or a disregard for the quality control measures presented in this paper.

Part I introduces testing protocols and procedures used to characterize incoming glycol streams. Test methods for identifying contaminants and potential processing difficulties are discussed. Familiar ASTM and USEPA SW-846 [*1*] tests, benchtop distillation, and an explanation of the significance of these tests to the vacuum distillation are presented. Part II describes pretreatments, distillation equipment and operation, and the polishing methods used to produce the finished glycol. Each facility is of different design, yet they both share very similar operating characteristics and capabilities. Part III characterizes the chemistry of the feedstreams and ethylene glycol product produced in actual production runs. Physical, compositional, and corrosion testing data are presented. Each facility processes both used automotive coolant and industrial glycol streams. The data reflect that within this quality control process, soundly designed and operated distillation systems can reliably produce glycol suitable for the production of engine coolants meeting the ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light Duty Service (D 3306-94) and other specifications from a variety of waste glycol streams.

Part I: Feed Characterization

With any physical or chemical process, if the outcome is to be consistent, it is essential to know your feedstock. Without a reasonable understanding of the contaminants and physical characteristics of the waste glycols, a consistent operation is difficult to maintain. Characterization of the feed is a process that begins in the design stage of the plant and continues for the life of the facility. At first, the feed is considered to be a complete unknown; gradually, its character becomes better understood. Depending on the source of the feed, it often becomes familiar.

The most common feed categories are:

1. **Used automotive coolant**—Collected from automotive service businesses by local used oil collectors. Complex mixture, but consistent in composite.
2. **Ethylene oxide sterilizer scrubber solution**—Low variability. Clear solution with variable water, EG, DEG, TEG, sulfate, and variable pH.
3. **Polyester waste**—Moderate variability. Fouling, solids, EG, DEG, phosphate, sulfate, esters, and terephthalic acids possible.
4. **Runway deicer**—Two types: (i) EG urea mixture, or (ii) PG acetate mixture. Water content variable, often very high. On-site concentration generally required to reduce transportation.
5. **Other**—High variability. Includes any waste of unknown source including partially processed wastes. Problems can include odor, color, higher glycols, sulfate, phosphate, acids, esters, unknowns.

Controlling feed variability and identifying potential processing problems are the functions of feed characterization. Some feedstreams are typically very steady within a given geography. For example, used automotive coolant is a complex mixture that is both well known and consistent. Although each individual generator will demonstrate some variability, the composite character of a large tank is very consistent. Day-to-day feed variable is low and operating problems are rare. Other streams, such as the polyester waste, sterilizer scrubber solution, and runway deicer glycols, are consistent with respect to a single generator, but can vary considerably from source to source. Last of all, there are the one-of-a-kind streams, where nothing short of a complete work-up would be adequate. This will include benchtop distillation, metals testing, GC work, anion testing, and corrosion testing of finished antifreeze produced on the benchtop.

Typically, a vacuum distillation plant will have considerable testing equipment available for quality control. Some of this equipment will be an artifact of process development work. In the case of the authors of the present paper, much of our equipment is required for quality control testing required in the recycling of used oil. See Table 1 for a list of common in-house testing capabilities. See Fig. 1 for a photograph of a benchtop distillation system.

The quality control process begins with prescreening and waste acceptance testing requirements. The extent of the testing will depend on whether the feed is a familiar type (used automotive antifreeze), from a familiar source, or is something new to the facility. In the design stage and beginning operation, everything is new. Then gradually, as the plant is operated over time, more feeds become familiar. The operating characteristics of the plant become well known. The acceptance limits for the plant become well known. "Familiar" in this case means either used automotive antifreeze from an in-house collection fleet, or any stream from a single tank or process unit which has been well characterized. See Fig. 2 for a typical prescreening/acceptance log. Familiar wastes are subject only to conformity testing, whereas unknown wastes are subjected to the entire range of tests. This will include a full compositional analysis, a pilot distillation, and corrosion testing of antifreeze formulated from the pilot distillate. Fortunately,

TABLE 1—*In-house testing capabilities.*

Physical Characteristics
- Glycol Content (refractive index)
- Glycol Content (gravity)
- Water (Karl Fisher)
- Appearance (visual comparison to "typical" for given stream)
- Viscosity (FSSU. High value for given glycol content indicates polymer or higher glycols)
- Ash furnace. (High value indicates high sulfate, phosphate, other)
- Bottom Sediment and Water (centrifuge. Oil and dirt contamination)
- Other Characteristics (reaction to pH swings, demulsifiers, etc.)
- pH (values below 8 will require pH adjustment before distillation.)
- Urea—Clinical blood check strips (Urea hydrolyzes to ammonia. Remove prior to distillation.)

Compositional Analysis
- GC (FID for glycols, alcohols, BTEX)
- GC (ECD for halogenated solvents, PCBs)
- AA or ICP (metals, silicate)
- LC (liquid chromatograph) or other methodology for anion analysis
- UV/Vis Spectrophotometer (color, other colorimetric methods)

Laboratory Distillation (bench-top)
- Sample waste water stream for treatability (varies with plant local requirements)
- Sample glycol stream for:
  - carryover of key contaminants (color, pH, odor, anions)
  - glycols, other volatile (GC)
  - recovery percentage
- Polish and retest for key contaminants
- Sample bottoms for:
  - disposal criteria (metals, ash, BTUs, viscosity, compatibility)
  - disposal percentage
  - physical characteristics (crystallization/precipitation, low temperature viscosity, etc.)

NOTE Benchtop distillation is generally run on the isolated sample, the sample mixed with the most common feed, and the sample mixed with the feed and various pretreatments, as required.

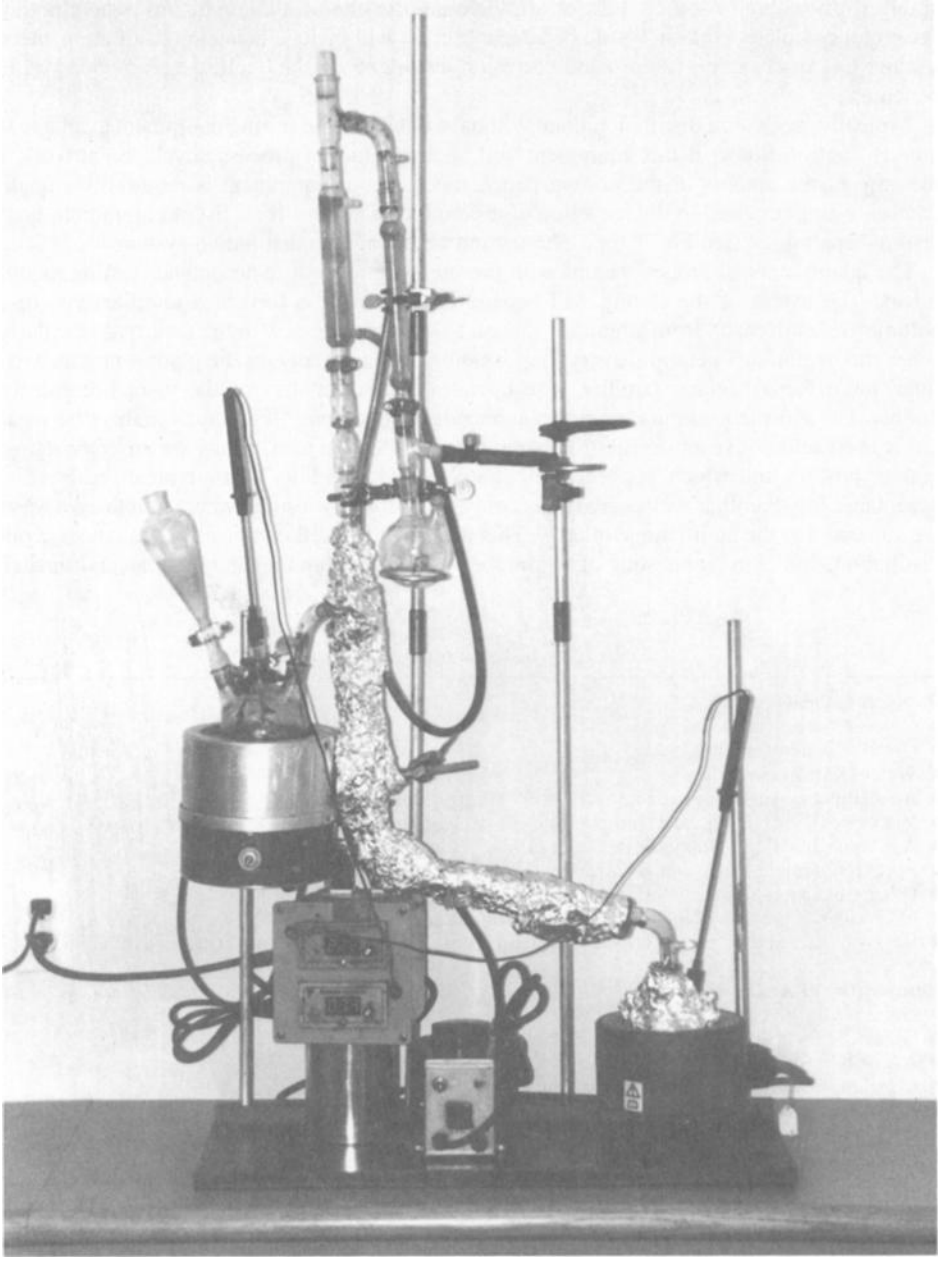
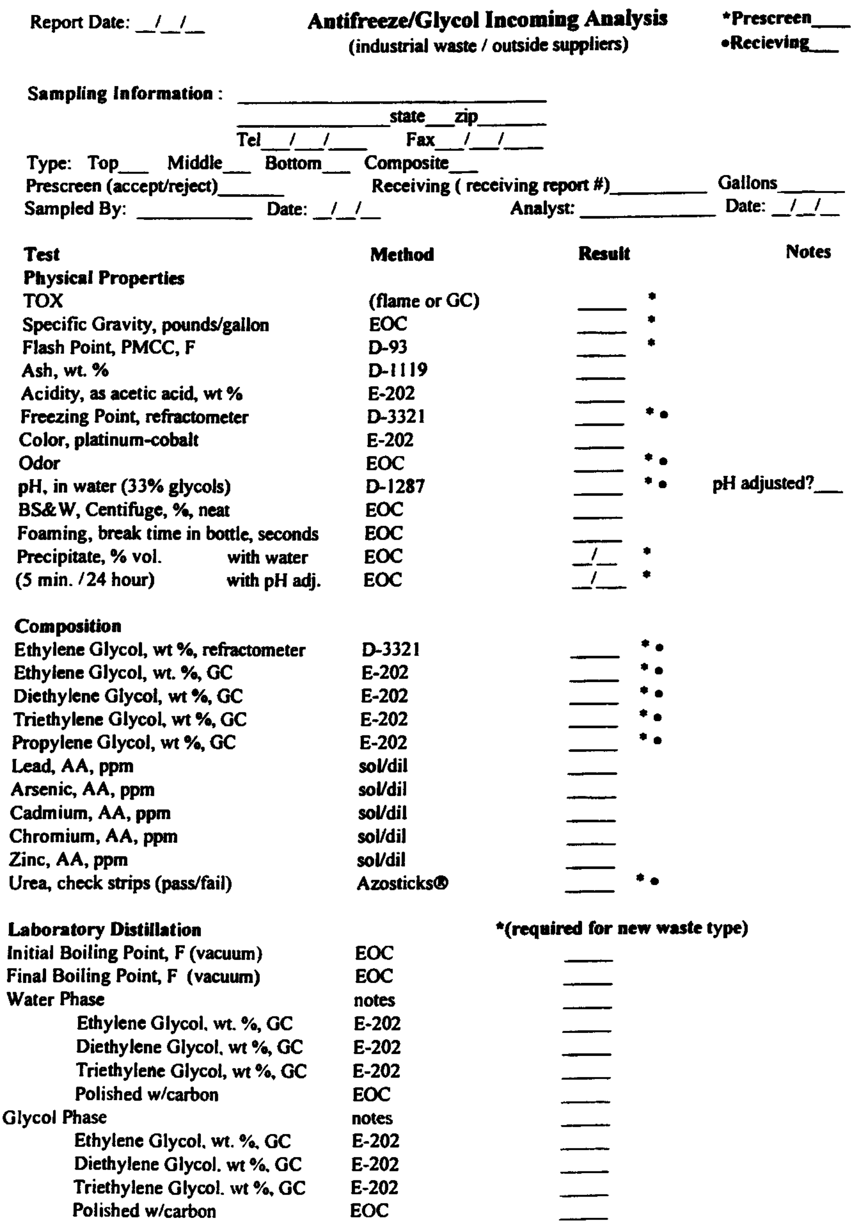


FIG. 1—*Photograph of a benchtop distillation system.*



Report Date: __/__/__

Antifreeze/Glycol Incoming Analysis
(industrial waste / outside suppliers)

***Prescreen____**
•Recieving___

Sampling Information : ______________________________
________________state___zip______
Tel___/___/____ Fax___/___/____
Type: Top___ Middle___ Bottom___ Composite___
Prescreen (accept/reject)______ Receiving (receiving report #)_________ Gallons______
Sampled By: ___________ Date: __/__/__ Analyst: _____________ Date: __/__/__

Test	**Method**	**Result**		**Notes**
Physical Properties				
TOX	(flame or GC)	____	*	
Specific Gravity, pounds/gallon	EOC	____	*	
Flash Point, PMCC, F	D-93	____	*	
Ash, wt. %	D-1119	____		
Acidity, as acetic acid, wt %	E-202	____		
Freezing Point, refractometer	D-3321	____	* •	
Color, platinum-cobalt	E-202	____		
Odor	EOC	____	* •	
pH, in water (33% glycols)	D-1287	____	* •	pH adjusted?___
BS&W, Centifuge, %, neat	EOC	____		
Foaming, break time in bottle, seconds	EOC	____		
Precipitate, % vol. with water	EOC	__/__	*	
(5 min. /24 hour) with pH adj.	EOC	__/__	*	
Composition				
Ethylene Glycol, wt %, refractometer	D-3321	____	* •	
Ethylene Glycol, wt. %, GC	E-202	____	* •	
Diethylene Glycol, wt %, GC	E-202	____	* •	
Triethylene Glycol, wt %, GC	E-202	____	* •	
Propylene Glycol, wt %, GC	E-202	____	* •	
Lead, AA, ppm	sol/dil	____		
Arsenic, AA, ppm	sol/dil	____		
Cadmium, AA, ppm	sol/dil	____		
Chromium, AA, ppm	sol/dil	____		
Zinc, AA, ppm	sol/dil	____		
Urea, check strips (pass/fail)	Azosticks®	____	* •	
Laboratory Distillation		***(required for new waste type)**		
Initial Boiling Point, F (vacuum)	EOC	____		
Final Boiling Point, F (vacuum)	EOC	____		
Water Phase	notes	____		
Ethylene Glycol, wt. %, GC	E-202	____		
Diethylene Glycol, wt %, GC	E-202	____		
Triethylene Glycol, wt %, GC	E-202	____		
Polished w/carbon	EOC	____		
Glycol Phase	notes	____		
Ethylene Glycol, wt. %, GC	E-202	____		
Diethylene Glycol, wt %, GC	E-202	____		
Triethylene Glycol, wt %, GC	E-202	____		
Polished w/carbon	EOC	____		

FIG. 2—*Typical prescreening/acceptance log.*

these unfamiliar streams are generally available in sufficient quantity that detailed qualification is justified.

Part II: Glycol Processing

Standard Pretreatments

The information gained in the testing of samples is intended to lead to one of four outcomes. The decision points for each plant and each test are determined by operating experience:

1. **Normal Feed**—The waste is within the range of normal for the distillation system and can be processed without special consideration or pretreatment.
2. **Blendable Feed**—The waste is processable by blending at a fixed ratio with other feed.
    - **Excessively low pH**—pH between 7 and 8.5. Can cause excessive carryover of anions, such as chloride, sulfate, glycolate, nitrate, and nitrite. Mixing at low ratios with used antifreeze will generally buffer the pH sufficiently. Caustic addition is often needed.
    - **Foaming**—Generally moderated by mixture with used antifreeze by contact with residual defoamers. These tend to accumulate in the distillation evaporator. Test in benchtop still.
    - **Fouling**—Generally moderated by residual descaling additives in used antifreeze. May require processing at high dilution, softening, or treatment with fouling preventatives. Test in benchtop still.
3. **Pretreatable Waste**—The waste will require special pretreatment.
    - **pH adjustment**—pH lower than can be managed by dilution, typically <7. Caustic addition required to reach pH = 8.5 to 10.0.
    - **Flocculation/filtration/settling**—Fouling solids present at excessive levels.
    - **Oil and grease removal**—High levels can cause carryover and foaming. Chemical or physical treatment is needed.
    - **Additional post-distillation polishing**—Laboratory distillation or prior experience show difficulty with color, odor, or certain anions.
    - **Chemical pretreatment**—Urea, organic acids, and certain other contaminants can be chemically removed or neutralized.
4. **Reject**—The waste should be rejected, treated by incineration, or handled through waste water treatment. Rejection criteria varies by plant. It may not be possible or economical to make acceptable product from the waste at a given facility. This can result from high dissolved solids levels, excessive urea contamination, low glycol levels, or difficult carryover problems. Often, better economics exist in alternative markets where lower quality glycols are commonly used.

Vacuum Distillation

Each vacuum distillation plant is built to different specifications and with different equipment. However, the basic process units and operating conditions are established by the consistent nature of used automotive coolants and practical engineering constraints. Both of the plants studied included the following steps achieved in similar manners but with quite different specific approaches:

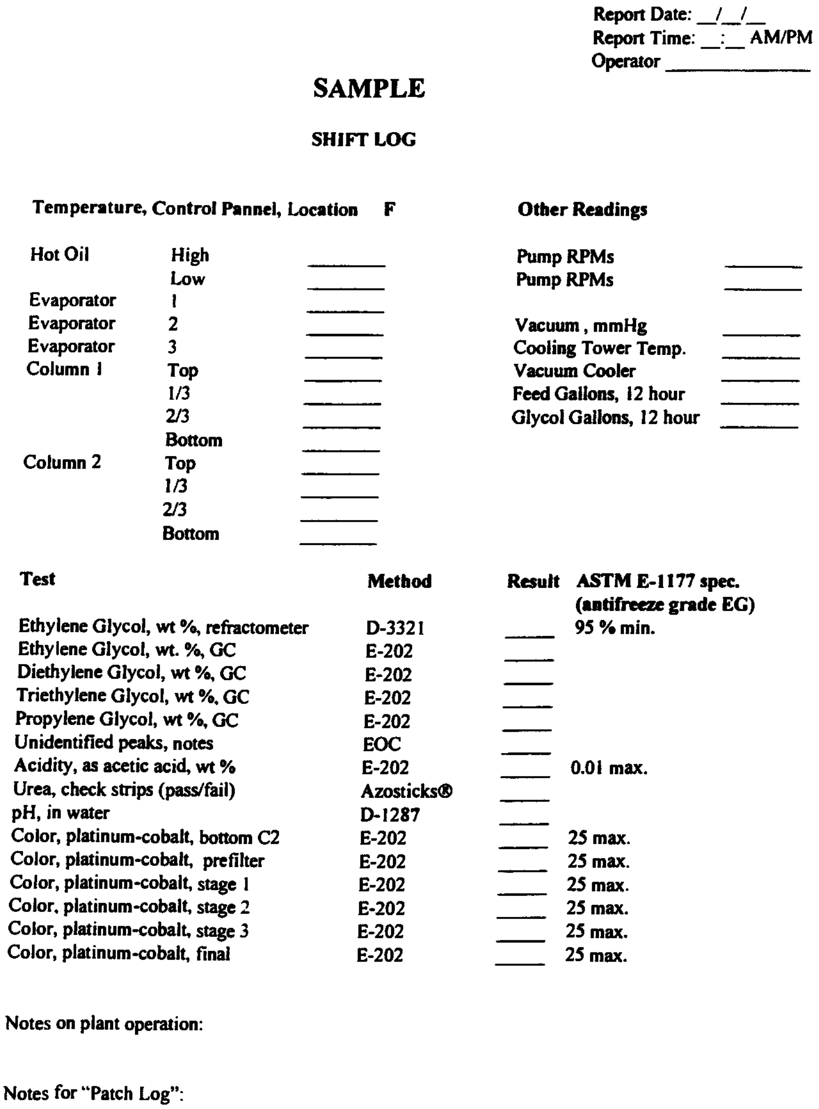
Equalization—Tankage and testing of incoming material combine to provide the distillation system with consistent feed.

Oil and dirt separation—This can be accomplished by any of the following methods: gravity separation, with or without the addition of polymers, demulsifiers, flocculants, heat, or pH adjustment; simple filtration; ultra filtration or reverse osmosis. Mixers and/or pumps are available for addition of chemical treatments.

Operation log—While not a process step, operator data logs and product testing are an essential part of the process. See Fig. 3 for sample operation log.

Feed/bottoms heat exchange—It is beneficial to preheat the feed to the bubble point for process stability and heat economy. It is generally necessary to cool the distillation bottoms prior to polishing.

Evaporation—Generally this is done in stages due to the wide boiling point difference between water and ethylene glycol. Stability, thermodynamic efficiency, and separation effi-



Report Date: __/__/__
Report Time: __:__ AM/PM
Operator ____________

SAMPLE

SHIFT LOG

Temperature, Control Pannel, Location		F	Other Readings	
Hot Oil	High	______	Pump RPMs	______
	Low	______	Pump RPMs	______
Evaporator	1	______		
Evaporator	2	______	Vacuum , mmHg	______
Evaporator	3	______	Cooling Tower Temp.	______
Column 1	Top	______	Vacuum Cooler	______
	1/3	______	Feed Gallons, 12 hour	______
	2/3	______	Glycol Gallons, 12 hour	______
	Bottom	______		
Column 2	Top	______		
	1/3	______		
	2/3	______		
	Bottom	______		

Test	Method	Result	ASTM E-1177 spec. (antifreeze grade EG)
Ethylene Glycol, wt %, refractometer	D-3321	____	95 % min.
Ethylene Glycol, wt. %, GC	E-202	____	
Diethylene Glycol, wt %, GC	E-202	____	
Triethylene Glycol, wt %, GC	E-202	____	
Propylene Glycol, wt %, GC	E-202	____	
Unidentified peaks, notes	EOC	____	
Acidity, as acetic acid, wt %	E-202	____	0.01 max.
Urea, check strips (pass/fail)	Azosticks®	____	
pH, in water	D-1287	____	
Color, platinum-cobalt, bottom C2	E-202	____	25 max.
Color, platinum-cobalt, prefilter	E-202	____	25 max.
Color, platinum-cobalt, stage 1	E-202	____	25 max.
Color, platinum-cobalt, stage 2	E-202	____	25 max.
Color, platinum-cobalt, stage 3	E-202	____	25 max.
Color, platinum-cobalt, final	E-202	____	25 max.

Notes on plant operation:

Notes for "Patch Log":

FIG. 3—*Sample of an operation log.*

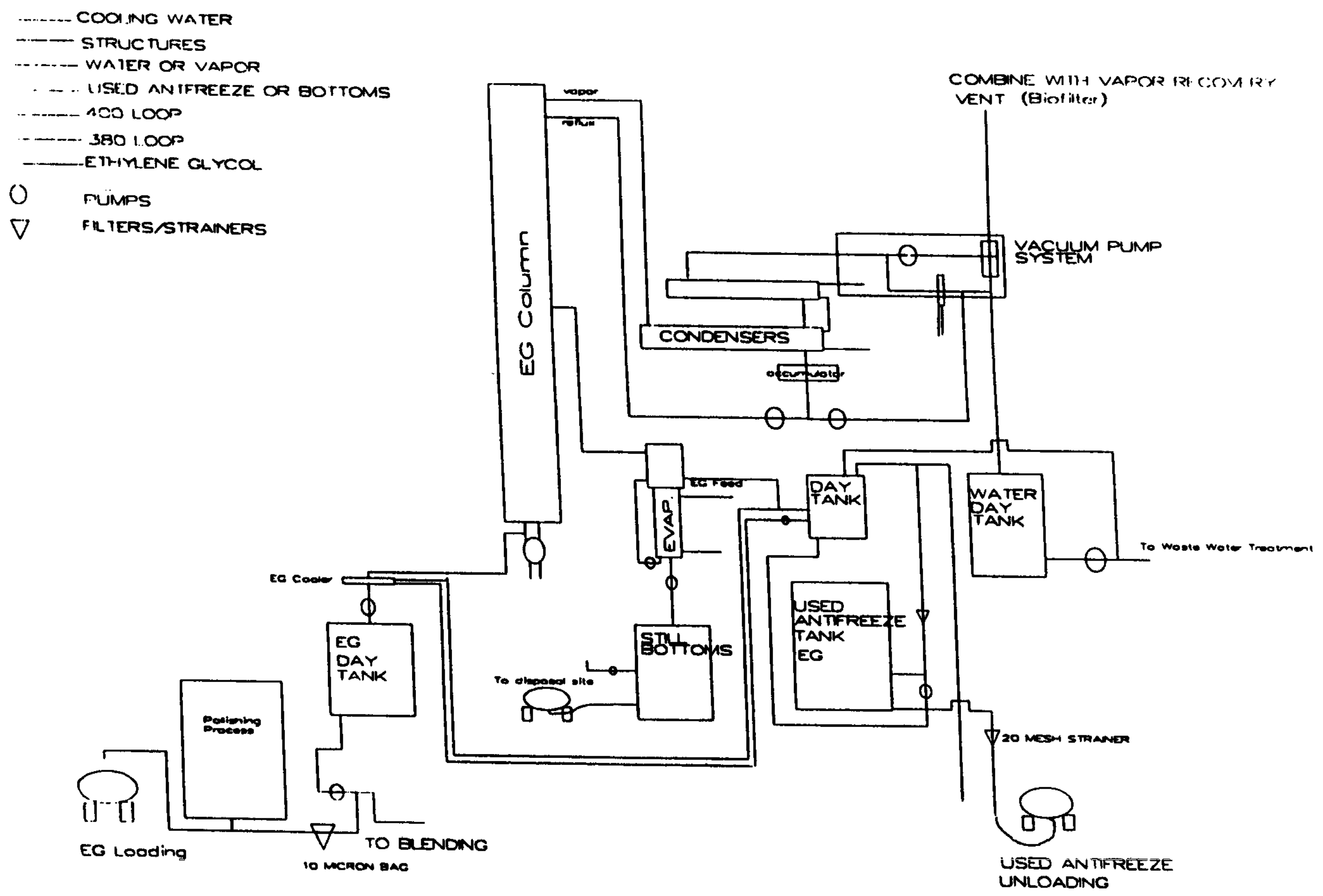


FIG. 4—*Antifreeze recycling unit process flow sheet.*

ciency are improved. This can be done in multiple columns under pressures varying from low pressure to 28 in Hg vacuum or in a single column at 24 to 28 in Hg vacuum with multiple evaporators. Evaporators can be falling film, vertical, forced circulation, kettle, or calandra type. Evaporators can be external with a vapor fed column, or all heat can be supplied in reboilers with product taken two to four trays up.

Fractionation—Either in packed or trayed columns. The separation requires 10 to 25 theoretical trays, depending on reflux and the separation efficiency desired.

Product polishing—Water overheads are treated for discharge as waste water or recycled within the plant. Glycol product is polished through one or more of the following steps: filtration (either simple or by UF/RO); carbon absorption in a fixed bed (either in a large bulk vessel or in transportable units); deionizing resins; additional filtration.

See Fig. 4 for representative flow sheet.

Product testing—Both participating facilities have QA/QC programs designed to formalize and document both the process and the products produced. The goals of the programs are:

1. To detect every problem as early as practical. To predict trouble, where possible.
2. To detect each problem at a point in the process where it can be corrected.
3. To check critical parameters in more than one way, when practical.
4. To collect operational data that will help develop a better understanding of the process.
5. To achieve these requirements without unnecessary duplication of effort.

An efficient quality control program is designed using operational experience to determine what indicators are available to predict both product quality and plant operation problems. Every item in the logs should serve a specific function, either in monitoring equipment status, product quality, or in predicting adjustments or maintenance. See Figs. 5 and 6 for sample product testing forms.

Part III: Test Data

For this paper the authors have chosen the present analytical data sets from nine different operational "points" representing the actual operation of the plant at that point. A variety of feed types is shown. Each data set includes "feed," "pre-polishing," and "post-polishing" samples. All were tested for a variety of physical parameters, as well as for a list of commonly identified contaminants of concern. Selected samples were subjected to rudimentary corrosion tests commonly used for screening purposes. Notes describe demonstration upsets (intentional, arranged for demonstration in this paper), operating conditions, and the generic source of the feed. The data are not intended to be sufficiently inclusive or systematic enough to be presented as a conclusive study. Much of the analytical data concerning feedstreams are considered to be proprietary, which has limited the scope of this portion of the paper. However, the data samples do represent a variety of widely differing streams treated by plants of different design, thousands of miles apart. Certain correlations are apparent in the data. The consistency of the finished glycol and the understanding of upset conditions are of interest.

Glycol Testing Data—The data collection phase of this paper included the collection of samples representing nine representative operation points. Each point is sampled as feed, as pre-polished distillate, and as post-polishing ethylene glycol product. This product was either blended into finished antifreeze or sold as industrial glycol. With the exception of several percent excess water, all of the samples collected meet the ASTM Test Method for Freezing Point of Aqueous Engine Coolants (D 1177-94) ethylene glycol specification. The water content of the finished antifreeze is addressed in corrosion inhibitor blending process. Lower water values could easily be obtained if required. See Tables 2 to 10.

As few other contaminants are present at detectable levels, data correlations are not presented;

Report Date: __/__/__

SAMPLE

GLYCOL ANALYSIS

Sampling Information : ____________________
____
____

Type: Top___ Middle___ Bottom___ Composite___
Tank Number _____ Gallons____ Invoice Number_____
Sampled By: __________ Date: __/__/__ Analyst: __________ Date: __/__/__

Notes: ____________________________

Test Information

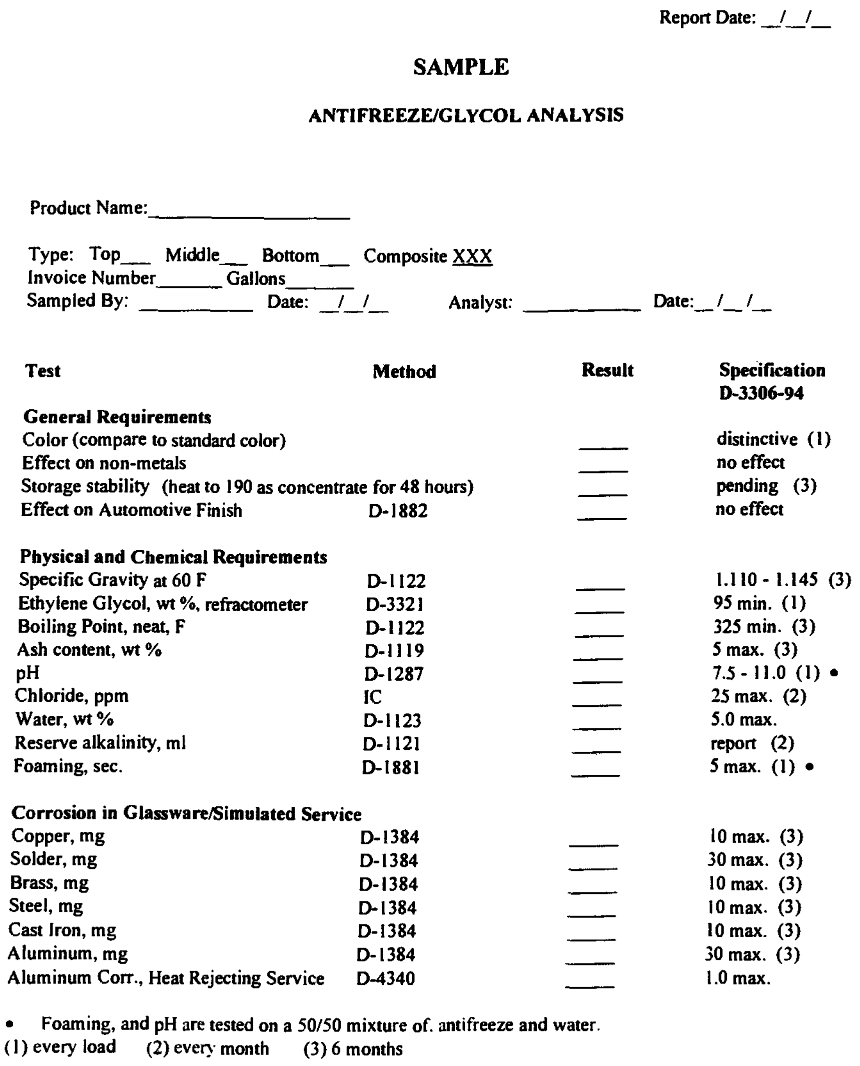
Test	**Method**	**Result**	**ASTM E-1177 spec. (antifreeze grade EG)**	
Specific Gravity, @ 60 F	D-1122	____		
Ash, wt. %	D-1119	____	<0.001	(3)
Ethylene Glycol, wt %, refractometer	D-3321	____	95 % min.	(1)a,b
Ethylene Glycol, wt. %, GC	E-202	____		(1)a,b
Diethylene Glycol, wt %, GC	E-202	____		(1)a,b
Triethylene Glycol, wt %, GC	E-202	____		(1)a,b
Propylene Glycol, wt %, GC	E-202	____		(1)a,b
Unidentified peaks, notes	EOC	____		
Total Glycols, wt %, GC	E-202	____	99.5 min.	(1)a,b
Acidity, as acetic acid, wt %	E-202	____	0.01 max.	(2)
Lead, AA, ppm	sol/dil	____		(3)
Arsenic, AA, ppm	sol/dil	____		(3)
Cadmium, AA, ppm	sol/dil	____		(3)
Chromium, AA, ppm	sol/dil	____		(3)
Zinc, AA, ppm	sol/dil	____		(3)
Water	E-202	____	0.5 max.	
Color, platinum-cobalt	E-202	____	25 max.	(1)b
pH, in water	D-1287	____		(1)b

(1)a On "customer sheet", with every load (1)b shift log (2) monthly (3) 6 months minimum

FIG. 5—*Sample product testing form.*

however, past laboratory distillation testing of samples high in chloride, sulfate, glycolate and terephthalate at varying pH suggests that low pH increases contaminant carryover. The effect begins strongly at feed pH less than 6.

Corrosion Testing Data—Corrosion testing was performed as a brief conformation that the glycol test data did not miss any overtly aggressive contaminant. Four of these glycol products were blended with an antifreeze additive package and subjected to the ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384-96) and the ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions (D 4340-96), to determine some measure of basic suitability. Additionally, from one of the "feed"



Report Date: __/__/__

SAMPLE

ANTIFREEZE/GLYCOL ANALYSIS

Product Name:__________________

Type: Top___ Middle___ Bottom___ Composite XXX
Invoice Number______ Gallons______
Sampled By: __________ Date: __/__/__ Analyst: __________ Date:__/__/__

Test	Method	Result	Specification D-3306-94
General Requirements			
Color (compare to standard color)		____	distinctive (1)
Effect on non-metals		____	no effect
Storage stability (heat to 190 as concentrate for 48 hours)		____	pending (3)
Effect on Automotive Finish	D-1882	____	no effect
Physical and Chemical Requirements			
Specific Gravity at 60 F	D-1122	____	1.110 - 1.145 (3)
Ethylene Glycol, wt %, refractometer	D-3321	____	95 min. (1)
Boiling Point, neat, F	D-1122	____	325 min. (3)
Ash content, wt %	D-1119	____	5 max. (3)
pH	D-1287	____	7.5 - 11.0 (1) •
Chloride, ppm	IC	____	25 max. (2)
Water, wt %	D-1123	____	5.0 max.
Reserve alkalinity, ml	D-1121	____	report (2)
Foaming, sec.	D-1881	____	5 max. (1) •
Corrosion in Glassware/Simulated Service			
Copper, mg	D-1384	____	10 max. (3)
Solder, mg	D-1384	____	30 max. (3)
Brass, mg	D-1384	____	10 max. (3)
Steel, mg	D-1384	____	10 max. (3)
Cast Iron, mg	D-1384	____	10 max. (3)
Aluminum, mg	D-1384	____	30 max. (3)
Aluminum Corr., Heat Rejecting Service	D-4340	____	1.0 max.

- Foaming, and pH are tested on a 50/50 mixture of. antifreeze and water.

(1) every load (2) every month (3) 6 months

FIG. 6—*Sample product testing form.*

samples, the same corrosion tests were run, both on straight used antifreeze (adjusted test specification glycol content) and on used antifreeze (adjusted test specification glycol content) blended with an antifreeze additive package. This additive package contained:

Sodium Tetraborate
Sodium Hydroxide
Sodium Nitrate
Sodium Nitrite
Sodium Molybdate
Sodium Tolytriazol
Sodium Silicate
Anti-foam
Dye

TABLE 2

Sampled 2-26-97 Tested 4-1-97
Distillation Facility 1
65% Polyester Waste, 35% Used Automotive Antifreeze

Analyte	Units	Polyester Waste	Feed	Pre-Polished	Polished
pH	SU	5.6	7.2	6.6	5.9
Color	alpha Pt/Co	425	light green	250	15
Specific Gravity	SU	1.067	1.006	1.117	1.117
Water Content	%	71	58	2.8	2.8
Ethylene Glycol	%	36	40.5	97.2	97.2
Propylene Glycol	%	<1	<1	<1	<1
Diethylene Glycol	%	<1	<1	<1	<1
Acidity	%				<0.005
Arsenic	ppm	<2.5	<2.5	<2.5	<2.5
Silicon	ppm	<2.5	8.8	<2.5	<2.5
Lead	ppm	<2.5	5.8	<2.5	<2.5
Iron	ppm	<2.5	27	<2.5	<2.5
Copper	ppm	<2.5	<2.5	<2.5	<2.5
Boron	ppm	<2.5	98	36	30
Chromium	ppm	<2.5	<2.5	<2.5	<2.5
Cadmium	ppm	<2.5	<2.5	<2.5	<2.5
Aluminum	ppm	<2.5	3.8	<2.5	<2.5
Zinc	ppm	3	7.5	<2.5	<2.5
Chloride	ppm	<5	<5	<5	<5
Sulfate	ppm	<5	<5	<5	<5
Nitrite	ppm	<5	<5	<5	<5
Nitrate	ppm	<5	234	<5	<5
Phosphate	ppm	1036	312	<5	<5
Glycolate	ppm	630	160	297	23
Oxylate	ppm	<10	<10	<10	<10

ASTM D 1384	Loss, Mg/ Sample
Copper	<2
Solder	<2
Brass	<2
Steel	3
Cast Iron	<2
Cast Aluminum	<2
ASTM D 4340	0.016

NOTES—

Run started with 100% polyester waste as test. Plant was switching to 100% automotive used antifreeze. See other Test sheets for typical values for used antifreeze.

pH was intentionally left unadjusted to document the effects (normally it is adjusted to about 8.5).

The testing data show that all glycol product samples pass these tests well. All glycol product samples performed in a very similar manner, displaying little corrosion above the laboratory detection limits. No product glycol coupon failed any test. No individual coupon, used antifreeze included, displayed more than double the average weight loss value. The used antifreeze

TABLE 3

Sampled 3-14-97 Tested 4-16-97
Distillation Facility 2
100% Used Automotive Antifreeze

Analyte	Units	Feed	Pre-Polished	Polished
pH	SU	8.4	6.7	6.4
Color	alpha Pt/Co	green	504	24
Specific Gravity	SU	1.068	1.117	1.117
Water Content	%	58	<2	<2
Ethylene Glycol	%	41	98+	98+
Propylene Glycol	%	<1	<1	<1
Diethylene Glycol	%	<1	<1	<1
Acidity	%			<0.005
Arsenic	ppm	<2.5	<2.5	<2.5
Silicon	ppm	35	<2.5	<2.5
Lead	ppm	<2.5	<2.5	<2.5
Iron	ppm	54	4.5	3.4
Copper	ppm	8	<2.5	<2.5
Boron	ppm	244	40	31
Chromium	ppm	<2.5	<2.5	<2.5
Cadmium	ppm	<2.5	<2.5	<2.5
Aluminum	ppm	12	<2.5	<2.5
Zinc	ppm	<2.5	<2.5	<2.5
Chloride	ppm	<5	<5	<5
Sulfate	ppm	256	<5	<5
Nitrite	ppm	<5	<5	<5
Nitrate	ppm	113	<10	<10
Phosphate	ppm	780	<10	<10
Glycolate	ppm	440	<10	<10
Oxylate	ppm	<10	<10	<10

ASTM D 1384	Loss, Mg/ Sample
Copper	<3
Solder	<3
Brass	<3
Steel	<3
Cast Iron	<3
Cast Aluminum	<3

NOTES—
No industrial glycol in feed. Feed is typical for this plant.
Carbon polishing system scheduled for change-out. End of run.
Column in upset condition/over temperature at bottom.

sample demonstrated marginal performance, with two glassware coupons failing, and 1 of 2 ASTM D 4340 pucks failing. The reinhibited used antifreeze glassware sample performed better, with all coupons passing, but not at the level new antifreeze is generally expected to perform. However, the additive package is one intended for use with distilled or virgin glycols, and was not optimized for use in recycling plain used antifreeze. No effort was made to filter or purify the used antifreeze prior to reinhibiting. This sample was run only to measure the

TABLE 4

Sampled 7-28-97 Tested 8-14-97, Set 3

Distillation Facility 2

100% Used Automotive Antifreeze

Analyte	Units	Feed	Pre-Polished	Polished
pH	SU	8.1	6.8	6.5
Color	alpha Pt/Co	green	>70	15
Specific Gravity	SU	1.06	1.117	1.117
Water Content	%	58	<1	<1
Ethylene Glycol	%	41	99+	99+
Propylene Glycol	%	<1	<1	<1
Diethylene Glycol	%	<1	<1	<1
Acidity	%			<0.005
Arsenic	ppm	<2	<2	<2
Silicon	ppm	31	2.6	<2
Lead	ppm	<2	<2	<2
Iron	ppm	17	<2.5	<2.5
Copper	ppm	<2.5	<2.5	<2.5
Boron	ppm	185	37	31
Chromium	ppm	<2.5	<2.5	<2.5
Cadmium	ppm	8.4	<2.5	<2.5
Aluminum	ppm	3.8	<2.5	<2.5
Zinc	ppm	9.1	<2.5	<2.5
Chloride	ppm	219	<5	<5
Sulfate	ppm	478	<5	<5
Nitrite	ppm	96	<5	<5
Nitrate	ppm	694	<5	<5
Phosphate	ppm	1135	<5	<5
Glycolate	ppm	1142	50	50
Oxylate	ppm	<10	<10	<10
ASTM D 1384	Loss, Mg/Sample	Feed W/Ad-Pak	Feed Only	
Copper	<3	<3	<3	
Solder	<3	<3	<3	
Brass	<3	<3	<3	
Steel	<3	<3	4	
Cast Iron	<3	5	11	
Cast Aluminum	<3	10	31	

NOTES—

Feed is 100% used automotive antifreeze. Typical for this plant.

Product rate, operating conditions, and product quality in normal range.

character of this particular feed sample and to confirm the laboratory method. The reinhibited used antifreeze was not tested by ASTM D 4340.

The data are not dissimilar from earlier work that studied the distillation of used propylene glycol based antifreeze in a small (47 liters/batch) batch stills [2]. A similar approach was taken, testing samples before and after distillation, followed by corrosion testing. However, the level of purity obtained in the commercial scale continuous plants presented in this study was better.

Test Data Significance—The intended focus of this paper is to review industry practice in used antifreeze and glycol distillation rather than to evaluate the effectiveness of distillation as

TABLE 5

Sampled 4-18-97 Sampled 4-21-97 Tested 5-2-97
Distillation Facility 2
100% Used Automotive Antifreeze

Analyte	Units	Feed	Pre-Polished	(4-18-97) Polished	(4-21-97) After Carbon Change
pH	SU	8.5	7.3	6.8	7.2
Color	alpha Pt/Co	green	720	12	6
Specific Gravity	SU	1.067	1.117	1.117	1.117
Water Content	%	65	0.3	0.3	0.3
Ethylene Glycol	%	41	99.7	99.7	99.7
Propylene Glycol	%	<1	<1	<1	<1
Diethylene Glycol	%	<1	<1	<1	<1
Acidity	%			<0.005	<0.005
Arsenic	ppm	<2.5	<2.5	<2.5	<2.5
Silicon	ppm	25	<2.5	<2.5	<2.5
Lead	ppm	<2.5	<2.5	<2.5	<2.5
Iron	ppm	15	8	<2.5	<2.5
Copper	ppm	<2.5	<2.5	<2.5	<2.5
Boron	ppm	166	31	40	32
Chromium	ppm	<2.5	<2.5	<2.5	<2.5
Cadmium	ppm	<2.5	<2.5	<2.5	<2.5
Aluminum	ppm	5	<2.5	<2.5	<2.5
Zinc	ppm	8.6	<2.5	<2.5	<2.5
Chloride	ppm	31	<5	<5	<5
Sulfate	ppm	143	<5	<5	<5
Nitrite	ppm	171	<5	<5	<5
Nitrate	ppm	668	<5	<5	<5
Phosphate	ppm	2108	<5	<5	<5
Glycolate	ppm	413	19	16	17
Oxylate	ppm	<10	<10	<10	<10

NOTES—
Feed is 100% used automotive antifreeze. Typical for this plant.
Product rate, operating conditions, and product quality in normal range.
Feed was not resampled after carbon change.

a recycling method. However, some limited evaluation of the finished glycols produced seems appropriate in order to establish some general points of reference. Also, there are relevant comments as to the likelihood of contaminants being present in distilled glycols. The significance of the corrosion testing methods used in this paper is included in the referenced methods[3–5].

Significance of Contaminants

Acidity—The ASTM E 1177 specification for acidity is 0.005%. May be indicator of organic acid carryover. Feed pH greater than 8.5 gives reduced carryover. Distilled EG should have pH > 7 without post distillation pH adjustments. pH reading and titrations can rise over a period of days if esters are present.

Metals—Present in waste, but did not carry over at detected levels. Tap water hardness

TABLE 6

Sampled 5-1-97 Tested 5-1-97
Distillation Facility 2
100% Used Automotive Antifreeze

Analyte	Units	Feed	Pre-Polished	Polished
pH	SU	8.4	6.9	7
Color	alpha Pt/Co	green	504	13
Specific Gravity	SU	1.068	1.117	1.117
Water Content	%	58	1.5	1.5
Ethylene Glycol	%	41	98+	98+
Propylene Glycol	%	<1	<1	<1
Diethylene Glycol	%	<1	<1	<1
Acidity	%			<0.005
Arsenic	ppm	<2.5	<2.5	<2.5
Silicon	ppm	28	<2.5	<2.5
Lead	ppm	17	<2.5	<2.5
Iron	ppm	80	4.5	3.2
Copper	ppm	13	<2.5	<2.5
Boron	ppm	218	38	37
Chromium	ppm	<2.5	<2.5	<2.5
Cadmium	ppm	<2.5	<2.5	<2.5
Aluminum	ppm	20	<2.5	<2.5
Zinc	ppm	<2.5	<2.5	<2.5
Chloride	ppm	57	<5	<5
Sulfate	ppm	240	<5	<5
Nitrite	ppm	111	<5	<5
Nitrate	ppm	490	<10	<10
Phosphate	ppm	950	<10	<10
Glycolate	ppm	620	<10	<10
Oxylate	ppm	<10	<10	<10

NOTE—No industrial glycol in feed. Feed is typical for this plant.

(calcium and magnesium as sulfates) typically runs 20 to 150 ppm. Individual metals levels over 10 ppm may indicate droplet entrapment.

Organic Acids—Glycolate/Oxylate. Glycolate is normally present in all antifreeze in use. Carries over at greatly reduced levels. Oxylate is commonly used at high levels to clean cooling systems in situ, and is followed by conditioning with borate solution [*6*]. Effect at trace levels glycol not known, as it forms quickly in use.

Terephthalic acid—Potentially present in polyester waste. Removal to a great extent by distillation. Tested as corrosion inhibitor in combination with other inhibitors and found not to be aggressive [*3*].

Chloride—Present in waste but did not carry over at detected levels. The ASTM D 3306 standard specifies 25 ppm maximum. Tap water commonly contains 2 to 75 ppm chloride. Corrosion inhibitor chemicals can contain chloride. Coolant concentrations above 50 ppm are thought to be detrimental. Stronger effect known at higher levels [*4*]. A 40 ppm maximum is recommended in D 3306 Appendix X1, Table X1, for service dilution water.

Nitrate/Nitrite—Present in waste, but did not carry over at detected levels. Not likely to cause compatibility problems with organic or conventional additive packages [*5*].

Boron—Boron carries over at reduced levels. Amount depends on design, feed, operating

TABLE 7

Sampled 8-5-97 Tested 8-14-97, Set 4
Distillation Facility 1
100% Used Automotive Antifreeze

Analyte	Units	Feed	Pre-Polished	Polished
pH	SU	8.1	6	6.8
Color	alpha Pt/Co	green	>70	15
Specific Gravity	SU	1.062	1.117	1.117
Water Content	%	61	<1	<1
Ethylene Glycol	%	38	98.5	98.5
Propylene Glycol	%	<1	<1	<1
Diethylene Glycol	%	<1	<1	<1
Acidity	%			<0.005
Arsenic	ppm	<2	<2	<2
Silicon	ppm	24	<2	<2
Lead	ppm	<2	<2	<2
Iron	ppm	11	<2.5	<2.5
Copper	ppm	<2.5	<2.5	<2.5
Boron	ppm	175	36	34
Chromium	ppm	<2.5	<2.5	<2.5
Cadmium	ppm	8.4	<2.5	<2.5
Aluminum	ppm	4	<2.5	<2.5
Zinc	ppm	8.1	<2.5	<2.5
Chloride	ppm	196	<5	<5
Sulfate	ppm	397	<5	<5
Nitrite	ppm	85	<5	<5
Nitrate	ppm	703	<5	<5
Phosphate	ppm	1132	<5	<5
Glycolate	ppm	880	53	38
Oxylate	ppm	<10	<10	<10
ASTM D 1384		Loss, Mg/Sample		
Copper		<3		
Solder		<3		
Brass		<3		
Steel		<3		
Cast Iron		<3		
Cast Aluminum		<3		

NOTES—
Feed is 100% used automotive antifreeze. Typical for this plant.
Product rate, operating conditions, and product quality in normal range.

conditions. Carryover amount is pH sensitive. Borate is a very common ingredient in conventional coolants, and does not interfere with performance. The effect of borate on organic acid inhibitor technologies (OATs) is not well documented in the literature, but levels below 10 ppm are believed to be acceptable. Higher levels are being investigated.

Phosphate—Present in waste, but did not carry over at detected levels. Not expected to be problematical at low levels. Effect on organic inhibitors is not well documented in the literature, but levels below 10 ppm are believed to be acceptable.

Sulfate—Present in waste, but did not carry over at detected levels. Not expected to be problematical at low levels. Effects have been documented at higher levels. Tap water com-

TABLE 8

Sampled 6-16-97 Tested 6-20-97
Distillation Facility 1
100% Used Automotive Antifreeze

Analyte	Units	Feed	Pre-Polished	Polished
pH	SU	8.7	7.6	7.8
Color	alpha Pt/Co	green	42	8
Specific Gravity	SU	1.064	1.117	1.117
Water Content	%	53	<1	<1
Ethylene Glycol	%	45	98.6	98.4
Propylene Glycol	%	<1	<1	<1
Diethylene Glycol	%	<1	<1	<1
Acidity	%			<0.005
Arsenic	ppm	<2	<2	<2
Silicon	ppm	24	<2	<2
Lead	ppm	<2	<2	<2
Iron	ppm	45	<2.5	<2.5
Copper	ppm	<2.5	<2.5	<2.5
Boron	ppm	210	9.8	12
Chromium	ppm	<2.5	<2.5	<2.5
Cadmium	ppm	<2.5	<2.5	<2.5
Aluminum	ppm	8	<2.5	<2.5
Zinc	ppm	11	<2.5	<2.5
Chloride	ppm	160	<5	<5
Sulfate	ppm	130	<5	<5
Nitrite	ppm	154	<5	<5
Nitrate	ppm	630	<5	<5
Phosphate	ppm	2100	<5	<5
Glycolate	ppm	400	50	32
Oxylate	ppm	<10	<10	<10

NOTES—
Feed is 100% used automotive antifreeze. Typical for this plant.
Product rate, operating conditions, and product quality in normal range.

monly varies between 5 ppm and 200 ppm. A 100 ppm maximum is recommended in D 3306 Appendix X1, Table X1, for service dilution water.

Silicate—Present in waste, but did not carry over at detected levels. Effect on organic inhibitors is not well documented in the literature, but levels below 10 ppm are believed to be acceptable.

Color—General indicator of physical cleanliness. Less than 25 Pt/Co color units. Antifreeze grade ethylene glycol must meet the ASTM Specification for Anti-Freeze Grade Ethylene Glycol (E 1177-92) of 25 units. Industrial-grade ethylene glycol must meet the ASTM Specification for Industrial Grade Ethylene Glycol (E 1119-92) of 10 units. Not a direct indicator of chemical purity. Emulsified oil is a common source of minor turbidity.

pH—Very sensitive to acidity in dehydrated glycol. A pH greater than 5 will generally insure compliance with ASTM E 1177 acidity specification. A range of 5.5 to 9 is recommended in D 3306 Appendix X1, Table X1, for service dilution water. pH greater than 7 after distillation and prior to polishing or additive addition correlates with lower contaminant levels.

PG/DEG/TEG—The ASTM D 3306 standard allows up to 15% other glycols. Levels that high are generally unknown in the used antifreeze and industrial waste streams, when taken as a composite.

TABLE 9

Sampled 8-22-97 Tested 9-24-97
Distillation Facility 1
100% Used Automotive Antifreeze

Analyte	Units	Feed	Pre-Polished	Polished
pH	SU	9.2	8	7.5
Color	alpha Pt/Co	green	155	15
Specific Gravity	SU	1.084	1.117	1.118
Water Content	%	48	1.4	1.6
Ethylene Glycol	%	52	98.5	98.4
Propylene Glycol	%	<1	<1	<1
Diethylene Glycol	%	<1	<1	<1
Acidity	%			<0.005
Arsenic	ppm	<5	<5	<5
Silicon	ppm	33	<20	20
Lead	ppm	<5	<5	<5
Iron	ppm	32	<5	<5
Copper	ppm	<5	<5	<5
Boron	ppm	365	<20	<20
Chromium	ppm	<5	<5	<5
Cadmium	ppm	<5	<5	<5
Aluminum	ppm	<20	<20	<20
Zinc	ppm	22	<2.5	<2.5
Chloride	ppm	442	<10	<10
Sulfate	ppm	1755	<10	<10
Nitrite	ppm	323	<10	<10
Nitrate	ppm	1401	<10	<10
Phosphate	ppm	1287	<10	<10
Glycolate	ppm	2435	16	<10
Oxylate	ppm	<10	<10	<10

NOTES—
Feed is 100% used automotive antifreeze. Typical for this plant.
Product rate, operating conditions, and product quality in normal range.

Water—Finished antifreeze can contain up to 5% water. Antifreeze blenders can adjust process to ensure compliance with specifications. Vacuum distillation systems can practically achieve less than ½% water if customer specifications require.

Summary

We have attempted to give an overview of how the reprocessing of waste glycols by vacuum distillation into product is a process including prescreening, processability studies, process control and Q/C testing, and finished antifreeze testing. It is not a "black box" process in which untested feed is blindly pumped through a machine. Used, surplus, by-product, and waste glycols conforming to industry accepted types are well characterized and valuable feed stocks. It has been demonstrated that waste glycols from differing sources are being processed by vacuum distillation into ethylene glycol meeting all ASTM specifications required for the production of D 3306 specification engine coolant. The plants vary considerably in their geography, design, feed, and operational characteristics, but the finished glycol and antifreeze products they produce are consistent and indistinguishable.

TABLE 10

Sampled 8-24-97 Tested 9-24-97
Distillation Facility 1
100% Used Automotive Antifreeze

Analyte	Units	Feed	Pre-Polished	Polished
pH	SU	8.8	7.9	7.4
Color	alpha Pt/Co	green	140	20
Specific Gravity	SU	1.084	1.117	1.117
Water Content	%	46	<1	<1
Ethylene Glycol	%	54	98.6	98.4
Propylene Glycol	%	<1	<1	<1
Diethylene Glycol	%	<1	<1	<1
Acidity	%			<0.005
Arsenic	ppm	<5	<5	<5
Silicon	ppm	24	<20	<20
Lead	ppm	<5	<5	<5
Iron	ppm	15	<5	<5
Copper	ppm	<2.5	<2.5	<2.5
Boron	ppm	230	<20	<20
Chromium	ppm	<2.5	<2.5	<2.5
Cadmium	ppm	<2.5	<2.5	<2.5
Aluminum	ppm	<20	<2.5	<2.5
Zinc	ppm	12	<2.5	<2.5
Chloride	ppm	480	<5	<5
Sulfate	ppm	1680	<5	<5
Nitrite	ppm	240	<5	<5
Nitrate	ppm	1350	<5	<5
Phosphate	ppm	1220	<5	<5
Glycolate	ppm	2600	18	<10
Oxylate	ppm	<10	<10	<10

NOTES—

Feed is 100% used automotive antifreeze. Typical for this plant.

Product rate, operating conditions, and product quality in normal range.

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Marvin E. Haddock[1] *and Edward R. Eaton*[2]

Recycling Used Engine Coolant Using High-Volume Stationary, Multiple Technology Equipment

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REFERENCE: Haddock, M. E. and Eaton, E. R., "**Recycling Used Engine Coolant Using High-Volume Stationary, Multiple Technology Equipment,**" *Engine Coolant Testing, Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 251–260.

ABSTRACT: Recycling used engine coolant has become increasingly desirable due to two significant factors. First, engine coolant frequently merits designation as a hazardous waste under the Federal Clean Water Act. Federal and some state environmental protection agencies have instituted strict regulation of the disposal of used engine coolant. In some cases, the disposal of engine coolant requires imposition of waste disposal fees and surcharges. Secondly, ethylene glycol, the principal cost component of engine coolant, has experienced dramatic price fluctuations and occasional shortages in supply. Therefore, there are both environmental and economic pressures to recycle engine coolant and recover the ethylene glycol component in an efficient and cost-effective manner.

This paper discusses a multistage apparatus and a process for recycling used engine coolant that employs a combination of filtration, centrifugation (hydrocyclone separation), dissolved air flotation, nanofiltration, reverse osmosis, continuous deionization, and ion exchange processes for separating ethylene glycol and water from used engine coolant. The engine coolant is prefiltered through a series of filters. The filters remove particulate contaminates. This filtered fluid is then subjected to dissolved air flotation and centrifugation to remove petroleum. Then it is heated and pressurized prior to being passed over a series of two different sets of semipermeable membranes. The membrane technologies separate the feed stream into a "permeate" solution of ethylene glycol and water and a "concentrate" waste solution. The concentrate solution is returned to a concentrate tank for continuous circulation through the apparatus. The permeate solution is subjected to final refining by continuous deionization followed by a cation and anion ion exchange polishing process. The continuous deionization reduces ionic contaminants, and the ion exchange system eliminates any ionic contaminants left by the previous purification methods. A mechanical blender is used to mix the purified recovered fluid with fresh ethylene glycol (to adjust freeze point) and performance enhancing chemicals.

KEYWORDS: radiators, antifreeze, diesel, engine, ethylene, coolant, extended service, recycling, fully formulated, inhibitors, propylene, glycol, silicate

Engine coolants are formulated to provide internal combustion engines with protection from metal corrosion and to lower the freezing point of water. These coolants typically contain ethylene or propylene glycol at a concentration of about 30 to 70% by volume, and corrosion inhibitors at approximately 1 to 3% by weight. While engine coolants are universally used in "water-cooled" internal combustion engines, there are limitations to the useful life of such coolants. The inhibitor and antifreeze components of the coolant chemically break down over

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time into undesirable chemical compounds including sulfates and organic acids such as glycolic, formic and glyoxolic acids. The pH of the engine coolant composition also gradually decreases over time from a pH of approximately 10. In heavy-duty applications, the necessary addition of supplemental coolant additives (SCAs) increases the total dissolved solids (TDS) in the coolant until a saturation threshold is approached, at which point severe engine damage is probable.

Coolant with excessive TDS is associated with premature failure of radiators, water pumps, and other cooling system components. When the pH decreases below approximately 8.3, aluminum, steel, and iron corrode, weaken the components that they comprise, and result in eventual component failure. Copper and brass also corrode upon extended exposure to worn engine coolant. The lead alloy in radiators can degrade into lead oxide, allowing leaks to develop in the coolant system. Coolants, therefore, need replacement over time.

Motivation

The *Federal Register* of May 1994 stated that over 400 000 000 gal (151 416 000 L) of used engine coolant are disposed of each year. This used coolant is highly toxic, and has been identified in the deaths of pets and wildlife in many areas. The coolant poses a threat to humans as well. Disposing of it is also a waste of nonrenewable resource. A great deal of this volume could be recycled, recovering the resource and keeping the waste out of the environment.

In 1990, one of the authors elected to begin recycling used engine coolant in response to demand for such service in Central Texas. Initially, he purchased an early system that advertised recycling using ''chemically assisted filtration.'' The concept of the early system was that aeration and pH adjustment of coolant would precipitate contaminants, and the addition of chemical additives would restore adequate functionality to permit extended use of the coolant. While commercially successful, the author began to be concerned that the process may not be completely adequate. Customers expressed concerns regarding the appearance of the coolant, and debate in industry forums highlighted shortcomings of the filtration process.

After considering several alternatives, he purchased the reverse osmosis (R/O) process. This process was developed by Stanadyne Automotive Products [*1*] in 1989. The R/O process provided an intermediate fluid that was pure and offered a production rate that was fairly cost-effective, compared to distillation. The osmosis phenomenon is observed in nature as a distribution or equalization behavior of naturally occurring chemicals. It has been described in detail in the literature [2]. As the author worked with the Stanadyne process, he encountered unforeseen problems.

Regrettably, these problems, and market direction, motivated Stanadyne to withdraw from the market in 1995. Consequently, without the manufacturers' continuing support, all of the test experience and laboratory reports were in jeopardy of becoming invalid or unusable due to confidentiality agreements. Nevertheless, the author felt that the technology was too good to abandon, so he reengineered the R/O process on his own. In the course of reinventing the process, he addressed the shortcomings of the straightforward R/O system in recycling used engine coolant. In particular, he overcame an annoying problem caused when oil or similar petroleum products enter the R/O. Such chemicals coat the membranes, ''blinding'' them, and reducing production to a trickle. Further, discussions with OEM engineers suggested that the purity of recycled coolant would have to improve even further in order to permit reinhibition of the intermediate fluid either with traditional, inorganic technologies, or European-style carboxylate inhibitors. This would require that conventional inhibitor anions be reduced to trivial levels in the processed permeate. The challenge presented was to achieve this high degree of purity at an advantageous cost compared to virgin coolant.

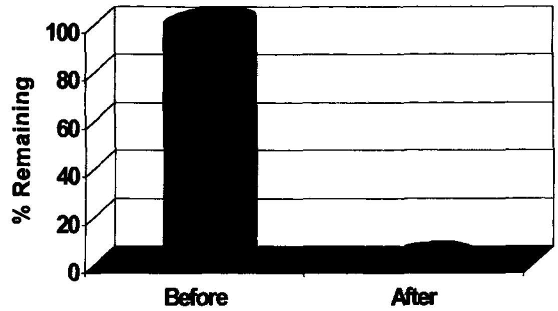

FIG. 1—*Petroleum removed by DAF.*

Providing for Oil Removal

The primary problem with the R/O unit proved to be presented by emulsified oil contamination in the used coolant. Emulsified oils are suspensions of microscopic oil droplets in the used coolant created in the process of removing, storing, transferring or disposing of the used coolant. The oil is usually a used engine (mineral) oil, but sometimes additives consisting of mineral oil combined with a petroleum sulfonate and/or amine soaps that facilitate emulsification are present. This oil coats the R/O membrane, fouling it. When fouling occurs, production rates are drastically reduced. If ignored, the membranes could become completely coated or "blinded," requiring frequent backflushing or some other regeneration procedure. Therefore, once this fouling is suspected, the system must be shut down, a soap solution mixed, and the membrane cleaned of the emulsified oil contaminates. This is a labor-intensive and onerous procedure. A pretreatment was needed to eliminate this emulsified oil problem.

Tests were run on various methods such as chemical flocculates, clarification treatments, and dissolved air flotation (DAF). A pretreatment sequence was developed that provides for the introduction of the used coolant into a large feed tank with a capacity of approximately 20 000 L (5283 gal). Some contaminates are gravity separated and removed as sludge. The remaining used coolant is filtered through commercial water filters rated at 50 and 10 μm, and next passed through dissolved air flotation, a process that efficiently removes petroleum contaminants (Fig. 1). A series of laboratory tests was conducted with representative feed samples to determine if traces of oil remained. Test results were conclusive that there was less than 2% of the original oil concentration remaining. To purge the remaining oils and particulates, a hydrocyclone separator was introduced. Tests of the coolant showed that no trace of oil was detectable in the R/O feed stream as it exited the hydrocyclone. The benefit of using the DAF/hydrocyclone pretreatment was to greatly extend the cleaning interval from once every two to five days to once per year. The resulting improvement in productivity was extremely encouraging.

Reengineering the R/O System

The next refinement involved reengineering the R/O architecture. An R/O unit was set up for initial testing. In the R/O process, a feed stream of used coolant is pumped through a membrane unit (Fig. 2). The pretreated feed stream consists of the ethylene glycol, water, and dissolved solids including molybdate, borate, nitrates, nitrites, phosphate, sulfate, metal ions, carboxylates, and chloride. In addition, some dissolved low molecular weight materials pass into the membrane under applied hydrostatic pressure. The input stream is a solution, having been treated to remove suspended matter.

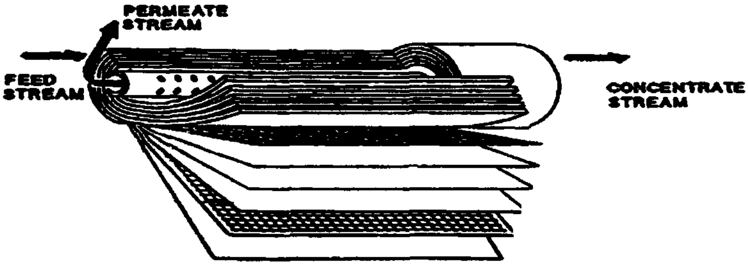

FIG. 2—*Diagram of a membrane unit.*

In choosing a membrane (and there is a great variety), the pore structure should provide for complete removal of contaminants. The selection of the porosity determines the degree of purification. Another important design criterion is the membrane capacity. This capacity is determined by multiplying the surface area by the "flux," defined as the volume of water permeated per unit membrane area per unit time. The standard units are GPD/ft^2 (m^3/m^2/day). Since capital cost and operating cost increase proportionally with membrane area, it is highly desirable to maximize membrane flux. The flux does not necessarily predict the volume of non-water permeate produced per unit area per unit time. Experimentation must be performed to measure actual production for a given type of fluid. Purity and flux are inversely proportional. To develop the commercial system, actual production rates were measured. These rates were then compared with flux values to develop a predictive conversion factor. The conversion factor was used to select the size of membranes required to achieve production goals.

The viscosity of the input varies with the type and ratio of glycol to water in the input stream. Viscosity also increases as temperature decreases. Tests were conducted to determine the influence of several process variables on permeate rate of flow: feed circulation rate, feed pH, operating temperature, operating pressures, the degree of feed concentration and time. The data show that productivity increases with temperature. Therefore, it is desirable to maintain a temperature as high as possible, but at which the membranes can operate without either short-term failure or long-term degradation. Flux was inversely proportional to glycol concentration. It was also inversely proportional to ion concentration. Other variables did not demonstrate significant influence upon flux.

Samples were pulled at regular intervals and chemically analyzed at independent laboratories. These analyses were used to determine membrane rejection efficiency on the feed concentrate contaminants. Flux versus time was recorded. Overall performance of the system was evaluated in terms of system productivity, permeate quality and operating cost.

The data show that this process recovers 96% of the ethylene glycol and water in the used coolant, leaving 4% of the input volume as waste to be disposed of either by incineration or contract hauling. It may be possible to further reduce the waste volume by recovering even more of the glycol and water through local vacuum distillation of the concentrate. About 90% of the concentrated waste consists of glycol and water.

In this system, the inventor implemented a two-stage membrane treatment strategy. Since product purity was the highest priority, a low-flux, small porosity membrane had to be used. The problem with this type of membrane was that it presented a severe bottleneck to system flow when used to directly process the pretreated used coolant. Using the data from the experimentation with various membranes, an investment was made to install two membrane systems in series. The first stage employed nano-filtration membranes, somewhat more porous than true reverse osmosis membranes, but along the same line of technology. The use of the two-stage membrane process presented a nanofiltered fluid to the R/O system that was dramatically lower

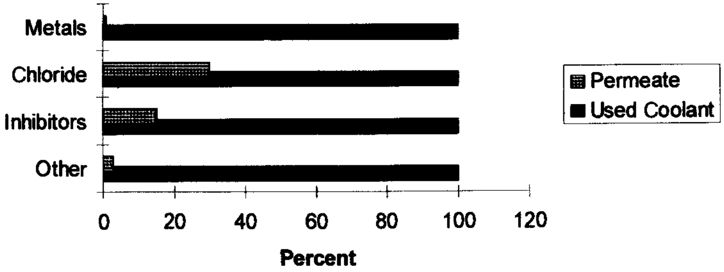

FIG. 3—*Percent of contaminants remaining in coolant after permeating through the R/O membrane.*

in solids content. This is the benefit of processing the coolant by nanofiltration to remove a majority of contaminants, and permitted optimum productivity of permeate through the R/O membranes. The permeate from the R/O unit is sufficiently pure (Fig. 3) to allow it to be reused in most engine coolant applications. In fact, it has been used very successfully and its performance reported heretofore [*3*]. This permeate varies in percentage of ethylene glycol depending on the percentage of EG in the input stream. However, to insure acceptability to all engine OEMs, a post-R/O polishing process has been developed. When this step is accomplished, an inhibitor package is added to complete the process of formulating coolant. This formulated coolant will meet ASTM D 6210 and TMC RP-329 specifications (Table 1).

Additional tests were conducted by the U.S. Army and the coolant was found to meet all their requirements. This R/O unit is one of the few processes that have been approved to recycle antifreeze for the U.S. Army. Detroit Diesel Corp. has also approved of the R/O process [*4*].

At recent ASTM and other industry meetings, the use of carboxylate inhibited coolant has been discussed. Since some newer cars and trucks are using this very different inhibitor package, it has become desirable to further purify the R/O permeate to reduce chloride and borate to less than 10 ppm. Such an extremely pure coolant will permit the option of inhibition with carboxylic acid type inhibitors of the type presently used in GM vehicles.

The authors were aware that dual-bed deionization was a candidate [*5*] to achieve the level of purity desired. Experimentation proved that the cost of purifying the R/O stream by deionization would be prohibitive. Turning to other wastewater purification systems, another candidate technology was identified: continuous electrolytic dialysis (CDI). The dialysis system removed ions remaining in the R/O permeate to a level of about 100 ppm, total. A final ion-exchange polish was not cost-effective on the CDI-processed coolant. After CDI and deionization, the purity of the final coolant is nearly perfect (Table 2).

A Review of the Process Stages

Waste coolant is typically a dark-green to brown, light-chocolate-milk-looking fluid. It contains oil, grease, glycols, glycol oxidation products, metals and metal oxides, and a mix of worn inhibitors. The objective is to recover the reusable water and glycols, with maximum efficiency, while removing all of the other chemistry. Please refer to Fig. 4 for a schematic of the system, and to Table 2 for sequential purification data.

Settling

The coolant as collected at the waste generation facility is often contaminated with external environmental matter. In spite of efforts to maintain the coolant separate from other waste, it

TABLE 1—*ASTM and TMC specifications.*

Property		ASTM/TMC Specification	Virgin Prediluted Coolant Data	Recycled Prediluted Coolant Data
Color		distinctive	green	green
Effect on nonmetals		no adverse effect	no adverse effect	no adverse effect
Specific gravity @ 15.5°C		1.110 to 1.145 EG 1.030 to 1.065 PG	1.040	1.040
Freeze point, °C		50 vol. % in water: −37 max EG, −32.2 max PG	−37	−37
Boiling point, (C)		163 min EG 151.7 min PG	152	152
Effect on automotive finish		no effect	no effect	no effect
Ash content, mass %		5.00% max	0.5%	0.5%
pH: 50 vol. % in distilled water:		7.5 to 11.0	10.4	10.4
Chloride, ppm		25.0 max	21	10
Water, mass %		5 max	50	50
Reserve alkalinity, mL		report	7.0	7.5
Corrosion in Glassware	D 1384			
copper		10 max	1	1
solder		30 max	8	7
brass		10 max	1	0
steel		10 max	0	0
cast iron		10 max	0	0
aluminum		30 max	0	0
Simulated Service	D 2570			
copper		20 max	3	1
solder		60 max	15	10
brass		20 max	3	0
steel		20 max	1	1
cast iron		20 max	1	1
aluminum		60 max	3	2
Corrosion of cast aluminum	D 4340	1.00 max	0.06	0.1
Foaming				
volume, mL	D 1881	150 max/5 max	45 mL	50 mL
break time, s			2.7 s	3.0 s

is commonly contaminated with dirt, oil, grease, nuts, fuel, bolts, and other shop artifacts. The coolant is heated and allowed to settle before being drawn from the holding tank to the processing plant.

Simple Filtration

The primary filtration provides separation of the gross contaminants. The chemistry of the coolant is unchanged after filtration. A bank of step-down filters strains the coolant of particulates with the final filters having approximately 20 μm ratings.

Dissolved Air Flotation (DAF)

The DAF system is a most interesting process that slowly floats petroleum contaminates to the top of the processing coolant, where the foamy oil layer is physically removed. The pro-

TABLE 2—*Progress of a batch of used coolant through the process stages.*

	Settle	Filter	DAF	Spin	Nano	R/O	CDI	DI	Mix
Lead	21	21	7	6	4	0	0	0	0
Copper	8	9	6	6	2	0	0	0	0
Iron	3	4	2	2	0	0	0	0	0
Alum.	33	30	21	19	10	0	0	0	0
Phos. (P)	1757	1769	1752	1650	925	39	4	0	0
Silicon	606	615	512	489	118	12	2	0	113
Boron	684	678	691	680	593	312	298	0	159
MbO$_4$	381	399	391	378	129	19	2	0	0
Chloride	45	51	49	50	40	18	6	1	12
Sulfate	218	224	221	230	147	39	12	0	...
RA	15.2	15.0	14.5	14.3	8.1	4.1	3.0	1.9	5.7
pH	10.3	10.0	9.1	9.0	8.9	8.4	8.3	8.1	10.4
FP°C	−20	−20	−21	−20	−18	−15	−15	−14	−34
Cond.[a]	3620	3590	3521	3412	2742	2694	1592	782	1218
NO$_2$	2838	2840	2812	2800	1298	657	152	0	1412
NO$_3$	347	369	327	356	156	102	60	0	389
Color	brown	brown	brown	green	light yellow	none	none	none	green
Clarity	cloudy	cloudy	foggy	foggy	clear	clear	clear	clear	clear
Odor	solv.	solv.	solv.	solv.	glycol	glycol	glycol	glycol	TT/EG

[a] Conductivity, in umhos, of a solution comprised of 10 mL sample and 90 mL distilled water.

cessed coolant is visibly greener and cleaner, but still contains visible traces of petroleum products. Interestingly, the DAF also helps control the heavy metals content of the input stream. While it does not remove all of the dissolved metals, the process does appear to reduce them, perhaps by oxidation. Analysis of the collected sludge does not reveal any leachable metals, further suggesting that they have been removed as oxides.

Centrifugation

The coolant from the DAF is centrifuged to remove the remaining petroleum contaminants. The centrifuged coolant has a green appearance, but is foggy.

The preliminary treatments prevent premature blinding of the membranes in the nanofiltration or reverse osmosis machines or both.

Nano-filtration

To optimize production by reducing viscosity, the coolant is preheated to about 100°F (38°C). The nanofiltration and reverse osmosis units are similar in appearance and function. The nanofiltration machine differs from its R/O sister in that it operates at a slightly lower pressure and has a larger porosity set of membranes, giving it a more generous flux or rate of production. This system recovers about 90% of the fluid introduced; the remaining 10% is returned to the primary holding tank. The nanofiltrate is light yellow to pale green in color. Most of the metals, such as iron, aluminum, lead, and copper, have been removed. The EG concentration has been weakened about 1 or 2% compared to the input stream. The concentrate that has been returned to the holding tank is about 15% higher in EG content than the input stream.

High-Pressure Reverse Osmosis (R/O)

The concept of using R/O is well documented. It serves this process as the workhorse technology, because it addresses the difficult-to-remove contaminates that are of concern in used

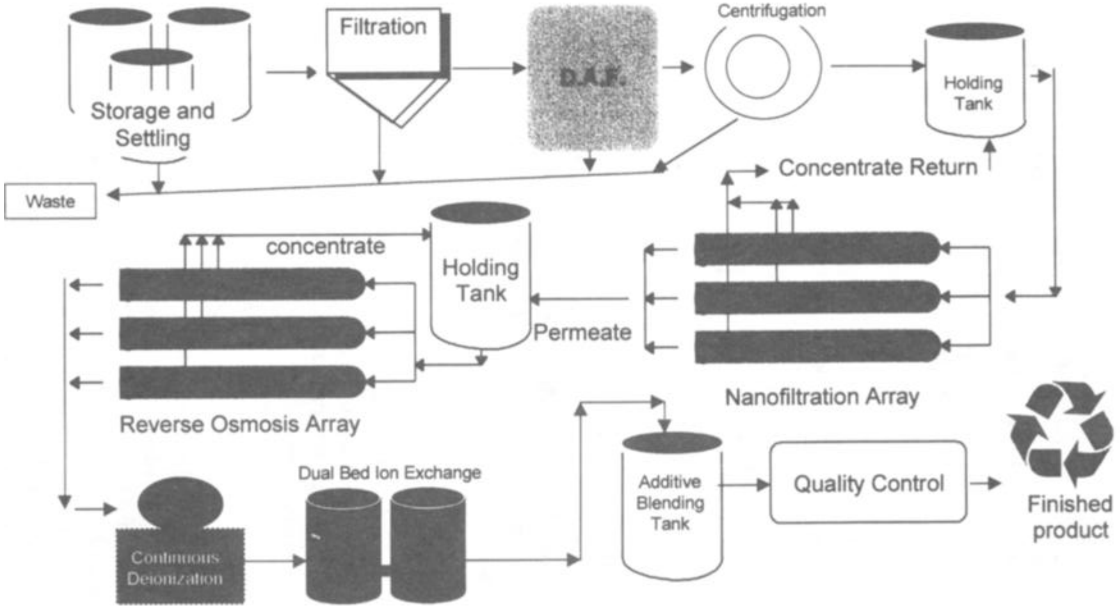

FIG. 4—*Multiplestage high-volume stationary coolant recycling plant.*

coolant. The particular R/O membranes used in this process are selected because they produce the following stripping efficiencies:

Dissolved metals:	over 99% removed
Formate/glycolate	approximately 75% removed
Phosphate, silicate, molybdate	over 90% removed
Sulfate	over 50% removed
Nitrite, nitrate, borate	about 70% removed
Chloride	varies with the chemistry of the coolant, 40 to 70% removed

At this point, the coolant is clear, colorless, and has lost about 4% of its EG content to the membrane selection processing. Coolant permeate of this type has previously been reinhibited and operated with great success. It is approved for use in warranted vehicles by multiple vehicle or engine OEMs or both.

Continuous Electrolysis Deionization (CDI)

To take the coolant to even more pure levels has been motivated by the State of California's limit on chloride content in recycled coolant and other industry discussions. Sometimes R/O processed coolant can meet "new" coolant property specifications (that is, 25 ppm chloride), but other times a badly contaminated coolant will require several time-consuming and expensive passes to purify the coolant to that low concentration. The CDI unit has been identified as a much more efficient method of removing the low-level monovalent ions such as chloride and nitrite that escape the R/O. In addition, boron manages to find its way through the R/O process, which is not a problem for coolant destined for reinhibition with boron-buffered inhibitor packages, but conflicts with carboxylate inhibitor chemistries. The CDI removes over 90% of these ions. After passing through the CDI, coolant is crystal-clear and colorless. It now contains less than 150 to 200 ppm total dissolved solids.

Dual-Bed Deionization (DI)

To insure consistent low-chloride and low-boron finished products that will satisfy the desires of GM and other engine OEMs, the proven dual-bed deionization process is used as the final purification step. Coolant passed over the anion and cation exchange resins exits with less than 10 ppm TDS. The DI process could be applied to the raw coolant as received by the plant with excellent technical results, but the ion beds would be exhausted at such a rapid rate as to drive the cost of recycled coolant to several times the cost of new. As a final polishing step, however, it contributes only pennies per gallon to the processing cost.

Reinhibition Process

The purified coolant is pumped into a stainless steel mixing vessel where the pure glycol (usually EG) and the desired inhibitor package are carefully added and mechanically stirred into the coolant. Mechanical stirring is preferred to prevent dissolving air in the fluid. Dissolved air may contribute to premature aging, undesirable because these coolants are frequently formulated into "extended service" or "Fill-For-Life^{SM}" technologies. Finally, samples are drawn and verified for quality by simple refractometer and titration checks, and the coolant is packaged for shipment.

Conclusions

Major advantages of recycling coolant by multiple-stage technology include:

- High productivity (up to 100 000 L (26 417 gal) per day) with moderate capital equipment, installation, and operating investment requirements. Lower operating cost than single-stage R/O, distillation or ion exchange technologies.
- Exceptional contaminant removal efficiency, offering like-new chemical, physical and performance properties. The system can consistently meet requirements for less than 25 ppm chloride content, and can remove old inhibitors so efficiently as to preclude the possibility of any inhibitor conflict with the reinhibition chemistry.
- The coolant may be reinhibited to meet any type of coolant specification, including traditional automotive, RP-329 diesel/universal, or carboxylic acid ''extended service'' technologies.
- The final product is ''ready-to use,'' ensuring that water hardness and other water contaminants (that is, chlorine) from tap water are not introduced, and preventing the possibility that uninformed end-users might, unintentionally, deviate from recommended glycol/water concentrations.
- No pre-process chemicals are required.
- Concentrated waste that can be further reduced by on-site distillation recovery.

In short, the multistage process is a highly attractive commercial alternative in solving the problem of used coolant disposal.

Summary

The process of recycling used coolant has been perfected. The evolution of a high-volume stationary plant architecture now permits much higher rates of production. The system employs the knowledge acquired over the past ten years to combine technologies to produce a pure, high-quality extract of glycol and water. The extract may be treated to emulate various antifreeze technologies, and has been tested and found to compare favorably with new (virgin) coolant formulated with the same inhibitor technology.

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William Kughn[1] *and Edward R. Eaton*[2]

Development of Mobile, On-Site Engine Coolant Recycling Utilizing Reverse-Osmosis Technology

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REFERENCE: Kughn, W. and Eaton, E. R., "**Development of Mobile, On-Site Engine Coolant Recycling Utilizing Reverse-Osmosis Technology,**" *Engine Coolant Testing, Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 261–269.

ABSTRACT: This paper presents the history of the development of self-contained, mobile, high-volume, engine coolant recycling by reverse osmosis (R/O). It explains the motivations, created by government regulatory agencies, to minimize the liability of waste generators who produce waste engine coolant by providing an engine coolant recycling service at the customer's location. Recycling the used engine coolant at the point of origin minimizes the generators' exposure to documentation requirements, liability, and financial burdens by greatly reducing the volume of used coolant that must be hauled from the generator's property. It describes the inherent difficulties of recycling such a highly contaminated, inconsistent input stream, such as used engine coolant, by reverse osmosis. The paper reports how the difficulties were addressed, and documents the state of the art in mobile R/O technology. Reverse osmosis provides a purified intermediate fluid that is reinhibited for use in automotive cooling systems. The paper offers a review of experiences in various automotive applications, including light-duty, medium-duty and heavy-duty vehicles operating on many types of fuel. The authors conclude that mobile embodiments of R/O coolant recycling technology provide finished coolants that perform equivalently to new coolants as demonstrated by their ability to protect vehicles from freezing, corrosion damage, and other cooling system related problems.

KEYWORDS: reverse osmosis, hazardous waste, engine coolant, antifreeze, recycling

Abbreviations

RP	A Recommended Practice published by TMC
R/O	Reverse Osmosis
SAE	Society of Automotive Engineers
TMC	The Maintenance Council of The American Trucking Association

As the engine coolant recycling market began to emerge, many types of systems were developed to fill the demand created by the combination of environmentally driven legislation and the necessity to dispose of waste engine coolant. These systems included simple filtration, flocculation-assisted filtration, ion exchange, microfiltration, reverse osmosis, and distillation. Some systems were readily adaptable to mobile operations. In considering the alternative technologies, low operating cost and the ability of the process to produce high-quality coolant were evaluated. Mobility requirements restricted or even precluded some technologies (that is, distillation) because of their size or power requirements. Others proved incapable of dealing with inconsistent waste streams. Commercial considerations such as high equipment or operating costs or both differentiated the remaining candidate technologies.

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During the early 1970s, and again in the 1980s, American society faced new problems created by a shortage of ethylene oxide-based products, including ethylene glycol. In addition, concern relative to environmental issues increased. These shortages, combined with new laws concerning hazardous waste, gave birth to coolant recycling. The recycling challenge energized many research efforts that explored various technologies. Almost a half-billion gallons of waste coolant are disposed of every year in the United States.

All these factors led to the development of coolant recycling technologies. There were many companies, including some of America's premier engineering companies, involved. Tremendous dedication of engineering resources were pressed into service to address the challenge. The membership of the ASTM D15 Engine Coolants Subcommittee swelled as scientists and engineers sought each other's assistance and advice.

Engineers had to address the needs to:

1. Recapture the nonrenewable resource.
2. Minimize waste.
3. Provide consistent, high-quality recycled coolant.
4. Provide a commercial service at a price competitive with virgin coolant.
5. Return a fair profit on the business investment.
6. Protect public safety.
7. Limit liability.

Minimizing waste by processing it at the location where it is generated limited both the liability and risk to public safety. Transporting hazardous wastes over public roadways places the generator at financial risk and exposes the public to the possibility of a release of hazardous material while transporting. Until the waste reaches the ultimate destination and is properly and permanently decomposed, the waste presents a continuing liability exposure to the generator due to ''cradle to grave'' legislation.

Various types of filtration systems were explored. Filtration proved incapable of removing chemistry and total dissolved solids to a satisfactory level. Flocculation was explored as an adjunct to filtration. This, too, was very limited as to the ability to remove the existing chemical contaminants and inhibitor technology.

Distillation was immediately recognized as far too power-intensive to integrate into a mobile embodiment. Ion exchange, while compact, energy efficient and highly productive, operated at a cost that was a multiple of two or three times that of virgin coolant!

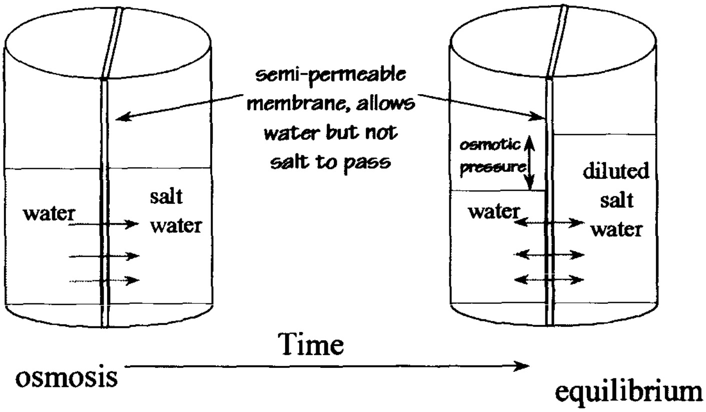

FIG. 1—*Concept of natural osmosis.*

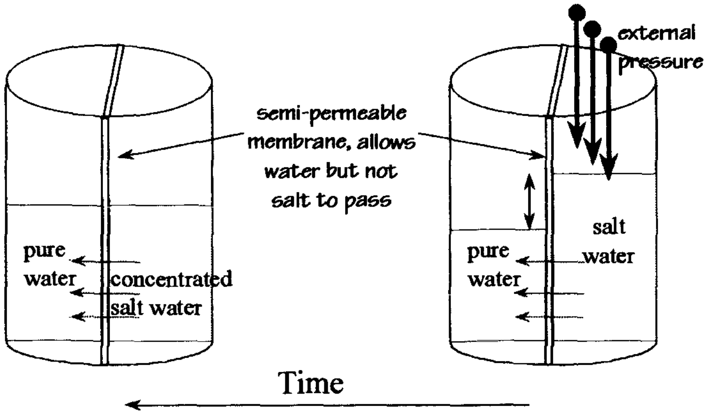

FIG. 2—*Concept of reverse osmosis.*

History

Prior to 1992, R/O as an engine coolant recycling technology struggled to attain recognition. Although R/O is a very selective purification process, the technology was in its infancy and had yet to gain acceptance in the industry. It would take the next four years for the R/O systems to grow in acceptance and become a preferred means of engine coolant recycling. In 1991, Stanadyne Automotive Corporation established a few beta operations with on-site equipment to test prototype systems in actual commercial conditions. One was established on the West Coast in Sacramento, California. Another was established in New York, and a third in Austin, Texas. Other sites and manufacturers participated in the R/O technology in the early 1990s. All of the beta sites grew into commercial operations and continue to apply the technology to coolant recycling today. Stanadyne manufactured and marketed smaller, stationary units targeted for use by individual shops who wished to do coolant recycling on their own. A number of these systems were sold and continue in service today, but the system was not sufficiently successful to justify continued attention at Stanadyne. Stanadyne withdrew from the marketplace in 1994, before commercializing the larger system.

In the past two years, the volume of coolant recycled by R/O has grown exponentially. The focus of R/O recyclers includes both the automotive market and the larger fleet market, with its higher volumes of waste. In a proactive move to maintain positive public experience and attitude towards R/O coolant recycling, the R/O recyclers have established an industry association called the "Reverse Osmosis Coolant Recyclers Association" (ROCRA). ROCRA is organized to insure the uniform high quality of coolant produced by R/O as the technology expands. It is in the process of establishing minimum quality standards and voluntary monitoring practices to provide for the protection of R/O coolant users.

Reverse Osmosis Systems

Reverse osmosis and other so-called "stripping" technologies differ from filtration in that R/O is able to remove emulsified oils, dissolved solids and old inhibitor chemistry. It is a purification process that works at the molecular level, allowing only certain types of molecules to pass through a membrane. This passing of molecules is called "permeation."

Membranes are selected that allow only some types of molecules to permeate, so the membranes are called "semi-permeable" membranes. In an engine coolant recycling system, water, ethylene glycol and propylene glycol are allowed to pass through or *permeate* (verb), the membrane. The fluid that is collected is called "permeate" (noun). Mineral scaling in engines can be reduced because hard water contaminants are rejected (they do not permeate) by the membrane and are not returned to the engine in the recycled coolant. Of course, all the "other stuff" that does not permeate is concentrated into a small volume of fluid. This fluid is referred to as "concentrate," and is either disposed of or further reduced by distillation recovery of the glycol and water in the concentrate. Relatively few companies manufacture R/O equipment. Even fewer of these manufacturers have operated the systems in actual commercial environments. The companies who have been involved in research and development of the coolant recycling systems have become acutely aware of the complexity and idiosyncrasies of R/O. Reverse osmosis is sensitive to some waste stream contaminants and requires careful attention to maintain system productivity. The drawbacks of R/O, however, are outweighed by the purification capability available from the technology. Only distillation and ion exchange have been demonstrated to be able to duplicate the crystal clarity of R/O permeate. This reclaimed permeate provides the purified base from which the recycler can reformulate high-quality engine coolant. Even early R/O systems were able to produce pure permeate, but at such a slow rate (1 to 2 L/h) as to make them impracticable.

Maintenance issues involving the frequent cleaning of the membranes that became plugged (fouled) with input stream contaminants frustrated pioneer operators and fabricators. It was sometimes necessary to interrupt the processing of a batch of coolant at a customer's location to perform a cleaning procedure. These procedures are time-consuming, generate waste water, employ expensive detergents, and dramatically reduce the productivity of the system by reducing its "uptime" percentage. It was feared that inconsistencies in the waste stream created insurmountable problems. Fortunately, perseverance and experimentation with pre-treatment and pre-filtration eventually provided adequate control of the problem contaminants, preventing the premature system maintenance aggravation. Scheduled cleaning and flushing of the equipment serves to maintain the system productivity for extended periods and prevents contaminant impingement on the elements. If systems are maintained on a regular basis, they will continue to provide a high level of efficiency and extended life of R/O elements.

Objective of Reverse Osmosis (R/O) Technology

The R/O product had to demonstrate to end-users that it could meet the performance requirements of both automotive and heavy-duty engines. In order to insure and maintain high quality, the process must be capable of satisfactorily removing contaminants and old inhibition chemistry. One of the first reports of success was the adaptation of water desalination tech-

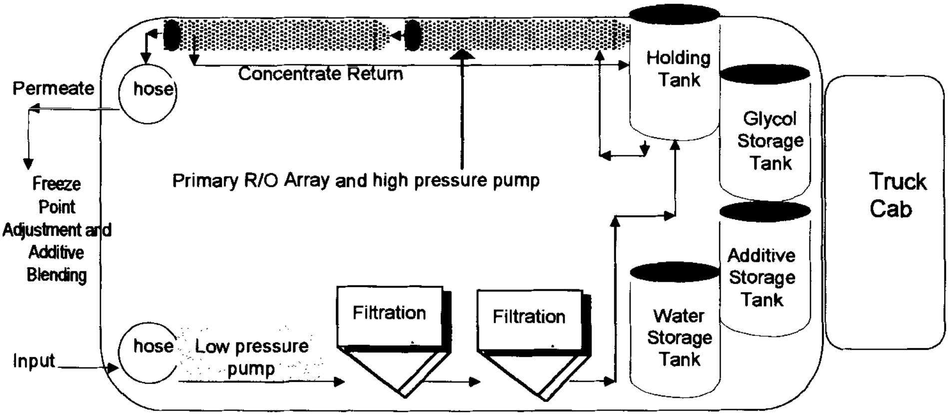

FIG. 3—*Diagram of single stage reverse osmosis mobile plant.*

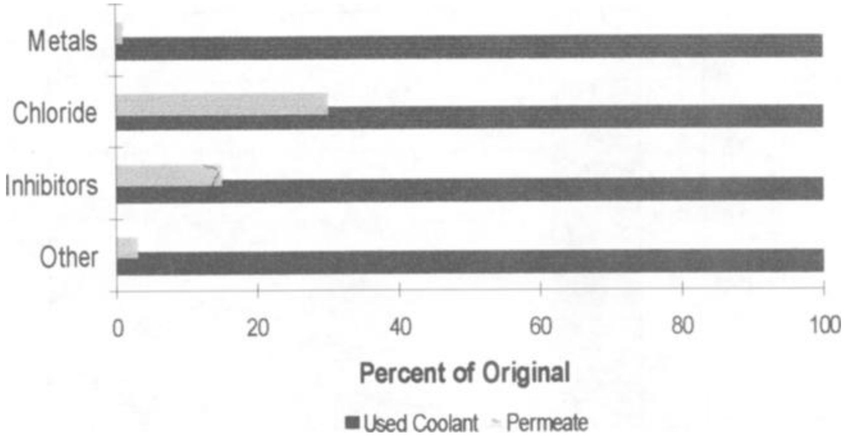

FIG. 4—*Percent of contaminants remaining after processing.*

nology by Stanadyne Automotive Corp. [*1*]. The Stanadyne technical paper reports the ability of reverse osmosis (R/O) to successfully recover ethylene glycol (EG) and water mixtures in a purified state. The recovered solution (permeate) could be reinhibited as an engine coolant. Testing demonstrated that the permeate, properly reinhibited, would meet accepted industry coolant standards [*2*]. These include ASTM and The Maintenance Council (TMC) performance requirements. The permeate could be prepared either for automotive or heavy-duty/universal application, depending on the inhibitor used.

Market Acceptance

The industry has accepted and recognized R/O technology. Technical papers have been written and businesses utilizing R/O have grown exponentially. Extensive testing (see the Appendix) has demonstrated the comparable performance between virgin and R/O recycled coolant. The ability of reverse osmosis to demineralize the solutions is an added benefit of recycling. In many applications it has been difficult to determine the difference between virgin coolant and R/O recycled coolant, except that the virgin coolant mixed with typical tap water will sometimes show the traces of minerals, contaminants and chemicals typically found in municipal water supplies. This has greatly aided the R/O recycler in gaining credibility in the market. Some large fleet operators, OEMs and municipalities have not only recognized the R/O technology but place R/O on par with distillation and ion exchange as methods preferred over filtration coolant recycling. Reverse osmosis has become the most practicable means for on-site mobile volume recycling. In 1996, with the aid of selected R/O recyclers and extensive client cooperation, an SAE paper was written reporting extensive fleet data to validate the efficacy of R/O recycling [*3*]. This study encompassed several fleet operations including municipal, student transportation and extended duty police applications. A wide variety of records for various types of applications were scrutinized. The data exhibited sound validation of the ability of R/O recyclers to recycle for large mixed vehicle fleets. Few cooling system-related problems were noticed. In fact, some problems disappeared when the fleet changed to recycled coolant!

Summary

Extensive evolution of the mobile R/O concept for recycling of used engine coolant has occurred. Early embodiments of mobile systems that generated about two liters of permeate

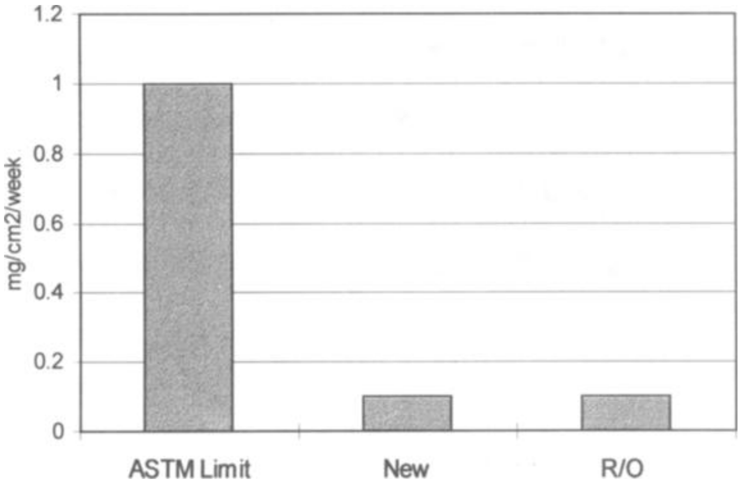

FIG. 5—*ASTM D 4340 results. Corrosion of aluminum heat-rejecting surfaces.*

per hour have been reengineered. The new systems now generate nearly 100 times that volume. The permeate—a clear, colorless solution of ethylene glycol and water—contains only small amounts of contaminants [*4*]. These contaminants are frequently residual inhibitors that further enhance the desirability and performance of the finished coolant. Several reinhibition chemistries are applicable to the permeate. The most common is a technology that prepares the fluid to comply with TMC RP-329 specifications. This is attractive because the TMC RP-329 requires that the coolant be compatible with conventional factory-fills, and meet both automotive and heavy-duty performance requirements. The permeate may alternatively be reinhibited to mimic phosphated American factory-fills of years past (that is, *Prestone II*) or newer carboxylic-acid type products (that is, *Peak Extended Life*). The performance of the finished coolant has been previously investigated and reported to be most satisfactory. The R/O technology has achieved the objectives of providing a universally applicable coolant, comparable to new coolant, at a reasonable cost. Reverse osmosis can be provided in a mobile embodiment, offering minimum waste liability exposure and maximum convenience for the generator.

Conclusions

1. Reverse osmosis is an acceptable means to recycle waste coolant while maintaining high coolant performance standards meeting industry requirements for both light and heavy-duty engines.
2. Reverse osmosis recyclers have solved problems related to the ability of the process to provide a consistent industry-accepted product to the user.
3. Reverse osmosis is accepted as a viable means to reduce the risk to public safety by reduction of ''over the road'' hauling of antifreeze hazardous waste.
4. Reverse osmosis coolant properties are essentially the same as those of virgin coolants.

Acknowledgments

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The authors wish to thank Richard DeGruccio of Superior Products, Sacramento, California, and Marvin Haddock, Recycled Engine Coolants, Inc. for their assistance.

APPENDIX 1

Standard Coolant Performance Data

Data Table 1: General Properties

Property	ASTM Method	ASTM Specification	New Performance	R/O Performance
Color		Distinctive[A]	Green	Green
Effect on non-metals		No adverse effect	No adverse effect	No adverse effect
Storage Stability		TBD	TBD	TBD

Data Table 2: TMC RP-329 performance

Property	ASTM Test Method	ASTM Specification	New	R/O
Specific Gravity @ 60 F	D-1122	1.0650min	1.07	1.07
Freezing Point (C)	D-1177	-37 max	-37	-37
Boiling Point[A], F (C)	D-1120	108 min	108	108
Effect on Automotive Finish	D-1882	No Effect	No Effect	No Effect
Ash content, mass %	D-1119	2.50% max	0.28%	0.29%
pH: 50 vol % in distilled water:	D-1287	7.5 to 11.0	10.4	10.2
Chloride, PPM	by IC	25.0 max	20.0	21.0
Water, mass %	D-1123	50 max	50	50
Reserve Alkalinity, ml	D-1121	Report[B]	3.5	4.0

Data Table 3: TMC RP-329 and Analysis Data

	TMC Specification	New	R/O
Nitrite (NO_2)	1200	1350	1580
Nitrate(NO_3)	-	441	651
Phosphorus (P)	-	10	50
Silicon (Si)	<125	113	120
Molybdate (MoO_4)	Type A - 0	0	0
Pb	0	0	0
Cu	0	0	0
Fe	0	0	1
Al	0	0	0
Total Hardness	170	9	15

ATA TABLE 4: TMC RP-329 PERFORMANCE

Property	ASTM Test Method	ASTM Specification	New	R/O
Corrosion in Glassware Weight loss, mg/specimen	D 1384			
Copper		10 max	1	1
Solder		30 max	8	7
Brass		10 max	1	1
Steel		10 max	0	1
Cast iron		10 max	0	0
Aluminum		30 max	0	0
Simulated Service Weight loss, mg/specimen	D 2570			
Copper		20 max	3	2
Solder		60 max	15	12
Brass		20 max	3	2
Steel		20 max	1	1
Cast iron		20 max	1	1
Aluminum		60 max	3	4
Corrosion of Cast Aluminum Alloys at Heat Rejecting Surfaces, mg/cm^2/week	D 4340^A	1.00 max	0.06	0.10
Foaming Volume, ml Break time, seconds	D 1881	150 max 5 max	45 2.7	50 3.0
Cavitation Erosion Rating for pitting, cavitation or erosion of the water pump	D 2809	8 min	10	10

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[*1*] Huff, J., ''Using Reverse Osmosis to Recycle Engine Coolant,'' SAE Technical Paper Series 921635, Society of Automotive Engineers, Warrendale, PA.

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[*3*] Eaton, E. R., ''Engine Reliability Experience of Mixed Vehicle Fleets Operating on Engine Coolant Recycled with Reverse Osmosis Technology,'' SAE Technical Paper Series 962239, Society of Automotive Engineers, Warrendale, PA.

[*4*] Carr, R. P. and Eaton, E. R., ''Observations on the Reliability Effects of Operating Heavy Duty Engines with a Nitrite/Borate/Low Silicate Coolant with No Coolant Change Interval,'' SAE Technical Paper Series 960642, Society of Automotive Engineers, Warrendale, PA.

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Heavy-Duty Fleet Test Evaluation of Recycled Engine Coolant

REFEERNCE: Woyciesjes, P. M. and Frost, R. A., "**Heavy-Duty Fleet Test Evaluation of Recycled Engine Coolant,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335,* R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 270–291.

ABSTRACT: A 240 000 mile (386 232 km) fleet test was conducted to evaluate recycled engine coolant against factory fill coolant. The fleet consisted of 12 new Navistar International Model 9600 trucks equipped with Detroit Diesel Series 60 engines. Six of the trucks were drained and filled with the recycled engine coolant that had been recycled by a chemical treatment/filtration/reinhibited process. The other six test trucks contained the factory filled coolant. All the trucks followed the same maintenance practices which included the use of supplemental coolant additives. The trucks were equipped with metal specimen bundles. Metal specimen bundles and coolant samples were periodically removed to monitor the cooling system chemistry. A comparison of the solution chemistry and metal coupon corrosion patterns for the recycled and factory filled coolants is presented and discussed.

KEYWORDS: engine coolant, fleet testing, engine coolant recycling, supplemental coolant additive, SCA, corrosion test data, solution analysis, depletion rate, glycol degradation acids, chloride and sulfate

Over the past several years engine coolant recycling has received a lot of attention in both light duty and heavy duty engine applications. Numerous articles covering various technologies have been published describing the characteristics of used coolants and the efficiency of recycling technologies [*1*–*5*]. The Maintenance Council (TMC) has written a recommended practice as an aid to those considering the use or recycling of engine coolants [*6*]. The ASTM D15 committee on Engine Coolants is also working towards developing standards for recycled engine coolant.

With all of this activity, there still is a limited amount of published fleet performance data on recycled used engine coolants [*5*]. The bulk of the published performance testing has been directed towards laboratory testing. The purpose of this paper is to provide fleet test information on a used engine coolant that has been recycled by a chemical treatment/filtration/reinhibited process and field tested for 240 000 miles (386 232 km) in a fleet of Navistar International Model 9600 trucks.

Background

Currently, TMC recommends draining and replacing the engine coolant in heavy-duty engine applications at least every two years or 250 000 miles (402 325 km) [*6*]. They indicated that coolant used for longer periods, without checking its condition, can result in engine and cooling system damage. The used engine coolant recycled in this test was collected from vehicles

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TABLE 1—*Profile of International Model 9600 trucks used for the fleet test. Initial odometer and glycol concentrations for test trucks.*

Truck Test Number	Initial Odometer Reading, Miles	EG% for Factory Fill Coolant	Truck Test Number	Initial Odometer Reading, Miles	EG% for Factory Fill Coolant
204	27 066	41.9	216	856	45.8
205	39 858	50.4	217	933	45.5
212	813	47.6	218	844	43.8
213	817	44.8	219	803	...
214	822	47.5	220	1235	44.5
215	915	45.6	221	910	43.0

NOTE—1 mile = 1.61 km.

running out of a central truck terminal. The used coolant was collected from vehicles with between 200 000 to 500 000 services miles (321 860 to 804 650 km).

The recycled/reinhibited coolant was evaluated in a fleet of 1992 Navistar International Model 9600 trucks equipped with Detroit Diesel Series 60 engines operating out of a central terminal located in the Northeastern United States. A summary of the trucks' initial odometer readings are given in Table 1.

All routine servicing and maintenance was conducted at this location under the direction of the fleet owner's employees. The fleet was well maintained and follows a preset maintenance schedule. Their coolant practices were to run factory fill coolant for the life of the truck and to drain, save, and reinstall the vehicles' coolant anytime maintenance was required on the cooling system components. The coolant maintenance schedule includes:

- Testing the nitrite level of the coolant every ~12 875 km (8000 miles),
- Adding Supplemental Coolant Additives (SCA) when the nitrite level is low,
- Adding coolant makeup as needed.

The fleet ran on a five day schedule: Monday through late Friday afternoon. They were parked at the central terminal on the weekends. Coolant samples were taken on Sunday when the largest number of vehicles were parked on site overnight. This allowed entrance to the cooling system without the problem of residual pressure and loss of coolant. As a result of this procedure, the samples may not have contained representative amounts of suspended solids since the cooling systems were idle overnight. Initial pretest samples were taken from the deaeration surge tank because the radiators in the Detroit Diesel trucks were not equipped with a radiator cap. The coolant samples were clear, showing no visible sign of suspended material or insoluble precipitate.

This test involved a 12 vehicle fleet. Six of the vehicles were tested on the factory filled coolant. In the other six vehicles, the factory filled coolant was removed and replaced with a 50% solution of recycled/reinhibited engine coolant.

Analytical Techniques

A variety of analytical techniques and procedures were used to characterize the coolant samples (Table 2). Refractive index was used to provide total percent glycol. High performance liquid chromatography (HPLC) was used to identify the organics (that is, glycol degradation products, azoles, etc.) and ion chromatography (IC) was used for inorganic anions. Standard

TABLE 2—*Analytical test methods used in the characterization of the engine coolant and other test samples.*

Analysis Required	Test Method
Total glycols	refractive index
Glycol degradation products TTZ, MBT, BZT	high performance liquid chromatography
Nitrate, nitrite, chloride, sulfate	ion chromatography
pH, reserve alkalinity	ASTM D 1287, ASTM D 1121
Elemental analysis: Al, B, Ca, Cu, Fe, Mg, Mo, Na, P, Pb, Si, Sn, Zn	inductively couple plasma emission spectroscopy
Total dissolved and suspended solids	gravimetric analysis

laboratory techniques were used for pH (ASTM Test Method for pH of Engine Coolants and Antirusts (D 1287)) and reserve alkalinity (ASTM Test Method for Reserve Alkalinity of Engine Coolants and Antirusts (D 1121)).

Inductively coupled plasma emission spectroscopy (ICP) was one of the key methods of analysis. All coolant samples were analyzed by ICP, which measures the concentration of a broad range of elements commonly found in a cooling system and coolant. Recognizing the importance and sensitivity of this method, special care was taken to avoid errors caused by interferences from this complex matrix or by different coolant sample viscosity (caused by glycol concentration differences between samples and the standards). In addition, all samples were filtered through a 0.07 μm filter before being analyzed.

Total dissolved solids (TDS) and total suspended solids (TSS) were done by gravimetric analysis. The coolant samples were filtered through a 0.07 μm filter. The filtrate was dried to a constant weight in a 180°F (82.2°C) oven to give the TDS. The total suspended solids were measured by drying the filter to a constant weight in a 180°F (82.2°C) oven and measuring the residual weight gain on the filter.

Fleet Testing

Test Vehicles and Test Setup

The Navistar International 9600 COE Tractors were equipped with 677CID (11.1 L) Series 60 Detroit diesel engines. The engine's turbo was equipped with an air-to-air charge cooler mounted in front of the engine brass "high-flow" radiator. Nominal cooling system capacity is 50 qt (47.3 L).

As each truck was prepared for test, the engine coolant was drained as completely as possible to allow installation of the test hardware. Coolant drained averaged 45.3 L or 90% of the total cooling system contents. It is extremely difficult to completely drain a cooling system once it has been filled as a small amount of coolant always gets trapped in the heater core, hose loops, and cavities in the head and block. These vehicles were not equipped with coolant filters.

Special brackets were constructed of ⅛ in. (3.2 mm) thick cold rolled steel to facilitate the mounting of the metal specimen capsules, Fig. 1. The capsules were fabricated with heavy duty 2¼ in. (57 mm) inside diameter hose with the inlet and outlet supplied by ⅜″ in. (9.5 mm) inside diameter reinforced power steering hose. The two capsules were connected in series with an inlet hose which came from a tee at the inlet side of the passenger compartment heater line. The capsule return hose was connected to a fitting on the suction side of the water pump. Thus, flow was maintained through the specimen capsules any time the engine was running. Each of

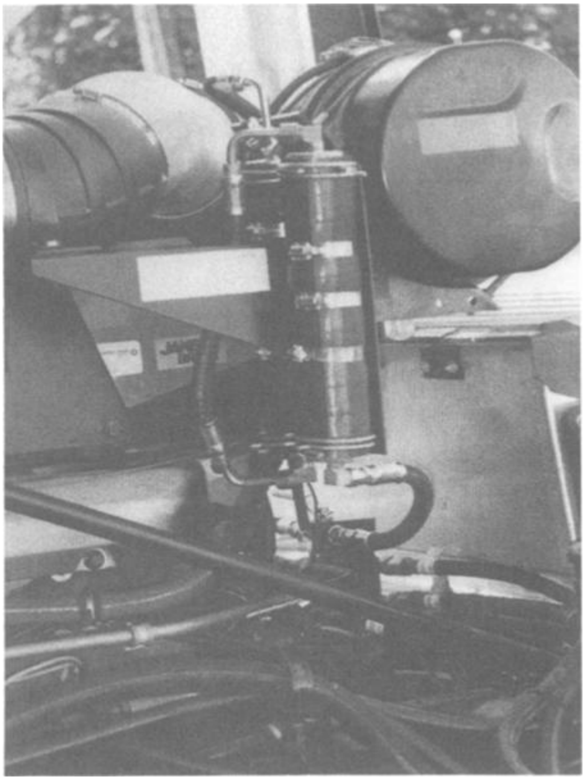

FIG. 1—*Metal specimen by-pass arrangement for Navistar International 9600 COE Tractors equipped with Detroit Diesel Series 60 engine.*

the specimen capsules held five specimen bundles, each bundle containing seven 2 by 1 in. (50.8 by 25.4 mm) metal coupons of the common engine metals (modine solder or 97/3 solder, copper, Sn30a solder, or ASTM solder, brass, steel, cast iron, and cast aluminum) [*7*].

Trucks that were to run on the recycled engine coolant were drained completely, test hardware and specimens were installed and the cooling system was refilled with the recycled coolant. The trucks that ran on OEM coolant received a similar treatment, but were refilled with the coolant that had been drained prior to hardware installation.

Each truck carried a 2½ gal (2.09 L) makeup jug in the driver's compartment behind the cab door for makeup needs if required when the truck was away from the home dispatch area. The trucks were examined every weekend, and during this time the coolant level was checked, makeup added if needed, and hoses tightened if required (a frequent "must" during periods when night time temperatures dipped below +32°F (0°C)).

Coolant samples were taken every 8000 miles (12 875 km). Samples were taken with the engine running following a 10 min idle period through a sample valve affixed to the top of one of the specimen capsules. Specimen bundles were removed at 24 000 mile (38 623 km) intervals. Coolant chemistry was closely monitored throughout the test period and SCA was added whenever nitrite levels dropped to 800 ppm.

Logs were maintained on all cooling system maintenance and makeup requirements. Over the course of the 220 000 mile (354 046 km) test, an average of 3 and 2.4 gal (2.5 and 2.0 L) of makeup coolant was required for the trucks containing factory fill and recycle coolant, respectively.

Test Coolants

Recycled/Reinhibited Engine Coolant

The used engine coolant recycled in this test was collected from vehicles running out of a central terminal with between 200 000 to 500 000 service miles (321 860 to 804 650 km). A total of 150 gal (125.4 L) was collected. An analysis of the composite used coolant is given in Table 3.

The used coolant was recycled/inhibited by a multistage chemical recycling process followed by filtration [5]. An analysis of the recycled coolant prior to reinhibition is given in Table 3. The recycle process removes most dirt, oil, heavy metals, corrosion products, and other insoluble contaminants from the used coolant leaving a base fluid which contains a low level of useful inhibitors. To this recycled engine coolant, a two part commercial reinhibitor package was added to adjust the inhibitors concentrations back to a balanced mixture. At this point, a fully formulated engine coolant is ready for the addition of a supplemental coolant additive (SCA) of choice that meets the performance requirements outlined in ASTM Specification for Low Silicate Ethylene Glycol Base Engine Coolant for Heavy Duty Engines Requiring a Pre-Charge of Supplemented Coolant Additive (SCA) (D 4985). The corrected amount of SCA was added to the recycled/reinhibited product prior to filling the trucks' cooling system. The composition of the SCA used in this test is given in Table 4.

TABLE 3—*Composition of the used engine coolant before and after recycling (before reinhibition).*

Property	Used Engine Coolant	After Recycling/ Before Reinhibition	% Change
% Glycol	47.2	46.8	
pH	8.6	6.9	
RA (ASTM)	8.8	. . .	
Nitrate (NO_3^-), μg/mL	1306	6223	
Nitrite (NO_2^-), μg/mL	856	487	43
Tolyltriazole (TTZ), μg/mL	374	186	50
Elemental analysis (soluble), μg/mL			
Borate (as B)	1048	726	31
Potassium	2639	1404	47
Molybdate (as Mo)	58	48	17
Sodium	3334	2966	11
Silicate (as Si)	92	46	52
Phosphate (as P)	1000	232	77
Corrosion products, μg/mL			
Copper	2	0	100
Iron	3	0	100
Zinc	3	0	100
Glycol degradation acids, μg/mL			
Acetate	216	170	21
Formate	30	0	100
Glycolate	810	870	0
Contaminants, μg/mL			
Chloride	88	79	10
Sulfate	400	388	0

TABLE 4—*Composition of: the factory fill coolant (removed from six trucks and comingled) used for makeup, the commercial heavy-duty coolant used to adjust glycol concentration of factory fill coolant and the SCA.*

Property	Factory Fill Coolant (Comingled Coolant)	Coolant Used to Adjust EG Content	SCA: Maintenance Charge
% Glycol	43.4	95+	
pH	9.5	10	
RA (ASTM)	8.7	17.4	
Nitrate, μg/mL	1094	2198	86
Nitrite, μ/mL	ND	0	231
TTZ, μg/mL	401	802	56
MBT, μg/mL	244	488	143
elemental analysis (soluble), μg/mL			
Boron	703	9730	55
Molybdenum	32	140	0
Silicon	75	150	42
Phosphorus	575	3742	15
Contaminants, μg/mL			
Chloride	29	...	6
Sulfate	23	...	3

Factory Fill Coolant

Analysis of the factory filled coolant is given in Table 4. The engine coolant is a borate/phosphate buffered, low silicate engine coolant containing tolyltriazole, mercaptobenzothiazole, and nitrate as additional inhibitors. A check of the factory fill coolant showed it to contain no nitrite. A precharge level of SCA was added to each truck as recommended by the SCA manufacturer. Next the glycol concentrate of each vehicle was checked. The average glycol percent in the factory filled trucks was only 45.5%, which provides freeze point protection to −20°F (−29°C). It is the practice of this terminal to maintain a glycol percent of ~50% for −34°F (−37°C) freeze point protection. The glycol content of the factory filled trucks was adjusted to 50% using a commercial heavy duty engine coolant, Table 4. The commercial coolant was a borate/phosphate buffer, low silicate formulation similar to the factory fill coolant.

The factory fill coolant removed from the trucks put on test with recycled/reinhibited coolant was saved for use as makeup fluid for the six test trucks containing factory fill coolant. The analysis of the comingled factory fill coolant, to be used as makeup coolant, is given in Table 4.

Coolant Chemistry

The basic coolant chemistries of the two test fluids are very similar. Both the factory fill and recycled coolants utilize a borate/phosphate buffer, have low initial levels of silicate, contain nitrate, TTZ, and MBT, and require an initial charge of SCA. The largest difference is one fluid was prepared with new glycol and the other from recycled used engine coolant. Figures 2 to 5 show the depletion rates of several key inhibitors for the recycled and factory filled engine coolants, respectively.

The average inhibitor depletion rates for the recycled used engine coolant shows the borate (measured as boron), molybdate (measured as molybdenum), phosphate (measured as phosphorus), and nitrate concentrations to be fairly constant over the first 70 000 test miles (112 651

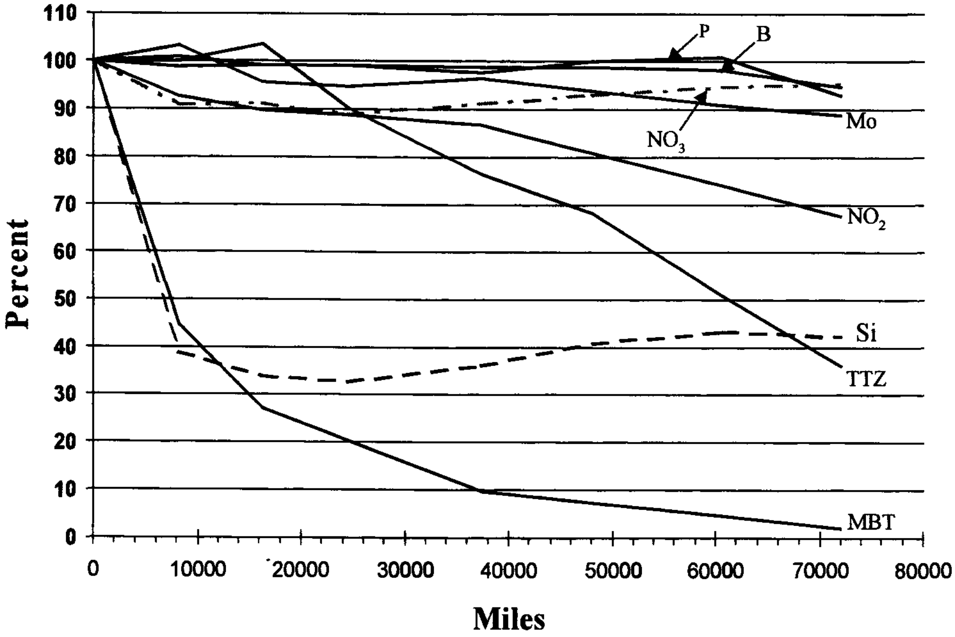

FIG. 2—*The average inhibitor depletion rate of the trucks containing recycled engine coolant.*

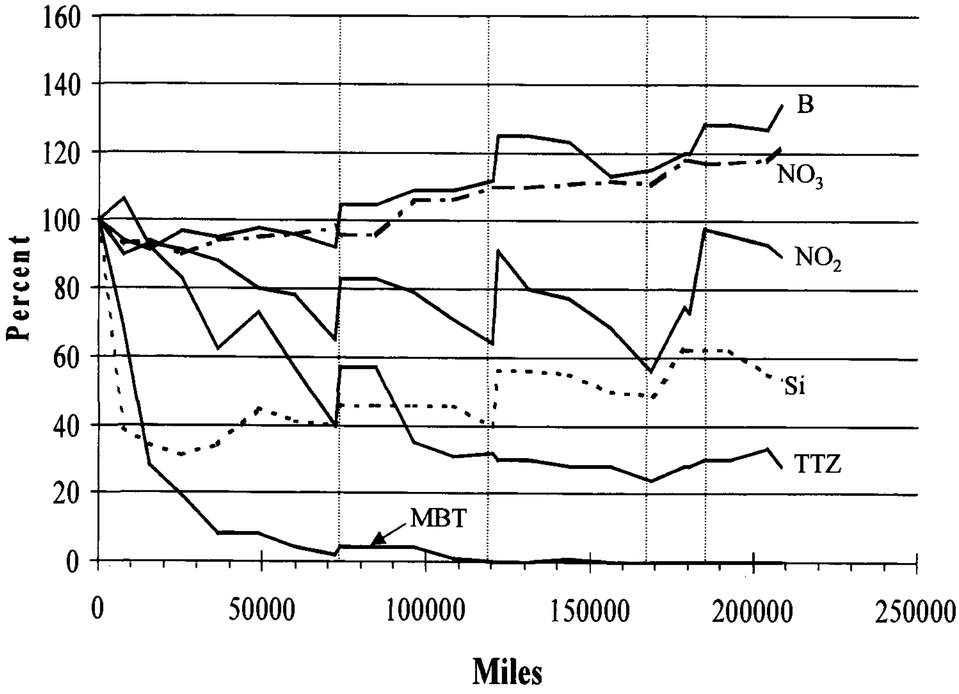

FIG. 3—*The inhibitor depletion rate for recycled coolant in Truck 215. The dashed vertical line indicates mileage where SCA was added.*

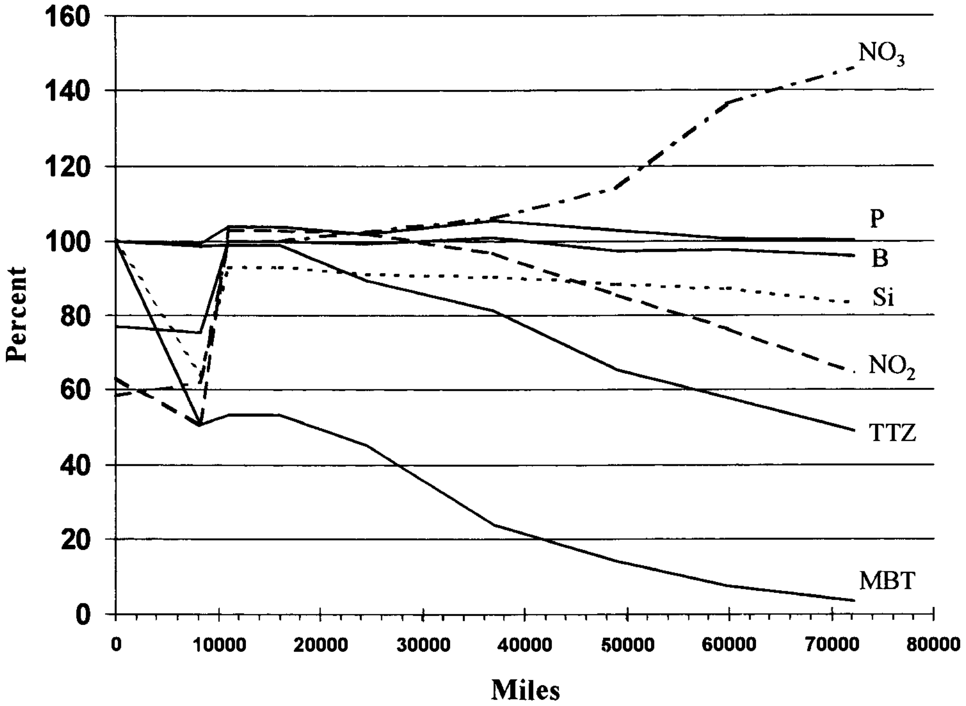

FIG. 4—*The average inhibitor depletion rate for the factory filled trucks. At about 10 000 miles (16 093 km) a supplement of SCA was added.*

km). Figure 3 shows that the levels of borate and nitrate increase with time as a results of the contribution of additional borate and nitrate with each SCA addition.

The silicate level (measured as silicon) in the recycle coolant drops ~60% within the first 10 000 miles (16 093 km) and levels out over the next 60 000 miles (96 558 km). This depletion pattern is consistent with the corrosion protection mechanism for silicate. Silicate is known to quickly set up a protective layer on metal surfaces while maintaining a reserve of soluble silicate in solution to repair any damage that may occur to the protective film over time. As in the case of borate and nitrate, the silicate level increases with each addition of SCA. It is interesting to note that the average soluble silicate level at 200 000 miles (321 860 km) is well above what would typically be seen in light duty vehicle service that use high silicate engine coolants.

The mercaptobenzothiazole (MBT) and tolyltriazole (TTZ) both deplete with time. The MBT depletes rapidly and is only 10% of the initial concentrate after 40 000 miles (64 372 km). The addition of SCA has little affect on the concentration of MBT through the test. At 100 000 miles (64 372 to 160 930 km) there is no detectable level of MBT. Tolyltriazole depletes slower. At 70 000 miles (112 651 km), TTZ is at approximately 40% of its initial concentration. The depletion rate of TTZ is nonlinear and levels out at ~30% between 100 000 to 200 000 miles (160 930 to 321 860 km).

The nitrite level in the recycled coolant depletes at a slower rate than MBT or TTZ. However, the depletion rate is such that periodic supplements are required with time to maintain a safe level of nitrite for protection against cavitation erosion corrosion (CEC) of the wet sleeve liners. The nitrite depletion curve is consistent with earlier report depletion curves.

The depletion curves for the factory filled trucks are complicated by the addition of SCA at

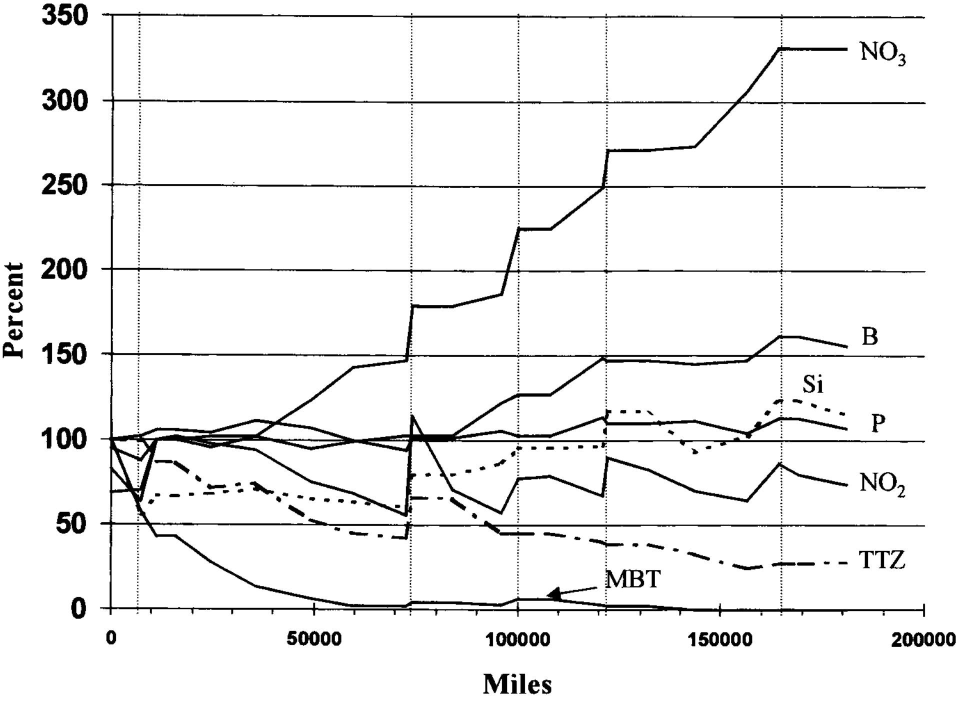

FIG. 5—*The inhibitor depletion rate for the factory filled truck 217. The dashed vertical lines include mileage where SCA was added.*

~10 000 miles (16 093 km) into the test. This supplement of inhibitors caused a jump in the percent inhibitors present in the factory fill coolant. Still it is useful to evaluate the depletion rates of the inhibitors up to the next addition of SCA.

The factory filled engine coolants showed the same average depletion rate patterns for borate (measured as boron) and phosphate (measured as phosphorus) over the first 70 000 miles (112 651 km) as the recycled coolant. The borate and phosphate level remained relatively constant over this period. The nitrate depletion curve appears quite different for the factory fill coolant versus the recycled coolant. In both cases, the nitrate concentration appears to level out at approximately 40 000 miles (64 372 km) and then starts to increase. The increase for the recycled coolant is 5% versus 40% for the factory filled coolant. This looks like a large difference, but the actual increase in parts per million of nitrate are comparable. The difference in percent increase is due to the large difference in the initial concentration of nitrate in the coolants.

In the factory filled trucks the actual initial, 0 miles, silicate level could not be determined because by the time the first sample was pulled from the vehicles the silicate level had already dropped. By 10 000 miles (16 093 km) the silicate would be expected to have reached equilibrium. With the first addition of SCA the silicate level should increase to a new equilibrium and level off as in the case of the recycle coolant. This pattern is seen in Fig. 4. With each subsequent addition of SCA the silicate level slowly begins to increase, Fig. 5. By the end of test, the average silicate level is well above what would typically be seen in a light duty vehicle which uses a high silicate engine coolant.

The mercaptobenzothiazole (MBT) and tolyltriazole (TTZ) depletion curves are very similar to the recycled coolant curves. The MBT depletes rapidly to 20% of the initial concentrate after

40 000 miles (64 372 km) and to 0% by 100 000 miles (160 930 km). The tolyltriazole depletes slower. At 70 000 miles (112 651 km), it is at roughly 50% of its initial concentration and starts to level out at ~30% by 100 000 miles (160 930 km) and remains level for the next 100 000 miles (112 651 km).

The nitrite level in the factory filled coolant showed a similar depletion pattern as the recycled coolant. The depletion rate is such that periodic supplements are required with time to maintain a safe level of nitrite for CEC protection of the wet sleeve liners.

Glycol Degradation Products

It is well known that ethylene glycol will degrade with time in the cooling system. The main degradation products are formic and glycolic acids. It has been demonstrated that the degradation of ethylene glycol is an auto-oxidation process that proceeds independently of the corrosion process. There are many factors that effect this process including pH, temperature, pressure, and metal catalyst. The level of glycol degradation products varies from vehicle to vehicle. These acids react with coolant to consume base and lower the reserve alkalinity of the coolant.

An earlier report [*1*] on used coolant suggests that the concentration of degradation products level out as a function of increased mileage. This conclusion was based on single data points from a large data base of vehicles at various mileage. In this study, the glycol degradation acid concentrations are followed as a function of time/mileage and are not single points in time.

A plot of the glycol degradation acids as a function of mileage for the factory fill and recycled coolants are given in Figs. 6 and 7 along with the best fit for the total acid data. The shape and

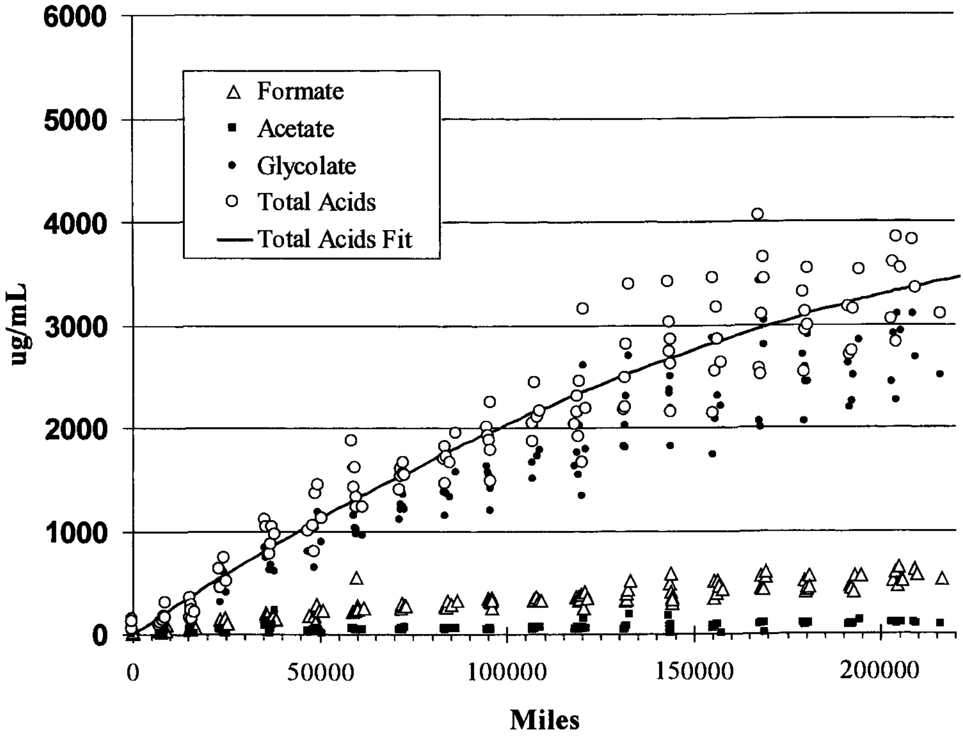

FIG. 6—*Glycol degradation acids as a function of test mileage for the six factory filled trucks.*

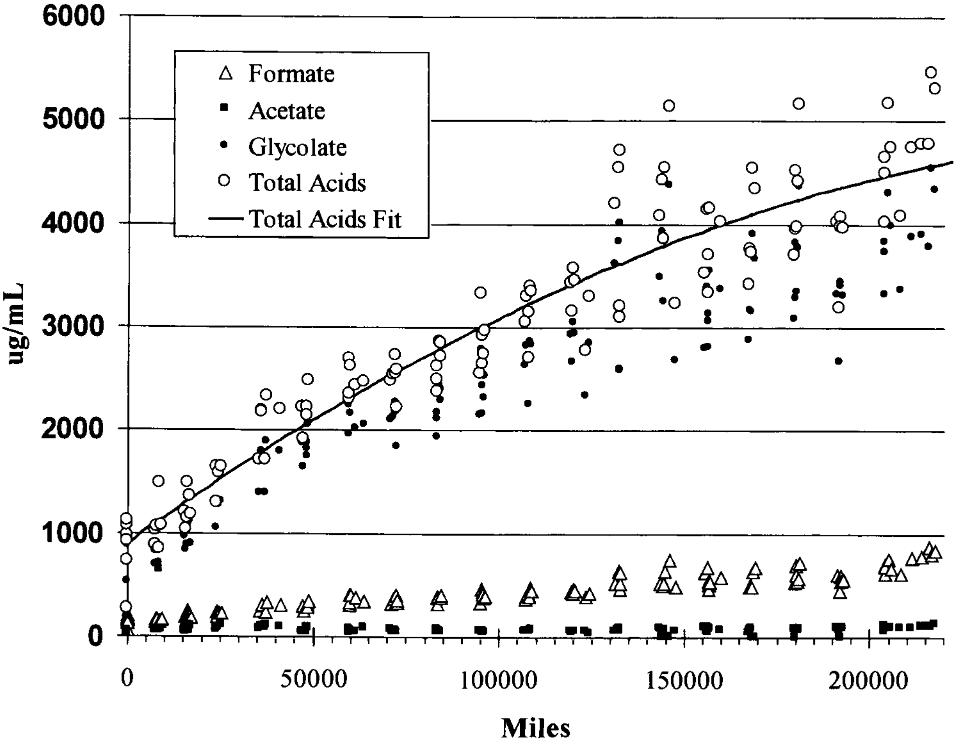

FIG. 7—*Glycol degradation acids as a function of test mileage for the six trucks containing recycled coolant.*

slope of the two curves are very similar. If the initial total degradation acid level is subtracted from the recycled coolant total acid numbers, the two line are superimposable within experimental error, Fig. 8. This suggests that the leveling out of the total acid concentration is not the result of the acids coming to critical equilibrium concentrations. It appears that the rate of glycol degradation acid formation is affected by the initial condition of the cooling system or properties of the coolant. With time/mileage the rate of formation decreases. This decrease most likely corresponds to a gradual change in the condition of the cooling system or the initial coolant properties.

Possible explanations for this gradual decrease in the rate of acid formation include: a change in the cooling system metal surfaces as a function of time as a result of the formation of protective films, or the change in the coolant initial properties, such as pH, as it provides protection to the cooling system. Both the factory fill and recycle coolant initial pH is above 10 and drops with mileage down to pH of 8.

Whatever the cause, the consequence is that with each refill of a new truck with recycled antifreeze the total glycol degradation acid concentration will be increased by the level of residual glycol degradation acids not removed by the recycling process. If the increase is due to the initial condition of the coolant, the total glycol degradation acid concentration would be expected to increase by the standard rate plus the cumulative carry over of acids with every refill of recycle product.

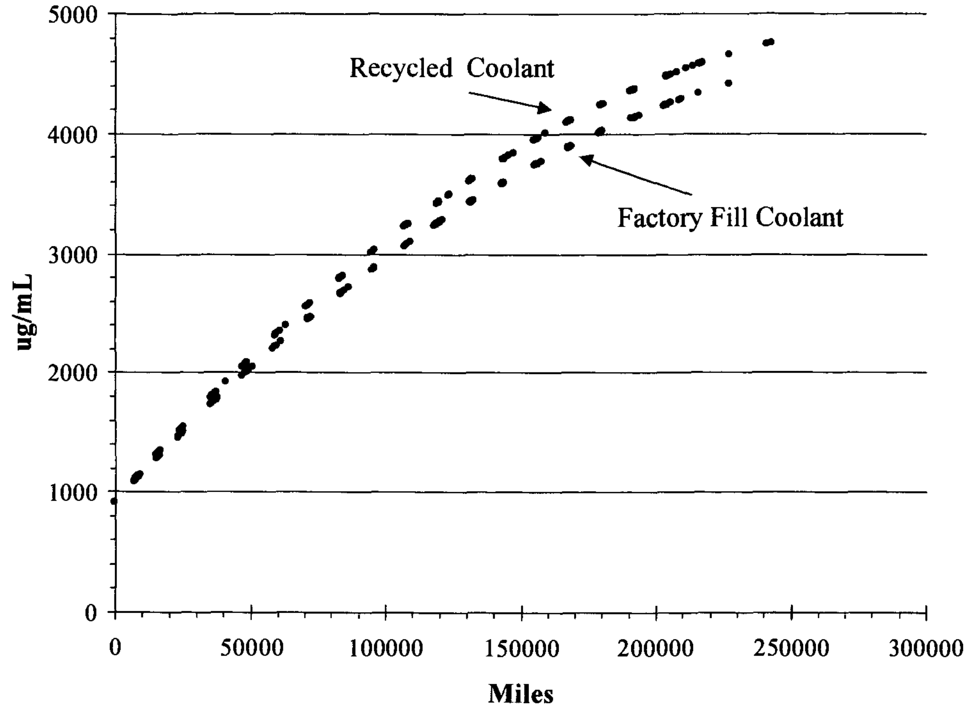

FIG. 8—*Statistical fits of total acid plus 905 μg/mL for factory fill coolant versus total acid for recycled coolant filled trucks.*

Corrosive Contaminants: Chloride and Sulfate

Two common contaminants found in the cooling system are chloride and sulfate. Chloride and sulfate can be introduced into the cooling system via the water used to dilute the coolant, top off water, during cleaning, and/or conditioning the cooling system, and from trace impurities found in the coolant's inhibitor or SCA package. Other possible sources of sulfate include the degradation of mercaptobenzothiazole, leaching of sulfur compounds from cooling system hoses, or from blow by of combustion gases.

The corrosive nature of chloride and sulfate is well known and documented. ASTM Standard Specifications for Ethylene Glycol Base Coolant for Automotive and Light Duty Service (D 3306), has for a long time limited the maximum amount of chloride to 25 ppm in a new coolant. Many of the new standards have adopted this chloride limit. There has been recent debate within the ASTM Coolant Committee as to whether this limit is set too low and if there should be a limit for recycled coolant products sold in the market place.

As part of the debate, Prestone undertook work to look at the effects that various levels of chloride would have on two different commercial coolants (GM-6043 [*1*] and GM-6038 [*8*] plus SCA) in ASTM glassware type testing [Test Method for Corrosion Test for Engine Coolant in Glassware (D 1384), Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants under Heat-Rejecting Conditions (D 4340), and Test Method for Cavitation Corrosion and Erosion-Corrosion Characteristics of Aluminum Pumps with Engine Coolants (D 2809)]. GM-6043 was selected as being representative of a typical North American high silicate coolant used for light duty service.

TABLE 5—*ASTM glassware results for GM-6043 with varying levels of chloride.*

ASTM D 1384 TEST RESULTS

Chloride Level, ppm	HiPb Solder	Copper	Sn30a Solder	Brass	Steel	Cast Iron	Cast Aluminum
blank	57	4	−4	2	−1	−4	−2
100	60	4	−3	1	0	−3	15
200	37	4	−5	2	1	−1	45
300	46	4	−5	3	0	−1	34

ASTM D 4340 TEST RESULTS

Chloride Level, ppm	Corrosion Rate, mg/cm^2/week
blank	0.17
100	0.14
300	0.14

ASTM D 2809 TEST RESULTS

	Pump Ratings		
Chloride Level, ppm	Impeller	Pump	Pump Cover
blank	10	10	10
300	10	10	10

The coolant is a high pH, high silicate, borate-phosphate buffer base coolant containing MBT, TTZ, molybdate, and nitrate as additional inhibitors. As can be seen in Table 5, the addition of up to 300 ppm chloride does not result in a failure of GM-6043 in the ASTM D 4340 and D 2809 tests. However, in ASTM D 1384 increasing concentration of chloride have a negative affect on the ability of GM-6043 to protect cast aluminum, resulting in a failure at 200 ppm Cl^-.

GM-6038 plus SCA was selected as being representative of a fully formulated engine coolant for heavy duty service. GM-6038 is a high pH, low silicate, phosphate-borate buffer coolant containing nitrate and TTZ as additional inhibitors. The SCA selected was a standard commercial product. The addition of chloride to the GM-6038 plus SCA showed no affect in ASTM D 1384, D 4340, and D 2809.

The two test coolants reacted differently to increasing chloride content. GM-6038 plus SCA could tolerate up to 300 ppm chloride and still pass the ASTM D 3306 requirements for ASTM D 1384, D 4340, and D 2809. The GM-6043 formulation was more sensitive to the concentration of chloride failing the D 1384 requirements for ASTM D 3306. The data clearly show that different inhibitor packages react differently to the level of chloride, and there is no easy way to predict how other formulations would perform at comparable chloride levels. Further it is dangerous to try to extrapolate what would happen beyond 300 ppm chloride. The best way to look at the effect chloride or other contaminants have on the cooling system is to generate field test performance data on the engine coolant containing the contaminants of interest over a broad concentration range. The laboratory glassware testing has been repeated by another lab-

TABLE 6—*ASTM Glassware results for GM-6038 plus SCA with varying levels of chloride.*

ASTM D 1384 TEST RESULTS

Chloride Level, ppm	HiPb Solder	Copper	Sn30a Solder	Brass	Steel	Cast Iron	Cast Aluminum
blank	379	5	−4	2	0	−2	8
100	361	3	−5	2	−1	−1	−1
200	370	5	−1	4	1	−2	3
300	339	5	−5	3	−1	−2	3

ASTM D 4340 TEST RESULTS

Chloride Level, ppm	Corrosion Rate, mg/cm^2/week
blank	0.34
100	0.21
300	0.43

ASTM D 2809 TEST RESULTS

Chloride Level, ppm	Pump Ratings		
	Impeller	Pump	Pump Cover
blank	10	9	9
300	10	10	10

oratory and the results show the same corrosive nature of chloride in GM-6043 and GM-6038 [*9*].

This fleet test was designed to look at the average chloride and sulfate levels that would be expected under normal operating conditions. As can be seen in Table 7, the coolant in the factory filled trucks started with an average 27 ppm chloride and after 220 000 miles (354 046 km) increased 73 to 100 ppm. The trucks containing recycled coolant start at an average of 73 ppm chloride and increased ~79 to 152 ppm by the end of test. In both cases over the duration of the test, the chloride level increased roughly the same amount.

The effect sulfate has on the performance of an engine coolant is less defined. One study reported at an ASTM D15.15 Recycled Coolant Committee meeting [*9*] suggested that GM-6043 and GM-6038 containing 700 ppm sulfate would fail the ASTM D 3306 requirement for D 1384 on cast iron (Table 8).

Surveys of used coolant have shown average sulfate levels in the range of 269 to 273 with a standard deviation of ~220 ppm [*2,3*]. The recycled engine coolant initial sulfate level is approximately at the average used coolant level, while the factory filled coolant contains substantially less. However in both cases, the sulfate level increases on average 1100 ppm over the course of the test. This increase is significantly greater than would be expected under normal operating conditions. A closer examination of the data shows that for both the factory fill and recycled coolant, the sulfate level increases as the MBT concentration is decreasing. The rate of increase in sulfate is inversely proportional to the decrease of MBT levels in both fluids. The excessive buildup of sulfate in these trucks appears to be due to the breakdown of MBT (Fig. 9).

TABLE 7—*Chloride levels at the start and end of fleet test for the factory filled and the recycled engine coolant.*

Trucks with Factory Fill Coolant Chloride Level, ppm			
Truck No.	Start	End	Increase
204	65	129	64
212	25	97	72
216	15	72	57
217	22	98	76
218	18	112	94
221	18	95	77
Average	27	100	73

Trucks with Recycled Coolant Chloride Level, ppm			
Truck No.	Start	End	Increase
205	84	175	91
213	74	177	103
214	73	141	68
215	69	141	72
219	71	132	61
220	67	132	76
Average	73	152	79

TABLE 8—*Sulfate levels at the start and end of fleet test for the factory filled and the recycled engine coolant.*

Trucks with Factory Fill Coolant Sulfate Level, ppm			
Truck No.	Start	End	Increase
204	272	1417	1145
212	38	1025	987
216	37	1145	1108
217	34	1265	1231
218	32	1354	1322
221	32	1319	1287
Average	74	1254	1180

Trucks with Recycled Coolant Sulfate Level, ppm			
Truck No.	Start	End	Increase
205	330	1324	994
213	370	1705	1335
214	341	1380	1039
215	347	1380	1033
219	336	1450	1114
220	348	1432	1084
Average	345	1445	1100

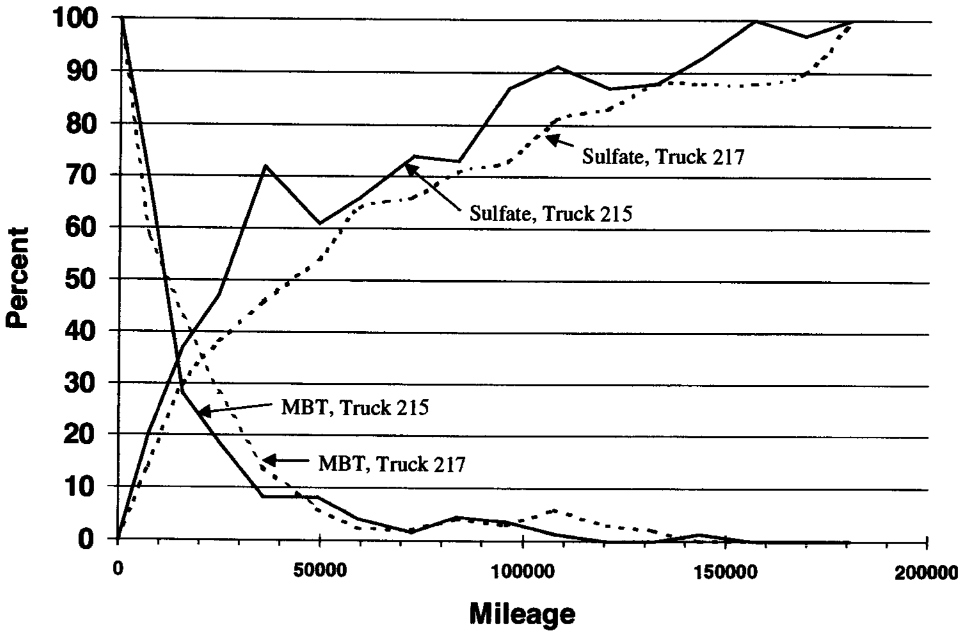

FIG. 9—*Percent MBT depletion rate and sulfate buildup in the factory filled Truck 217 and recycled coolant Truck 215 as a function of mileage.*

Total Dissolved Solids

High concentrations of total dissolved solids have the potential to cause or contribute to a number of cooling system problems once it reaches a critical level. A partial list of potential problems include [*10*]:

- water pump failure resulting from the deposition of the total dissolved solids on water pump seals,
- loss of cooling system efficiency by flow restriction and the formation of insulating barriers on heat accepting exchangers, and
- cracked heads and warped engine blocks caused by the formation of insulating scale barriers on heat rejecting engine surfaces.

The problem with reporting TDS is knowing, "What is a safe level?" Part of the problem is that many components contribute to the total TDS number. They include inhibitors necessary for the protection of the cooling system, as well as, contaminants, degradation, and corrosion products. The bulk of the initial concentration of total dissolved solids in a new coolant are the inhibitors or additive package. In recycled coolant, a larger portion of the initial TDS may be carry over of contaminants, degradation and corrosion products. The percent of each must be determined for each recycling process. An estimate of the initial TDS breakdown for the multistage chemical recycling process followed by filtration is roughly 2.9 weight % inhibitor package and 0.2 weight % attributed to carry over of contaminants.

A good measure for determining if the TDS level is too high is by monitoring the engine and cooling system component failure rate over the duration of the field test. In this fleet test,

TABLE 9—*Total dissolved solids (TDS) levels at the start and end of fleet test for the factory filled and the recycled engine coolant.*

Trucks with Factory Fill Coolant TDS Level, Weight %

Truck No.	Start	End	Increase
204	1.20	2.44	1.24
212	1.46	2.24	0.78
216	1.52	2.52	1.00
217	1.61	2.36	0.75
218	1.45	2.36	0.91
221	1.45	2.51	1.06
Average	1.45	2.40	0.95

Trucks with Recycled Coolant TDS Level, Weight %

Truck No.	Start	End	Increase
205	2.82	3.40	0.58
213	3.25	3.93	0.68
214	3.05	3.39	0.34
215	3.16	3.82	0.66
219	3.12	3.76	0.64
220	3.34	3.55	0.21
Average	3.12	3.64	0.52

there were no discernible pattern of cooling system or related engine component failures that could be traced to either test coolant. Another measure of the level of coolant system protection is monitoring the rate of increase in the TDS levels over time. A larger increase would suggest an increase in the amount of contaminants, corrosion, or degradation products. The factory filled coolant shows a larger increase in TDS levels over the life of the fleet test suggesting poorer protection (Table 9).

Metal Coupon Weight Loss Results

As discussed earlier in the section on test vehicle setup, each truck was equipped with a special bracket mounting that contained two metal specimen capsules. Each capsule held five metal bundles which contain seven 2 by 1 in. (508 by 254 mm) metal coupons of common engine metals. Bundles were periodically removed to assess the degree of protection the test coolant was providing over the 220 000 mile (354 046 km) fleet test. The average metal weight losses for the six trucks on each test coolant are shown in Figs. 10 and 11. The most pronounced weight losses are on the two solder specimens, high lead solder (97% Pb/2.5 Sn = alloy L50113) and low lead solder (Sn30a = SAE 3A). The recycle coolant provided better protection on the high lead solder, while the factory fill coolant provided slightly better protection of the low lead solder. Overall, the recycle coolant provides slightly better protection of the two solder types.

An examination of Figs. 12 and 13 provides a better comparison of the performance results on the other five metals. In all cases, the weight loss values are very low. Both fluids are providing excellent protection to the copper, brass, steel, cast iron, and cast aluminum coupons. The highest weight losses experienced are on the brass followed by the copper coupons. For both fluids, the corrosion of the brass and copper specimens is continuing as seen by the steady increase in metal weight losses as a function of test miles. The rate of corrosion on the copper

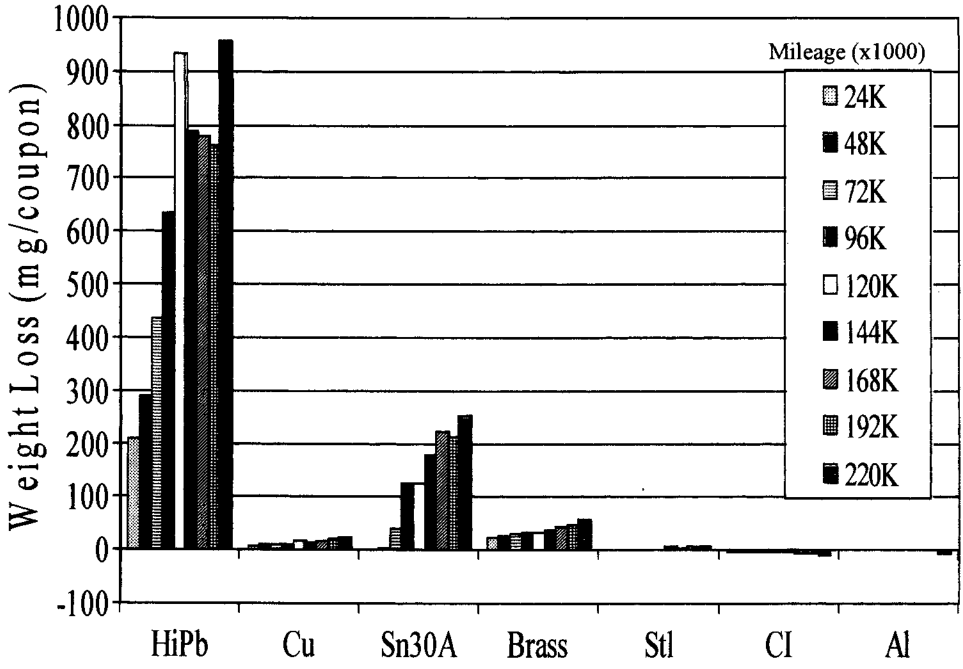

FIG. 10—*220 000 mile (354 046 km) fleet test corrosion results for the trucks containing factory filled coolant: Average weight loss (mg).*

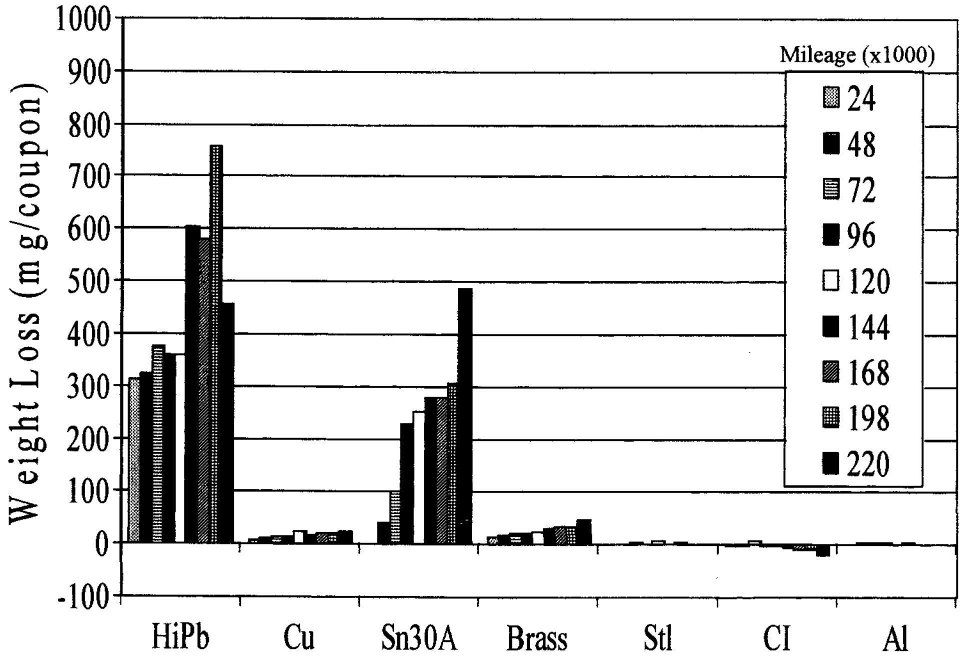

FIG. 11—*220 000 mile (354 046 km) fleet test corrosion results for the trucks containing recycled coolant: Average weight loss (mg).*

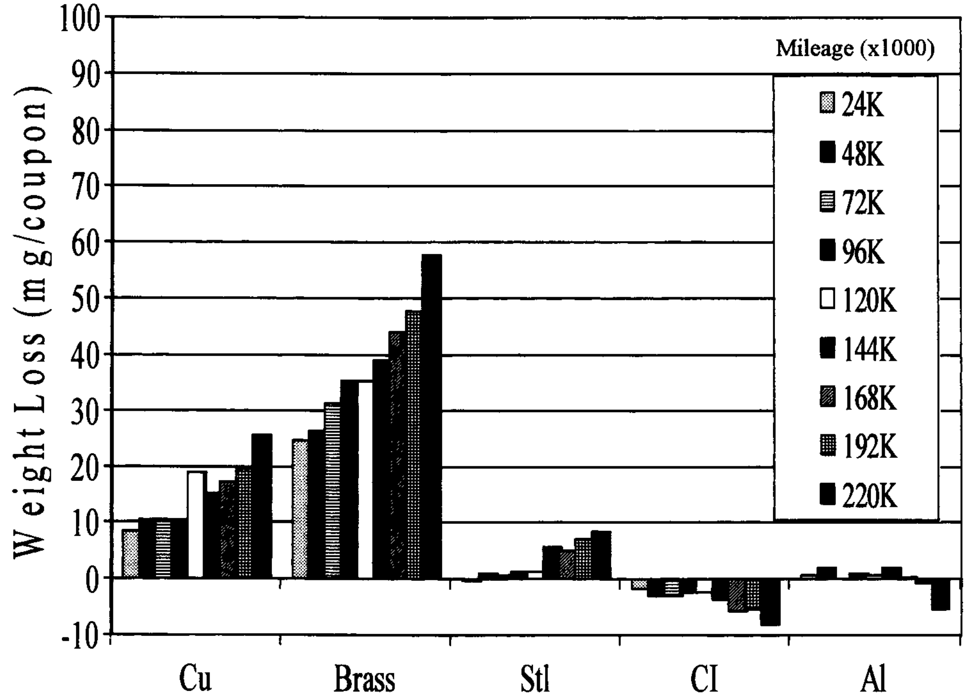

FIG. 12—*220 000 mile (354 046 km) fleet test corrosion results for the trucks containing factory filled coolant: Average weight loss (mg).*

coupons appears to be comparable for the factory fill and recycled coolant. The corrosion rate on the brass coupon is slightly higher for the factory fill coolant. Overall, in the course of the 220 000 mile (354 046 km) test both test coolants provided excellent protection to the cooling system metals. The recycle coolant may have provided slightly better overall protection.

Discussion and Conclusions

This paper provides 220 000 mile (354 046 km) fleet test data that directly compares the performance of a recycled engine coolant versus a factory filled coolant. The recycled coolant was obtained by a chemical treatment/filtration/reinhibited process of used engine coolant taken from trucks averaging 200 000 to 500 000 miles (321 860 to 804 650 km). A review of the corrosion data and the maintenance records showed that the recycled coolant provides equivalent or slightly better protection than the factory fill coolant.

Taking a closer look at the results we see that one of the key differences between the two test coolants is that the recycle coolant initially contains a small amount (~0.2 weight %) of carry-over products that consist of degradation acids, chloride, and sulfate. The initial levels of these components did not have any negative affect on the protection afforded by the recycled coolant to the metal surfaces in the cooling system.

Looking first at the depletion rates of the corrosion inhibitors, it is apparent that mercaptobenzothiazole quickly depletes to zero. The other inhibitors could be considered long life; phosphate, borate, nitrate, and molybdate depletion less than 10% in 72 000 miles (115 870 km) and actually increase in many cases over the 220 000 mile (354 046 km) test. Even silicate changed less than 10% once it has come into equilibrium with the cooling system. The increase

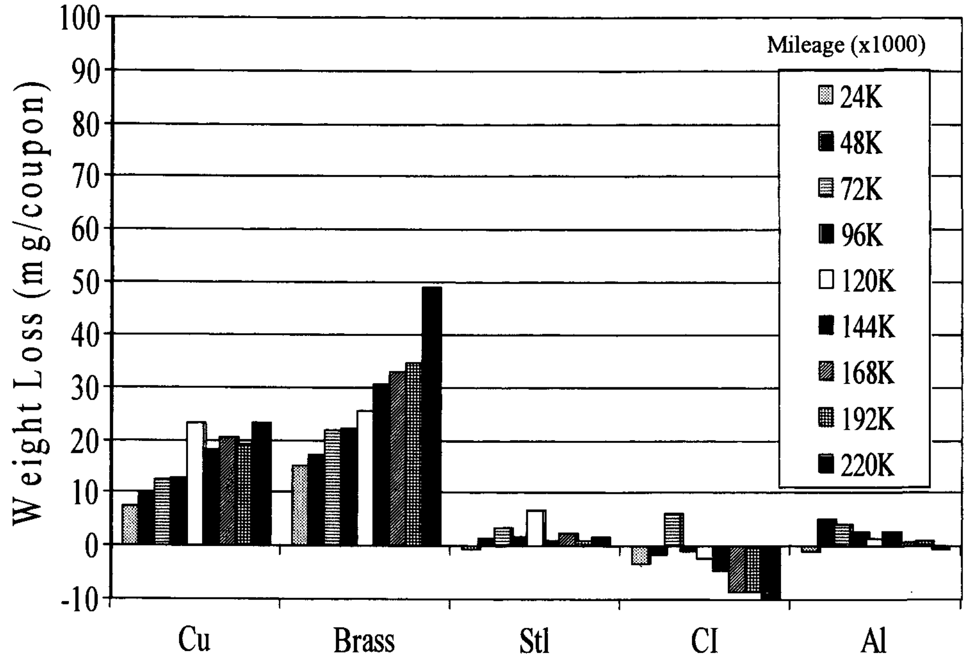

FIG. 13—*220 000 mile (354 046 km) fleet test corrosion results for the trucks containing recycled coolant: Average weight loss (mg).*

in the inhibitors is occurring because they are being supplemented with SCA at a greater rate than they are decreasing. This same pattern is seen in both the recycled and factory fill coolant. A closer look at the nitrite depletion data clearly shows that periodic additions of nitrite are required if it's concentration is to be maintained in a safe concentration range. In the test coolants, the other components found in the SCA are not necessary for maintaining an inhibitor balance. With each addition of SCA there is a rise in the TDS levels of the coolant and the balance of the inhibitor package is starting to be adversely affected. The inhibitor depletion rates for the fleet test are quite different than previously reported for a 50 000 simulated service test miles (80 465 km) [*11*]. In the simulated test, the depletion rates for phosphate and silicate were more accelerated.

The rate of glycol degradation acids buildup is not affected by the initial concentration of degradation acids. The initial level of total acids in the recycled coolant is ~900 μg/mL. The rate of acid buildup is identical for both coolants over the 220 000 mile (354 046 km) test. The rate of acid buildup changes over the course of the test. The initial conditions of the cooling system or coolants appears to increase the degradation rate early in the test. With time/mileage, these conditions change and the degradation rate starts to level off. An understanding of the mechanism involved would provide better guidance as to an acceptable initial acid level. The potential concern is that with each subsequent recycling of the coolant the carry over concentration of degradation acids could rise to a point, that over the course of use the total acid level will reach a detrimental or aggressive concentration.

The complete elimination of common contaminants such as chloride and sulfate is not practical. There are too many possible sources. However, it is also recognized that high levels of chloride and sulfate can have a very negative affect on the cooling system. The chloride and sulfate content of the test coolants did not have a negative affect on the corrosion rate of the cooling system metals as measured by the weight losses on the metal test coupons. In the recycled coolant, the chloride level started at an average of 73 ppm and finished at 152 ppm. An inspection of the aluminum coupons showed no obvious signs of corrosion and had minimal to no weight loss over the duration of the test. Aluminum would most likely be adversely affected by high chloride concentration if the coolant inhibitor package was not functioning properly. It has been shown in ASTM D 1384 glassware tests that as little as 200 ppm chloride can cause a good fluid to fail the requirements of ASTM D 3306 for cast aluminum.

Both fluids in this test showed an excessively high level of sulfate at the conclusion of the test. An examination of the test data showed that as the level of mercaptobenzothiazole decreased, the level of sulfate increased. Further, the concentration of sulfate started to level off at approximately the same point where the MBT went to zero. It appears that the sulfate is one of the by-products of the breakdown of MBT. The final concentration of sulfate in the factory filled and recycled coolant were 1254 and 1445, respectively. Sulfate has been shown to be aggressive to ferrous metals; however, an examination of the cast iron and steel coupons showed no sign of activity on either metal and virtually no weight loss. The corrosion inhibitor package is still providing excellent ferrous metal protection.

As stated earlier, the inhibitor package and other contaminants contribute to total dissolved solids (TDS). With each the addition of SCA the TDS of the coolant increases. Given that both test coolants have on average the same number of additions of the same SCA, any different in the rate of buildup TDS is the result of the buildup of other contaminants. An examination of the TDS in the two coolants shows the total level of TDS of the recycled coolant is twice as high as the factory fill coolant at the start of the test. The TDS level for the recycled coolant is 3.12 weight % which is slightly lower than 50% solutions of many commercial Asian coolants that can average up to 3.5 weight %.

Over the course of the test the TDS level of the recycled coolant rise ~0.52 weight % roughly half the rate as the factory fill coolant. At the end of the test the TDS level for the recycled coolant is ~1.5 times that of the factory filled coolant. The TDS level for factory fill coolant is increasing at almost twice the rate of the recycled coolant. This suggests the factory fill coolant is not holding up as well under the stress of the test and the levels of contaminants, degradation, or corrosion products are building up quicker. In terms of field test performance, the corrosion results and maintenance records do not show any problems with the factory fill coolant up to this point.

Summarizing the performance results, the recycle and factory fill coolant show the same slow depletion rates of their inhibitors, the same rate of increase in the level of glycol degradation acids, chloride, and sulfate, and equivalent corrosion protection of the metals found in the cooling system. They differ in that the factory fill coolant is made from virgin ethylene glycol while the recycled glycol product is obtained from recycled used engine coolant. Further the initial concentration of the inhibitors levels is higher in the recycled coolant leading to a higher initial TDS level with only ~0.2 weight % being carryover of contaminants. Based on the evaluation of the cumulative performance and fleet maintenance data, it is clear that the recycled coolant provides equivalent to slightly better performance than the factory filled coolant.

The results showed the recycled coolant to provide excellent protection to the cooling system of the test trucks. However, this information should not be extrapolated to other recycled engine coolants. Recycling technologies differ greatly in their ability to recycle and reinhibit used coolant. General Motors and the U.S. Military have conducted evaluation programs of recycling technologies which shows that certain technologies could not recycle used coolant back to a satisfactory condition.

An even more basic concern is the concept that all coolants will react in the same fashion to different levels of corrosive contaminant. Testing has shown that some good virgin commercial coolants are not able to protect cooling system metals from high levels of chloride and sulfate while others can. Knowing that there is even greater variation in used coolants, care must be taken when trying to use data from one recycling process to support the concept that all recycled coolants should behave similarly. The fact that the recycled coolant in this test was able to provide excellent protection to the cooling system while containing on average 152 ppm chloride and 1432 ppm sulfate does not mean a recycled coolant from another process will behave similarly. When considering using or buying a recycled coolant or recycling process, use caution. Require the recycler to supply a complete performance portfolio which should at minimal include: ASTM D 3306 performance testing, electrochemical testing, storage testing, compatibility testing, engine dynamometer testing and a multi vehicle fleet test. Key to understanding the performance portfolio will be an understanding of the quality and origin of the used engine coolant that was selected for testing. Make sure that the used coolant source is representative of the waste stream that you will be recycling and that it contains higher than normal (worst case scenario concentrations) of aggressive contaminants such as chloride and sulfate. In general, it is easier to pass performance requirements if the used coolant that is being recycled for the test was capable of passing the tests prior to being recycled.

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Evaluation of Engine Coolant Recycling Processes: Part 2*

REFERENCE: Bradley, W. H., "**Evaluation of Engine Coolant Recycling Processes: Part 2,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 292–318.

ABSTRACT: Engine coolant recycling continues to provide solutions to both economic and environmental challenges often faced with the disposal of used engine coolant. General Motors' Service Technology Group (STG), in a continuing effort to validate the general practice of recycling engine coolants, has conducted an in-depth study on the capabilities of recycled coolants. Various recycling processes ranging from complex forms of fractional distillation to simple filtration were evaluated in this study to best represent the current state of coolant recycling technology. This study incorporates both lab and (limited) fleet testing to determine the performance capabilities of the recycled coolants tested. While the results suggest the need for additional studies in this area, they reveal the true capabilities of all types of engine coolant recycling technologies.

KEYWORDS: corrosion, inhibitors, recycling processes, used reference coolant, virgin control coolant, laboratory testing, fleet testing

Engine coolant recycling, particularly in recent years, has become increasingly attractive to various sectors of the automotive repair industry. Evolving legislation seeks to encourage the recycling of used engine coolant. This, coupled with a stable glycol market, has helped keep coolant recycling competitive with virgin products and alternative methods of disposal. The North American market alone accounts for an estimated 757 million liters (200 million gallons) of ethylene glycol-based antifreeze yearly. Since the antifreeze/coolant concentrate is blended with water upon installation into the vehicle, as much as 1.5 billion liters (400 million gallons) of used coolant are generated every year. Only a very small fraction of this used antifreeze is currently being collected for disposal and a smaller portion of that amount is recycled. The ethylene glycol used in replacement antifreeze is manufactured from either natural gas or ethylene derived from cracked petroleum products. An obvious benefit from recycling ethylene glycol from used coolant is the corresponding decrease in the amount of new ethylene glycol required for the manufacture of the replacement antifreeze. Any reduction in the amount of virgin ethylene glycol required for antifreeze beneficially reduces the required amount of carbon-based natural resources, such as natural gas and petroleum products, to supply the antifreeze market in North America. These natural resources may then be employed in other areas such as natural gas, diesel fuel, home heating fuels, or gasoline for internal combustion engines or simply conserved [*1*]. These reasons, coupled with an ever-growing concern for the environment, have resulted in an expanded infrastructure of coolant recycling equipment and services now available.

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*Part 1 is in *Engine Coolant Testing: Third Volume, ASTM STP 1192*, pp. 276–288.

A Common Standard Required

A common method by which any engine coolant recycling process may be tested to determine its true capabilities is not currently available. As a result, original equipment manufacturers (OEMs) such as General Motors find it necessary to conduct studies, such as the one discussed in this paper, to determine which coolant recycling processes are capable of meeting their performance requirements. Just as passenger vehicles and heavy-duty trucks have different coolant performance requirements, different OEMs rely on different test procedures to satisfy their requirements. Consequently, coolant recyclers attempting to gain acceptance by various OEMs find it extremely difficult to satisfy all the necessary requirements. Participants in this study who successfully completed all the requirements were approved by General Motors, enabling them to recycle engine coolants for both light- and medium-duty vehicles without affecting cooling system warranty coverage.

Differences Between Part 1 and Present Study

GM's first study (henceforth referred to as Part 1) of the nature of recycled coolants was conducted in 1991 and focused primarily on the ability of recycled coolants to meet GM 1825M—an ethylene glycol based (concentrate) coolant performance specification for light- and medium-duty vehicles which contain aluminum (heat-rejecting) components. The details of the first study can be referenced under the title "An Evaluation of Engine Coolant Recycling Processes: Part 1," *Engine Coolant Testing: Third Volume, ASTM STP 1192*, R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 276–288. This second study was completed by General Motors in 1993, and is the subject of this paper. All the processes evaluated in this study are listed in (Table 1). For a comprehensive description of each process, refer to Part 1.

Format of the Study

Objective

The primary objective of this study was to evaluate the performance of recycled coolants formulated to meet GM 1899M—an ethylene glycol based (concentrate) coolant performance specification for light- and medium-duty vehicles without aluminum (heat-rejecting) components. An ancillary objective was to reevaluate the performance of recycled coolants formulated for aluminum applications (GM 1825M). For clarification purposes, Table 2 describes the relationship between coolant specifications GM 1825M, GM 1899M, and the ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light Duty Service (D 3306-94). The approach taken to accomplish these objectives was twofold. First, laboratory testing was conducted to determine if various engine coolant recycling processes were capable

TABLE 1—*Coolant recycling processes evaluated.*

1. Filtration, simple
2. Filtration, flocculation/coagulation
3. Filtration, flocculation/coagulation, oxidation
4. Deionization
5. Reverse osmosis
6. Filtration, centrifugation
7. Vacuum distillation
8. Chemical/deionization assisted filtration

TABLE 2—*Comparison of coolant specifications; ASTM D 3306, GM 1825M, and GM 1899M.*

	ASTM D 3306	GM 1825M	GM 1899M
Physical/Chemical Requirements			
Specific gravity, 60/60-F	1.11 to 1.14	1.11 to 1.14	1.11 to 1.14
Freezing point, °F, 50% vol.	−34 min.	−34 min.	−34 min.
Boiling point, °F undiluted/50% vol.	300 min./226 min.	300 min./not req'd.	300 min./226 min.
Effect on automotive finish	None	None	3% chg.-reflect.
Ash content, wt%	5 max.	5 max.	5 max.
pH, 50% vol.	7.5 to 11.0	7 to 11	7 to 11
Reserve alkalinity, mL	10 min.	10 min.	10 min.
Water, weight %	5.0 max.	5.0 max.	5.0 max.
Chlorides, ppm	25 max.	not required	not required
R.A., % loss after 1000 h	not required	25% max.	25% max.
General Requirements			
Color	distinctive	dist. green	dist. green
Odor	not offensive	not required	not required
Storage stability	not required	6 months	6 months
Performance Requirements			
CORROSION IN GLASSWARE			
Copper	10	10	10
Solder	30	20	20
Brass	10	10	10
Steel	10	10	10
Cast Iron	10	10	10
Aluminum	30	20	20
High lead solder	not required	not required	not required
SIMULATED SERVICE TEST			
Copper	20	20	20
Solder	60	40	40
Brass	20	20	20
Steel	20	20	20
Cast Iron	20	20	20
Aluminum	60	40	40
High lead solder	not required	not required	not required
Heat transfer corrosion of aluminum	1.0 mg/cm^2/wk	1.0 mg/cm^2/wk	not required
Foaming—max./break	150 mL/5 s	50/5 s	50/5 s
Cavitation erosion of Al water pump	8 min @ 100 H	8 @ 100	
Galvanostatic pitting test	not required	not required	not required
Engine dynamometer	not required	not required	not required
Circulation test	not required	not required	not required
Fleet test	not required	not required	not required

of recycling a reference used coolant to meet either GM 1825M or 1899M performance specifications. Secondly, limited fleet testing was utilized to observe the performance characteristics of these same recycled coolants when placed in a controlled fleet vehicle. As with Part 1, the results of this study were used to determine which recycling system would be approved by General Motors for use in vehicles without affecting the cooling system warranty.

Establishing the Reference Coolant

The used coolant that each recycling process was required to recycle in this study will henceforth be referred to as the *reference used coolant*. Unlike the reference used coolant from Part 1 which was removed from employee vehicles, the reference used coolant in the present study was obtained by collecting varying quantities of used coolant from local radiator and repair facilities. The primary reason for changing the source of used coolant was to provide adequate quantities of feedstock to allow for vehicle and additional laboratory testing. Frequent analysis of each drum of used coolant collected was conducted to assure that desired levels of ethylene glycol degraded acids, dissolved and suspended solids, as well as metal oxides and salts were achieved prior to adding to the composite reference used coolant. The reference used coolant was analogous to previous characterizations conducted on used coolant samples [*2*,*3*]. A complete characterization of the reference coolant can be seen in Table 3. This analysis, conducted in an independent laboratory, was accomplished by the following methods. All metals were determined by inductively coupled plasma (ICP). Tolyltriazole (TTZ), benzotriazole (BZT), and mercaptobenzothiazole (MBT) were determined by high-pressure liquid chromatography (HPLC). All anions, including glycolate and formate, were determined by ion chromatography (IC). In order to ensure a more consistent and abundant feedstock, future studies would benefit from the implementation of a (proven) synthetic reference coolant.

TABLE 3—*Analysis of reference coolant.*

Analysis, ppm	Solubles/Total
pH	8.9/n/a
RA ASTM	4.48/n/a
% Glycol	42.5/n/a
TTZ	261/n/a
BZT	ND/n/a
MBT	14/n/a
Chloride	87/n/a
Nitrite	97/n/a
Benzoate	471/n/a
Nitrate	752/n/a
Sulfate	268/n/a
Boron	180/183
Copper	2.5/2.5
Potassium	1271/1293
Molybdenum	29/29
Sodium	1660/1684
Phosphorus	580/595
Silicon	34/38
Iron	3.5/22.0
Lead	14/19
Zinc	4.3/4.3
Calcium	3.3/8.0
Formate	215/n/a
Glycolate	874/n/a
Acetate	47/n/a
% Total solids	1.4/n/a
% Total dissolved solids	1.24/n/a

n/a = Not applicable.
ND = Not detected.

Recycling the Coolant

As with Part 1, all portable coolant recycling processes were conducted at the General Motors Service Technology Group Headquarters building located in Warren, Michigan, before the author. Each equipment was operated per manufacturer guidelines and under the direct supervision of the manufacturer. Prior to recycling the reference used coolant, each recycling system was primed with the reference used coolant. Failure to prime recycling equipment could significantly influence the nature of the finished product. This affect is directly related to the internal volume of the recycling system being tested, the amount of coolant recycled, and the nature of the primer coolant. Recycled samples were individually coded and shipped to an independent test facility accustomed to performing ASTM testing of this nature.

Dissolved Solids

Table 4 contains the level of total dissolved solids of the recycled coolants from each process, both before and after reinhibition. Reinhibited coolants were analyzed in both the 1825M and 1899M configurations. As might be expected, the deionization and vacuum distillation processes (#s4 and 7, respectively) were the only ones capable of reducing the dissolved solids to negligible levels. Reverse osmosis (#5) was also effective in reducing dissolved solids though not nearly to the same degree as the deionization and vacuum distillation processes (the effectiveness of RO processes to address solubles is largely dependent upon the membrane design). Simple and chemically assisted filtration processes (Nos. 1, 2, 3, 6, and 8) had little affect on dissolved solids levels with the exception of process No. 8 which incorporated the use of a cation deionization bed. While the issue of total dissolved solids tends to be more relative to the coolant's designated application (that is, passenger versus heavy duty vehicles), it is reasonable to conclude that the recycling processes that address dissolved solids are less dependent upon their reinhibitor package and more likely to generate a consistent effluent.

Metal Oxides

A more comprehensive analysis of the recycled coolants prior to reinhibition is given in Table 5 where the processes' effectiveness in reducing metal oxides, chloride, and ethylene glycol degraded acids is portrayed. Metal oxides, having originated from the corrosion of various metals in the cooling system, are a testimony of the coolant's inability to perform its

TABLE 4—*Percent dissolved solids (%).*

Process # (see Table 1)	Preinhibited Coolant	Inhibited to Meet 1825M	Inhibited to Meet 1899M
1	1.1	1.6	1.2
2	1.2	2.1	1.7
3	1.2	1.7	1.5
4	<0.01	NA	0.9
5	0.8	1.5	1.4
6	1.3	NA	2.1
7	<0.01	1.2	1.1
8	1.0	2.5	2.2
Ref. coolant	1.3		
GM 6043		1.4	

All samples were 50% solutions.
NA = Process successfully met 1825M in Part 1 and was not rerun.

TABLE 5—*Post process analysis (uninhibited).*

	Soluble/Insoluble, ppm								
		Process No.							
Sample ID	Ref. Coolant	1	2	3	4	5	6	7	8
Aluminum	ND/5.3	ND/2.4	4/<2.0	<2.0/10	ND/ND	ND/2.7	ND/5.8	ND/2.5	ND/5.3
Calcium	3.3/8.0	2.1/2.7	11/<2.0	2.8/5.4	ND/<2.0	ND<2.0	2.4/4.3	ND<2.0	17/20
Copper	2.5/2.5	ND/ND	ND/<2.0	ND/3.9	ND/ND	ND/ND	ND/ND	ND/9.2	ND/4.3
Chloride	87/NA	76/NA	110/NA	80/NA	ND/NA	74/NA	86/NA	ND/NA	95/NA
Iron	3.5/22	ND/2.0	6.0/8.0	6.3/27	ND/ND	ND/3.0	5.2/9.3	ND/4.0	ND/ND
Lead	14/19	ND/ND	ND/2.0	ND/ND	ND/ND	ND/ND	ND/ND	ND/ND	ND/ND
Sulfate	268/NA	243/NA	265/NA	272/NA	ND/NA	25/NA	230/NA	ND/NA	259/NA
Zinc	4.3/4.3	3.6/4.1	6.0/<2.0	2.7/4.9	ND/ND	ND/ND	3.7/4.2	ND/ND	5.9/7.1
Total Degrad. Acids*	1136	890	933	1200	ND	883	1191	ND	1996

ND = Not detected.
NA = Not applicable.
*Total glycolic acids including formate, glycolate, and acetate.

basic function—protect cooling system components against corrosive attack. The significance of the ability to remove these corrosion products is dependent upon the nature of each metal as well as that of the coolant formulation (reinhibitor) and the design of the cooling system itself. However, failure to remove these products can lead to problems associated with clogged heat exchangers, increased susceptibility to galvanic attack, and even prevent subsequent coolants (added for service) from performing correctly. The reference coolant contained considerable amounts of these metal oxides.

Each process tested was capable of reducing iron, particularly at the soluble level, with the exception of process No. 3. Similarly, most every process tested was capable of reducing/eliminating copper. Significant levels of lead (14 ppm) were present in the reference coolant—far in excess of the 5 ppm EPA threshold for designation as a hazardous material. Each process was successful in completely eliminating all soluble lead. With the exception of process No. 2, all the insoluble lead was removed as well.

Chloride/Degradation Acids

The chloride content of the reference coolant was adequate (at 87 ppm) to provide a significant challenge to the recycling processes tested. Neither of the GM performance specifications contains a chloride limit—consequently, no maximum allowable level of chloride in the recycled coolants was enforced. Only deionization and vacuum distillation (processes Nos. 4 and 7) were capable of eliminating chloride, the other processes had little effect on the chloride level. As with total dissolved solids, those processes which do not reduce/eliminate chloride, rely more heavily on the strength of their inhibitor formulation to overcome potential deleterious affects resulting from the presence of this corrosive ion.

The formation of ethylene glycol degraded acids occurs as a natural process resulting from the thermal cycling of the coolant within the vehicle's cooling system. Elevated levels of these degradation acids (formate, glycolate, and acetate), coupled with a drop in the coolant's pH and depleted inhibitor levels, typically are responsible for imminent cooling system corrosion. Levels of formate, glycolate, and acetate in the reference coolant were representative of a depleted engine coolant. Once again, only deionization and vacuum distillation (processes Nos. 4 and 7) were capable of significantly reducing these acids with the exception of acetate which was eliminated by several processes.

Offsite recycling systems were addressed via the approval program which was established in the first study. The objective of this program has been to provide General Motors' dealers with information of the facilities capable of providing recycled coolant that meets GM 1825M requirements. Interested recycling facilities may submit a request to participate in this program which requires them to provide quality control information on their process, a characterization of their typical used coolant feedstock, along with the trade names and outlets of their product. With this information, a determination can be made as to the quality and consistency of the process, the relationship between their used coolant feedstock and the reference used coolant characteristics can be determined, and a sample product may be acquired for testing to GM performance specifications.

Testing the Recycled Coolants

In order to more fully comprehend the performance capabilities of the recycled coolants, both laboratory and vehicle testing were conducted. To accomplish this, adequate amounts of recycled coolant were generated to enable laboratory testing of GM 1825M and 1899M specifications and at least one vehicle test. While no statistical inference is made by the vehicle data generated in this study, some interesting results can be observed as recycled coolants from various processes are placed in both laboratory and field testing environments.

Laboratory Testing

As with Part 1, each recycled coolant was tested for specific chemical, physical, and performance characteristics as required by GM 1825M and GM 1899M specifications. The recycled coolants were preadjusted to a 50:50 water to ethylene glycol ratio. With the exception of the distillation systems, the recycling processes had no affect on the water to glycol ratio. Due to the prediluted nature of these coolants, adherence to the ASTM Specification for Prediluted Aqueous Ethylene Glycol Base Engine Coolant (50 Volume % Minimum) for Automobile and Light-Duty Service (D 4656-95) for prediluted coolants was maintained to insure proper test sample preparation.

Chemical/Physical Testing

To avoid unnecessary testing and expense, all the chemical/physical requirements had to be met prior to conducting the more involved performance based testing. The GM storage and compatibility test proved to be helpful in assuring that the coolant was sufficiently stable prior to conducting the more lengthy and costly tests such as the ASTM Test Method for Simulated Service Corrosion Testing of Engine Coolants (D 2570-96) and the ASTM Test Method for Cavitation Corrosion and Erosion-Corrosion Characteristics of Aluminum Pumps with Engine Coolants (D 2809-94). The results for both the storage/compatibility and foaming characteristics [as determined by ASTM Test Method for Foaming Tendencies of Engine Coolants in Glassware (D 1881-96)] are included in Table 6. The reference used coolant was unable to meet the requirements of both the storage/compatibility and the foam tests. Of the recycled coolants tested, only the recycled coolant from process No. 3 was unable to meet these requirements and consequently was disqualified from further testing.

ASTM D 1384 Results

The results of glassware testing [ASTM Test Method for Corrosion Test for Engine Coolant in Glassware (D 1384-96)] for both GM 1899M and 1825M recycled coolants can be observe

TABLE 6—*GM storage/compatibility and foaming tendencies results.*

Process	Storage/Compatibility 1825M/1899M	Foaming Tendencies 1825M/1899M
1	passed/passed	passed/passed
2	passed/passed	passed/passed
3	fail/fail	fail/fail
4	NA/passed	NA/passed
5	passed/passed	passed/passed
6	NA/passed	NA/passed
7	passed/passed	passed/passed
8	passed/passed	passed/passed
Ref.	failed	failed

NA = This process completed these requirements in Part 1 and was not rerun.

TABLE 7—*ASTM D 1384 glassware comparison data for GM 1899M recycled coolant.*

Metal	GM Spec.	Process Evaluated—Average Weight Loss, mg								
		Ref.	1	2	3	4	5	6	7	8
Copper	10	3	5	4	3	4	3	2	2	2
Solder	20	4	3	19	15	4	3	9	2	3
Brass	10	2	2	4	2	4	2	2	3	3
Steel	10	2	1	1	1	1	1	0	1	0
Cast iron	10	1	2	3	3	2	5	1	4	2
Cast aluminum	20	15	1	1	2	12	1	1	1	1

in Tables 7 and 8, respectively. Interestingly, the reference coolant met D 1384 requirements despite its condition. It is not, however, reasonable to assume that the reference coolant would be capable of providing adequate protection in a vehicle's cooling system. As will become obvious in the fleet data discussed in this paper, recycled coolants have been observed to pass laboratory performance tests but not perform adequately in a vehicle. All the recycled coolants, formulated for both GM 1899M and 1825M, met GM requirements of D 1384.

ASTM D 4340 Results

The results of the ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions (D 4340-96) can be observed in Table 9. The reference coolant performed extremely poor in this test. All the recycled coolants tested (formulated as GM 1825M) met the GM requirements for D 4340. The recycled coolants contained 3 to 6 times the amount of silicon as the reference used coolant.

ASTM D 2809 Results

The results of the cavitation and erosion testing of the water pump (as determined by D 2809) can be observed in Table 10. The reference used coolant was able to (marginally) meet the requirements of D 2809 with a rating of 8 (much deliberation was given to determine if the results were to be a 7 or 8). All the recycled coolants tested met the GM requirements of D 2809. Most of the post-test pumps were lightly coated with a thin black layer of anticorrosive material. This is a common occurrence in this test and is believed to be benign in nature. Three

TABLE 8—*ASTM D 1384 glassware comparison data for GM 1825M recycled coolant.*

Metal	GM Spec.	Process Evaluated—Average Weight Loss, mg								
		Ref.	1	2	3	4	5	6	7	8
Copper	10	3	3	4	2	NA	3	NA	2	1
Solder	20	4	3	13	14	NA	4	NA	2	1
Brass	10	2	4	3	3	NA	3	NA	1	2
Steel	10	2	1	1	1	NA	1	NA	0	0
Cast iron	10	1	6	1	3	NA	2	NA	2	9
Cast aluminum	20	15	1	2	1	NA	1	NA	1	1

NA = This process completed these requirements in Part 1 and was not rerun.

TABLE 9—*ASTM D 4340 results ($mg/cm^2/wk$).*

Process	Results
1	0.25
2	0.62
3	DIS
4	NA
5	0.15
6	NA
7	0.13
8	0.62
Ref.	7.4

NA = This process completed these requirements in Part 1 and was not rerun.

DIS = This process failed the chem./phys. requirements and was disqualified.

Note: GM 1825M allows a max. corrosion rate of 1.0 $mg/cm^2/$week.

of the recycled coolants (Nos. 1, 2, 8) accomplished a rating of 10, as was easily distinguished by the unroughened, unpitted, and noneroded surfaces. As an observation, levels of phosphate and nitrate were nearly double in those coolants which rated a 10 as compared to the reference used coolant which marginally passed. However, no such observation is made when comparing the recycled coolants which rated an 8 or 9 to those which rated a 10.

ASTM D 2570 Results

The results of simulated service testing (as determined by D 2570) are contained in Tables 11 and 12. Surprisingly, the reference used coolant fared quite well in this test, easily meeting all the weight loss requirements. The recycled coolants formulated for GM 1899M applications also met the GM requirements for D 2570 (Table 11). As should be expected, the recycled

TABLE 10—*ASTM D 2809 pump cavitation results.*

Process	1825M Results	1899M Results
1	10	10
2	10	9
3	DIS	DIS
4	NA	9
5	9	8
6	NA	8
7	9	8
8	10	10
Ref.	8*	. . .

Note. GM 1825M allows a max. corrosion rate of 1.0 $mg/cm^2/$week.—NA = This process completed these requirements in Part 1 and was not rerun.

DIS = This process failed the chem./phys. requirements and was disqualified.

*The reference coolant marginally passed this requirement.

TABLE 11—*ASTM D 2570 simulated service comparison data for GM 1899M recycled coolant.*

Metal	GM Spec.	Process Evaluated—Average Weight Loss, mg								
		Ref.	1	2	3	4	5	6	7	8
Copper	20	3	4	5	DIS	3	2	2	3	5
Solder	40	7	1	2	DIS	1	1	2	2	1
Brass	20	2	5	6	DIS	3	2	0	2	7
Steel	20	2	1	1	DIS	1	1	1	0	1
Cast Iron	20	9	1	2	DIS	1	0	1	1	13
Cast Aluminum	40	9	3	9	DIS	6	1	1	1	1

DIS = This process failed either the chem./phys. requirements or D 1384 and was disqualified.

coolants performed noticeably better than the reference used coolant. The performance of the recycled coolants formulated for GM 1825M applications (Table 12) was similar to the GM 1899M coolants with the exception of process No. 5 which was unable to adequately protect solder (GM's maximum allowable weight loss for solder in D 2570 is 20 mg less than the ASTM limit [40 mg versus 60 mg]). As a result, process No. 5 was disqualified from the test program. This is an ideal example of the capability of the recycling process (more specifically the reinhibitor formulation) to be of benefit or detriment to the coolant. While varying levels of coolant recycling effectiveness are prevalent where restoring the coolant's original qualities are concerned, each process, independent of its cost and complexity, is only as good as its / reinhibitor package. This has been observed repeatedly in the course of GM's coolant recycling studies—both in the portable and offsite recycling configurations. *In short—the **overall** effectiveness of the coolant recycling process has demonstrated itself to be dependent upon the appropriate combination of process and reinhibitor formulation.*

Vehicle Fleet Testing

In terms of performance requirements, ASTM D 3306 (or in this case GM 1825/1899M) outlines a regimen of progressively more strenuous tests, starting with glassware testing and proceeding to simulated service testing. Each test stresses different aspects of the coolant and provides minimum performance standards that the coolant should meet before it is considered for more advanced testing such as engine dynamometer and vehicle testing.

Key to the development of antifreeze/coolants is the ability to differentiate coolant perfor-

TABLE 12—*ASTM D 2570 simulated service comparison data for GM 1825M recycled coolant.*

Metal	GM Spec.	Process Evaluated—Average Weight Loss, mg								
		Ref.	1	2	3	4	5	6	7	8
Copper	20	3	4	3	DIS	NA	2	NA	5	2
Solder	40	7	1	1	DIS	NA	44	NA	1	2
Brass	20	2	5	3	DIS	NA	−3	NA	2	1
Steel	20	2	1	0	DIS	NA	1	NA	0	0
Cast Iron	20	9	3	1	DIS	NA	2	NA	1	1
Cast Aluminum	40	9	3	9	DIS	NA	1	NA	3	1

NA = This process completed these requirements in Part 1 and was not rerun.
DIS = This process failed either the chem./phys. requirements or D 1384 and was disqualified.

mance. A well designed development program, structured initially around the tests outlined in ASTM D 3306 provides the coolant scientist with minimum coolant performance to evaluate a test coolant against the information that could help avoid a catastrophic coolant related failure in fleet testing.

Ultimately, fleet testing is the best measure to differentiate coolant performance. It provides a direct measure of the performance and functionality of the coolant under field conditions and the needed significance to the data obtained from D 3306 testing [*4*]. A test protocol for the testing of engine coolants in light duty vehicles is contained in the ASTM Practice for Testing Engine Coolants in Car and Light Truck Service (D 2847-94). This fleet test was conducted in similar fashion as D 2847 with minor differences.

Fleet Description

In order to observe the performance of these recycled coolants when used in fleet testing, sufficient volume of recycled coolant was processed to enable both GM 1825M/1899M lab testing and fleet testing. Two groups of vehicles were utilized, one for recycled coolants formulated for GM 1825M and one for those formulated to GM 1899M. As previously mentioned, the scope of this fleet test was very limited in that nearly each vehicle contained a different recycled coolant. However, it was possible to maintain relatively good control over variables such as operating parameters, sample and coupon collection, and top offs.

The fleet utilized to observe the performance of the recycled coolants formulated for GM 1825M applications consisted of seven 1991 Chevrolet Luminas each with a 3.1 L engine (cast iron heads) and aluminum radiators. The fleet utilized to observe the performance of the recycled coolants formulated for GM 1899M applications consisted of six 1991 Chevrolet Caprices each with a 5.7 L engine (cast iron heads) and copper/brass radiators.

Vehicle Preparation

Vehicle preparation was different between the two fleet groups. This was primarily due to the existing condition of the cooling systems. The Luminas were in normal condition for vehicles with 40 500 km (25 000 miles). The Caprice fleet, however, was found to have been operated with a substandard coolant which caused deleterious effects to the cooling system as evidenced by varied degrees of solder bloom and the amount of corrosion products in the coolants. As a result, the following procedures were carried out respectively for each group.

Preparation of the Lumina fleet began by draining the pre-test coolant. This was accomplished via the utilization of (nonaqueous assisted) coolant exchange equipment. With the Luminas being relatively new, the presence of original inhibitors on the cooling system components was a concern; therefore, in accordance with ASTM D 2847, each cooling system was treated with an oxalic acid wash followed by a low pH, high borate conditioning coolant to remove the protective layer of the previous coolant and precondition the coolant system. The conditioner was kept in the vehicles for approximately 1621 km (1000 miles). The conditioning coolant was drained and followed by an aqueous flush. New radiators were obtained and thermally mapped and flowed prior to installation on each vehicle. To help assure the complete removal of the conditioning coolant, a used coolant was installed and used in each vehicle for approximately 810 km (500 miles). The used coolant was removed with the coolant exchange equipment used previously. Specimen capsules containing six metal specimen bundles per ASTM 1384 specifications were installed in the heater bypass circuit and the cooling system was filled with the recycled test coolants.

The preparation of the Caprice fleet differed from the Lumina fleet for reasons previously discussed. The pre-test coolant was drained in the same fashion as the Lumina fleet; however, the cleaning was omitted due to the poor condition of the cooling systems. New radiators were obtained and flow checked prior to installation. Specimen capsules were installed and the recycled test coolants inserted.

Before beginning testing, all vehicles were inspected for evidence of leaks, worn belts and hoses, and any components with questionable integrity to minimize the likelihood of failure during the test. The engine was run at high idle until normal operating temperature and flow through the bypass metal specimen capsule were achieved. With the engine off, a sample of coolant was taken and a final inspection for leaks was performed. A lead seal safety wire on the radiator cap was installed to prevent its unauthorized removal.

Test Protocol

A variety of recycled coolants originating from different recycling processes were utilized in the fleet test. Table 13 cross-references the vehicles with the respective process of recycled coolant utilized. The decision process to determine which recycled coolants would be used in the fleet test was based mainly on the volume of available recycled coolant after lab testing although some consideration was given to choosing processes which did not appreciably decrease soluble contaminants.

Mileage accumulation on the 1991 Chevrolet Lumina fleet was held to approximately 3240 km (2000 miles) per month and was comprised of a combination of city, rural, and highway driving. A total of 40 000 test miles (64 372 km) per vehicle was accumulated. Mileage accumulation on the 1991 Caprice fleet was variable due to the nature of their use as police vehicles. A total of 48 600 km (30 000 test miles) per vehicle was accumulated. All vehicles were checked routinely for evidence of cooling system leaks.

Fleet Test Results

Vehicle inspections conducted routinely revealed no leaking coolant pumps nor hoses. No radiator failures were observed during the test. Visual inspections of the coolant recovery tanks did not reveal any evidence of unstable coolants. Calorimeter and flow testing performed before and after testing did not reveal any significant difference in the characteristics of the radiators.

TABLE 13—*Vehicle to process cross-reference.*

Vehicle	Process	Performance Application
Caprice	0*	GM 1899M
Caprice	1	GM 1899M
Caprice	7#	GM 1899M
Caprice	8	GM 1899M
Caprice	Ref.	GM 1899M
Caprice	virgin	GM 1899M
Lumina	0*	GM 1825M
Lumina	0*	GM 1825M
Lumina	0*	GM 1825M
Lumina	8	GM 1825M
Lumina	2	GM 1825M
Lumina	Ref.	GM 1825M
Lumina	virgin	GM 1825M

*These vehicles were run with experimental processes.

Coupon specimen bundles were removed and inspected at 8100 km (5000 mile) intervals [following an initial 16 200 km (10 000 mile) interval].

Copper

Figures 1 and 2 show the resultant weight loss of copper in the Lumina and Caprice fleets, respectively. The GM 6043M control coolant in the Lumina fleet resulted in less than half the copper loss at each test interval than did the reference used coolant. Process 2 slightly outperformed the virgin control coolant while process 8 finished between the virgin control coolant and the reference used coolant. All the processes tested in the Caprice fleet performed comparably to the GM 6038M control coolant. There was a steady increase in corrosion over the course of both fleets, but there was no subsequent acceleration in weight loss. In general, this shows that there is still copper corrosion inhibition provided by the coolants. There is an increase in the spread of the weight losses as the mileage increases indicating that the corrosion inhibition may be breaking down in some of the coolants towards the end of the test (that is, GM 6038M in the Caprice fleet). There is no indication of significant differences between the coolants tested with regards to copper weight loss.

Brass

Figures 3 and 4 show the resultant weight losses for brass in the Lumina and Caprice fleets, respectively. There is some evidence of mileage dependent behavior in the brass weight loss data. There is a pattern of increasing corrosion during the course of the test, although there is little increase in brass corrosion between 16 200 km and 48 600 km in the Lumina fleet and

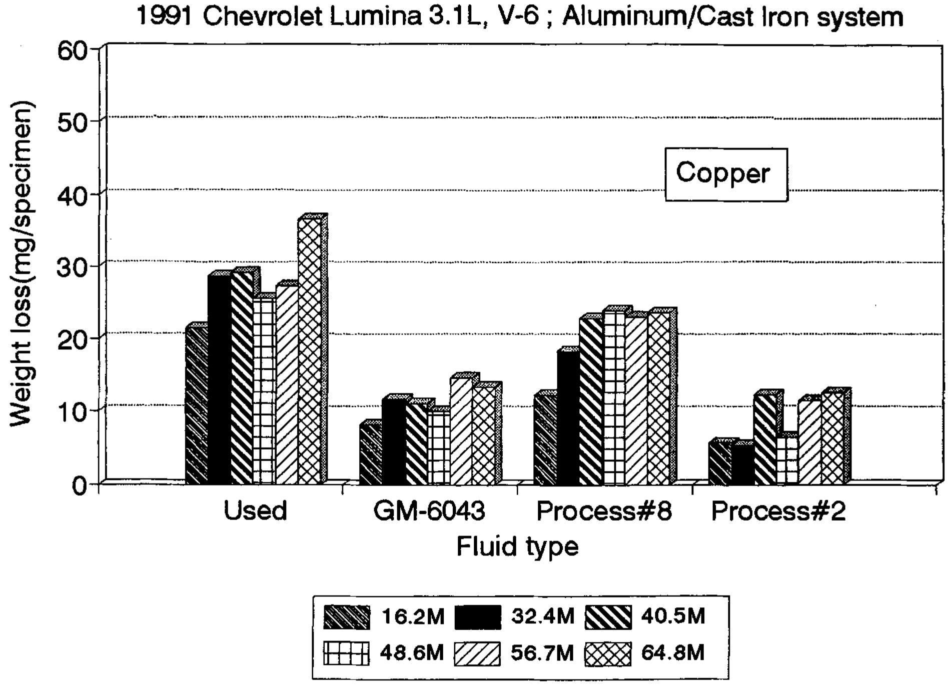

FIG. 1—*Recycled coolant fleet test: high silicate coolant/weight loss data.*

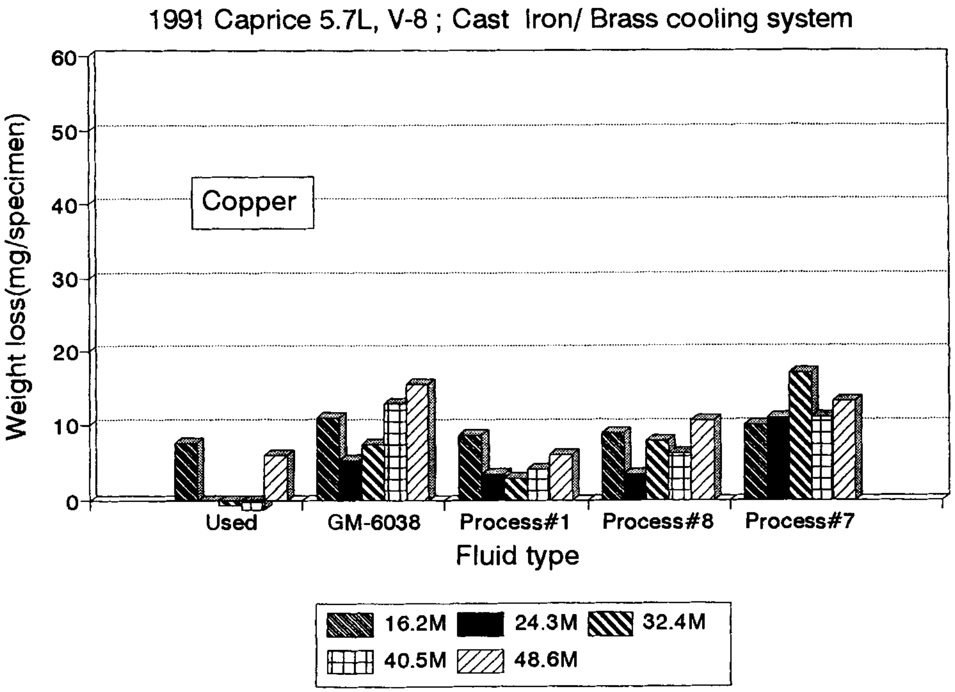

FIG. 2—*Recycled coolant fleet test: low silicate coolant/weight loss data.*

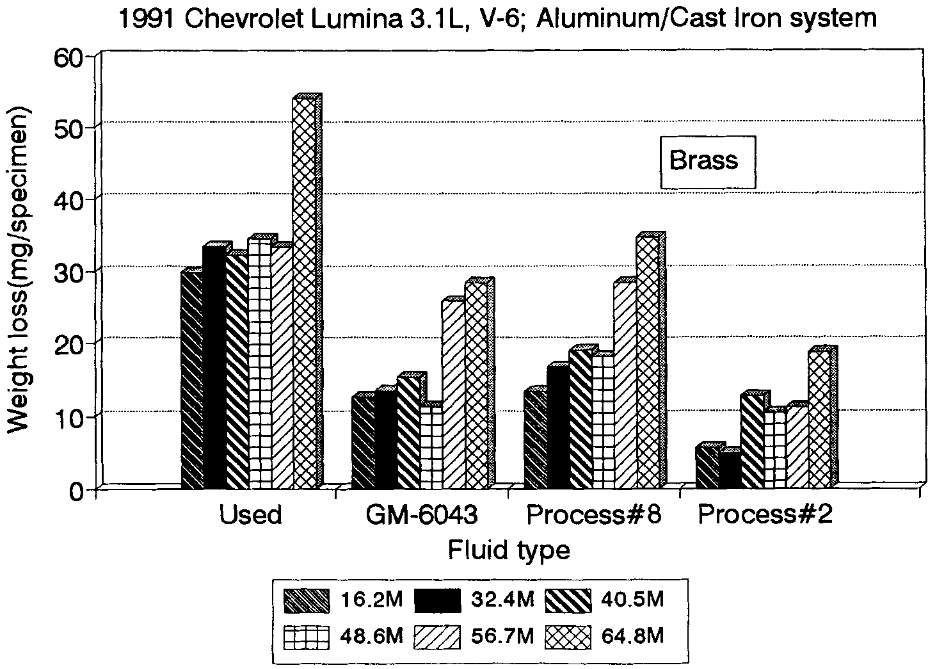

FIG. 3—*Recycled coolant fleet test: high silicate coolant/weight loss data.*

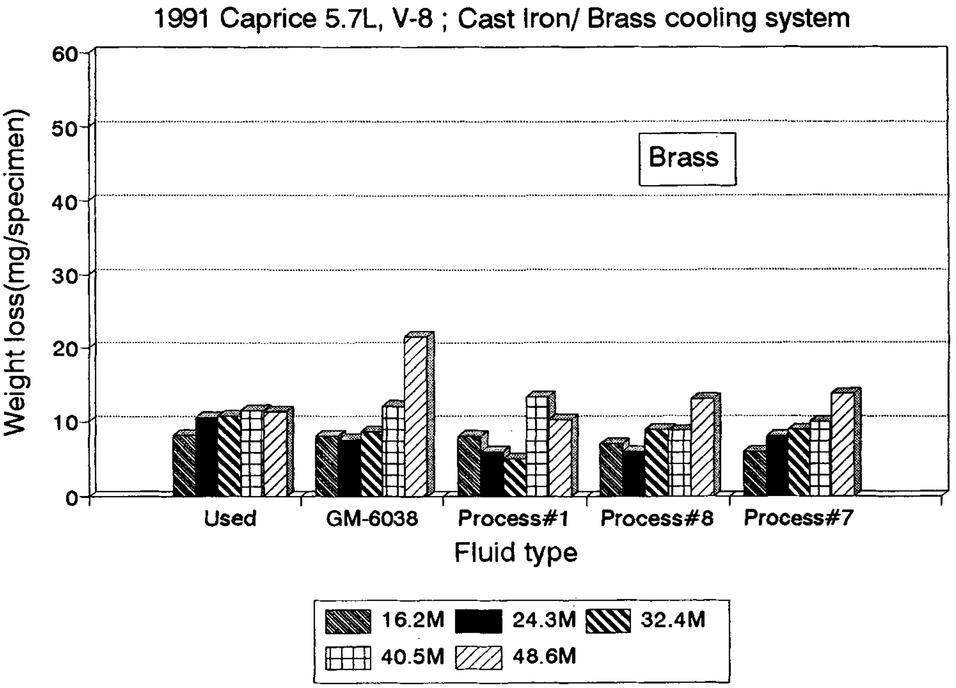

FIG. 4—*Recycled coolant fleet test: low silicate coolant/weight loss data.*

16 200 km and 40 600 km for the Caprice fleet (excluding process No. 7). Both processes tested in the Lumina fleet performed comparably with the GM 6043 control coolant. The reference used coolant resulted in significantly higher weight losses. In the Caprice fleet, all the processes tested performed comparably to the GM 6038M control coolant with the exception of the 48.6 km interval. There were essentially no performance differences between any of the test coolants.

ASTM Solder

Figures 5 and 6 show the resultant weight losses for ASTM solder in the Lumina and Caprice fleets, respectively. There is no indication in the weight loss data of a difference between the two groups of fleets when comparing acceptable and unacceptable coolants. In the Lumina fleet, it would appear that GM 6043M control coolant and the recycled coolant from process No. 8 provided acceptable corrosion protection for ASTM solder throughout the course of the test. In the Caprice fleet, processes Nos. 7 and 8, and the GM 6038M control coolant provided adequate solder protection.

The reference used coolant, and processes Nos. 1 and 2 resulted in unacceptably high weight losses from the beginning to the end of the test in their respective fleets. It is quite apparent that these coolants had no ability to protect the ASTM solder components in the cooling system. Of interest is the fact that the coolants from processes Nos. 1 and 2 passed both D 1384 glassware and D 2570 simulated service testing. Process 1 did extremely well in protecting ASTM solder throughout both the D 1384 and D 2570 tests (3 and 1 mg, respectively). While the solder loss in D 1384 for process No. 2 was below the GM limit of 20 mg, it was somewhat higher (at 13 mg) than the other processes (at 1, 2, 4, 3 mg). The only other process (No. 3) with a comparable weight loss (14 mg) failed D 4340 and consequently was disqualified from additional testing.

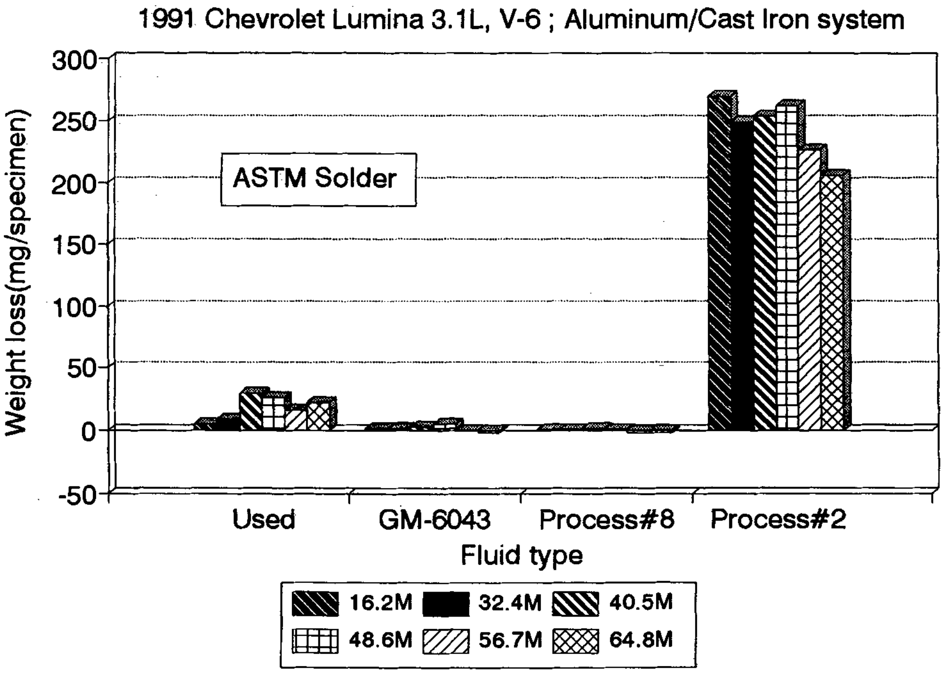

FIG. 5—*Recycled coolant fleet test: high silicate coolant/weight loss data.*

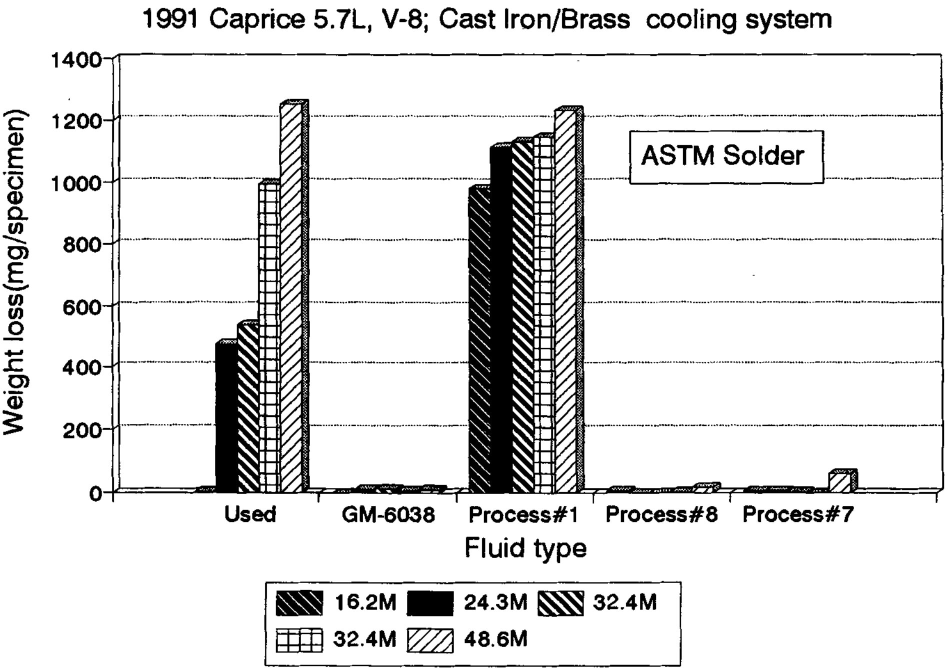

FIG. 6—*Recycled coolant fleet test: low silicate coolant/weight loss data.*

Steel

Figures 7 and 8 show the resultant weight losses for steel in the Lumina and Caprice fleets, respectively. In the Lumina fleet, both recycled coolants tested resulted in slightly lower weight losses than the GM 6043M control coolant. In the Caprice fleet, recycled coolants from processes Nos. 7 and 8 performed comparably to the GM 6038M control coolant. Both the virgin control coolants and the recycled coolants from the aforementioned processes proved capable of protecting steel throughout the test.

The reference used coolant and the recycled coolant from process No. 1 (Caprice fleet) generated high weight losses of steel. Recycled coolant from process No. 1 did extremely well in both the D 1384 and D 2570 laboratory tests (1 mg each). It is likely that the inability of the reference used coolant and the recycled coolant from process 1 to protect steel is attributable to the reference used coolant's low pH start point compared to the other coolants (see Fig. 14), as well as the characteristic depletion rate of phosphorus for both the reference used coolant and the recycled coolant from process No. 1 (see Figs. 13 and 15).

Cast Iron

Figures 9 and 10 show the resultant eight losses for cast iron in the Lumina and Caprice fleets, respectively. In the Lumina fleet, recycled coolants from both processes resulted in slightly lower weight losses than the GM 6043 control coolant. In the Caprice fleet, the GM 6038 control coolant performed very well with low weight losses, as did process No. 8.

The used reference coolant, and the recycled coolants from processes Nos. 1 and 7 (in the

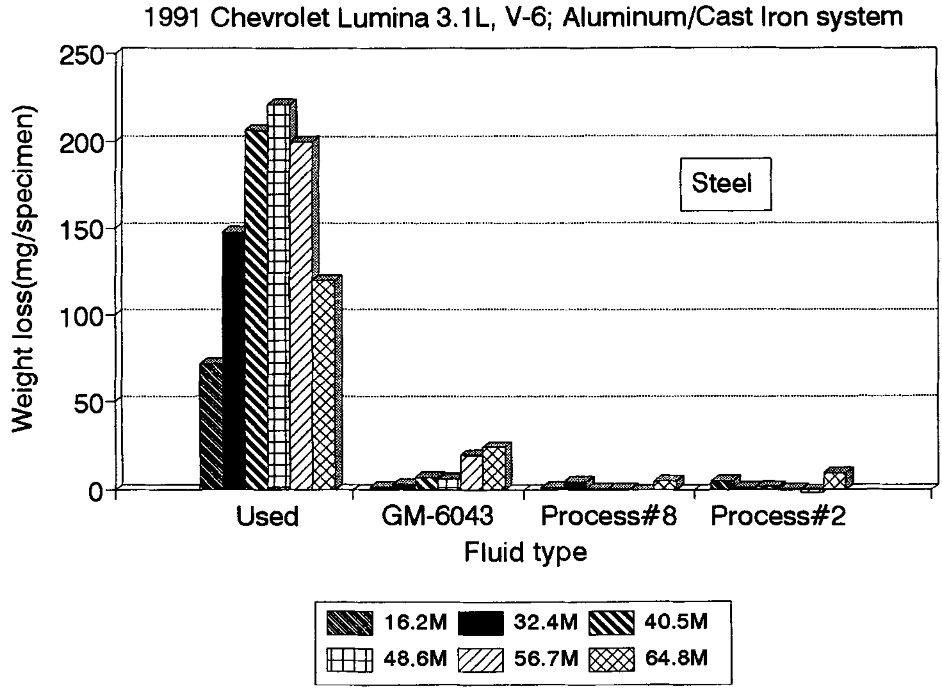

FIG. 7—*Recycled coolant fleet test: high silicate coolant/weight loss data.*

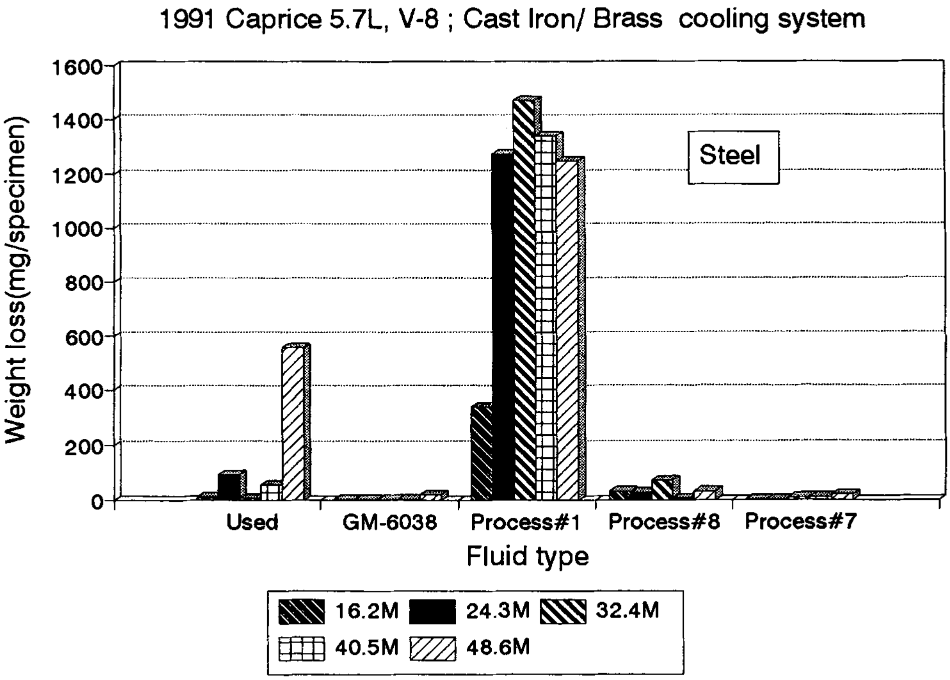

FIG. 8—*Recycled coolant fleet test: low silicate coolant/weight loss data.*

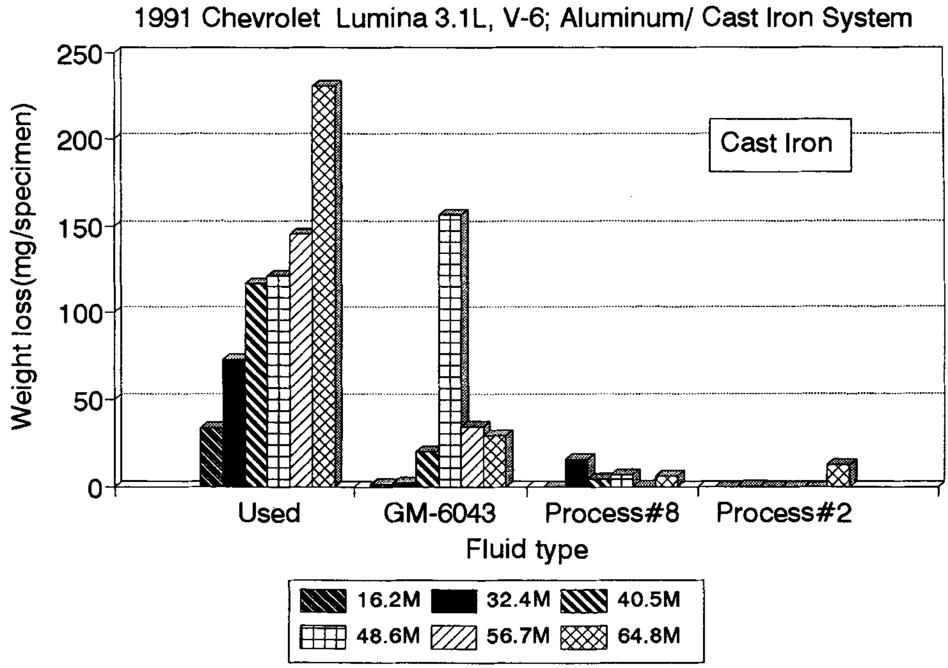

FIG. 9—*Recycled coolant fleet test: high silicate coolant/weight loss data.*

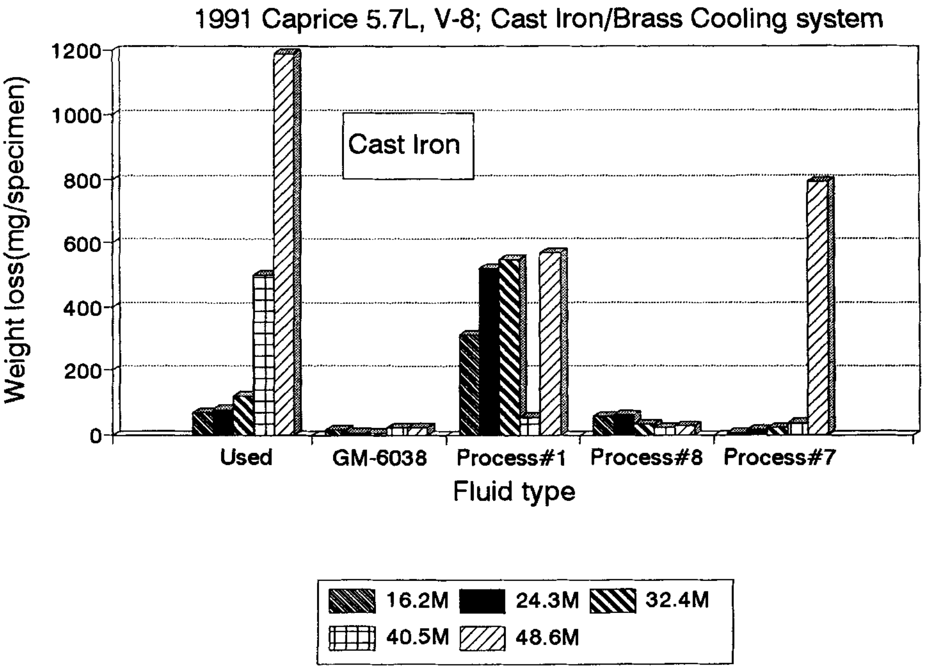

FIG. 10—*Recycled coolant fleet test: low silicate coolant/weight loss data.*

Caprice fleet) resulted in high levels of weight loss. Recycled coolant from process No. 1 performed extremely well in both the D 1384 and D 2570 tests (1 mg and 2 mg, respectively). As with the steel results, it is likely that the inability of the used reference coolant and the recycled coolant from processes Nos. 1 and 7 to protect cast iron is attributable to the reference used coolant's low pH start point compared to the other coolants (see Fig. 14), as well as the characteristic depletion rate of phosphorus for both the used reference coolant and the recycled coolant from processes Nos. 1 and 7 (see Figs. 13 and 15).

Aluminum

Figures 11 and 12 show the resultant weight losses for aluminum in the Lumina and Caprice fleets, respectively. There is indication of significant differences between the high and low silicate coolants where aluminum weight loss is concerned. In the Lumina fleet, aluminum remained well protected with the GM 6043M control coolant, both recycled coolants, and even the reference used coolant. Coupon weight gains were achieved indicating well passivated surfaces. Both processes Nos. 2 and 8 performed well in the D 1384 test (2 mg, 1 mg) and the D 2570 test (9 mg, 1 mg). The results of the Caprice fleet differed from the Lumina fleet. Processes Nos. 7 and 8 maintained effective corrosion protection throughout the test. However, the effectiveness of the GM 6038M control coolant appeared to be mileage dependent and resulted in significant weight losses in the last three test intervals. Process No. 1 experienced the highest weight losses, its performance on D 1384 was 1 mg, and 3 mg on D 2570. The reference used coolant displayed a pattern of increasing corrosion during the test, resulting in a relatively high weight loss.

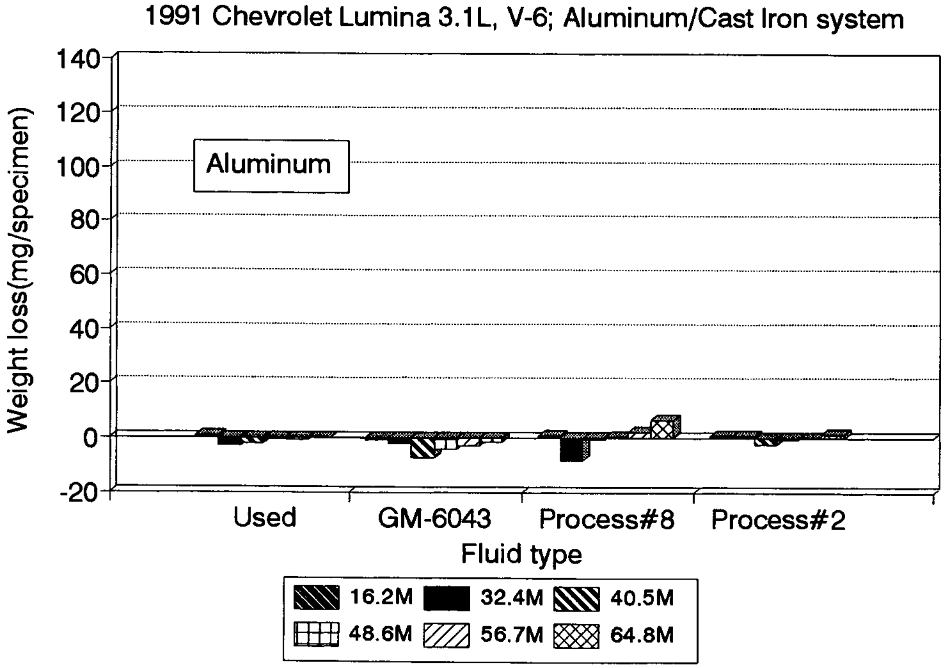

FIG. 11—*Recycled coolant fleet test: high silicate coolant/weight loss data.*

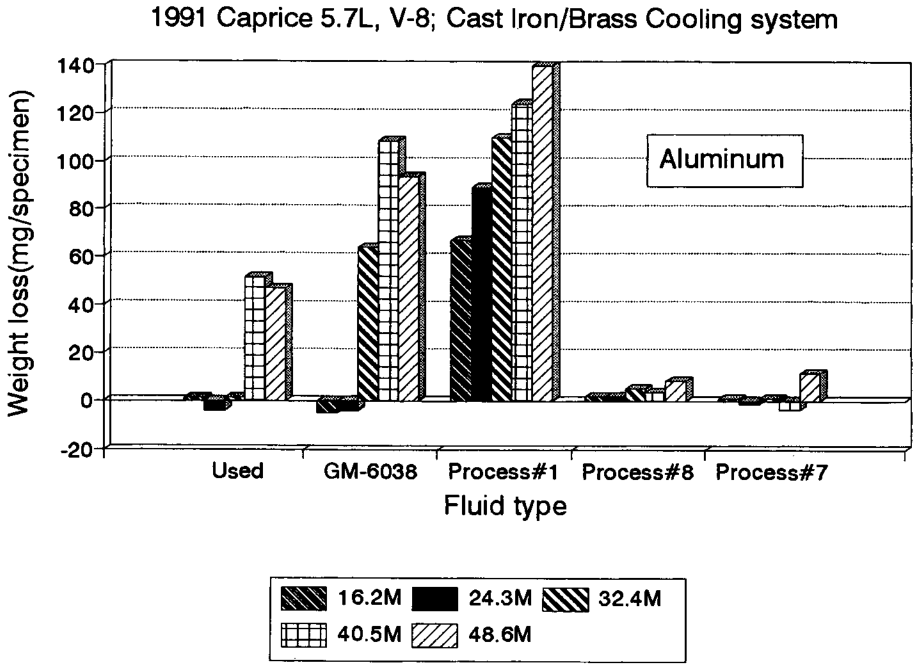

FIG. 12—*Recycled coolant fleet test: low silicate coolant/weight loss data.*

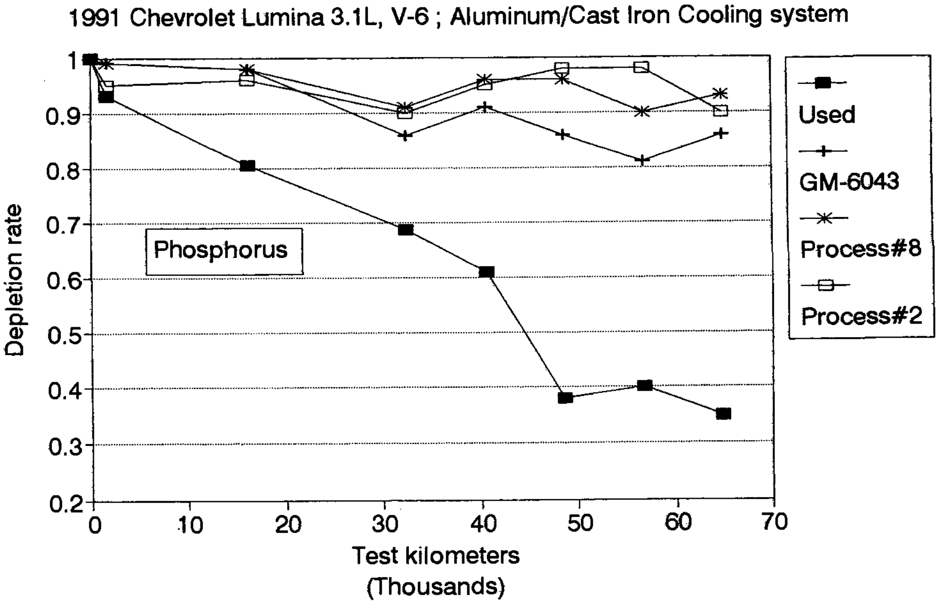

FIG. 13—*Recycled coolant fleet test: high silicate coolant/solution data.*

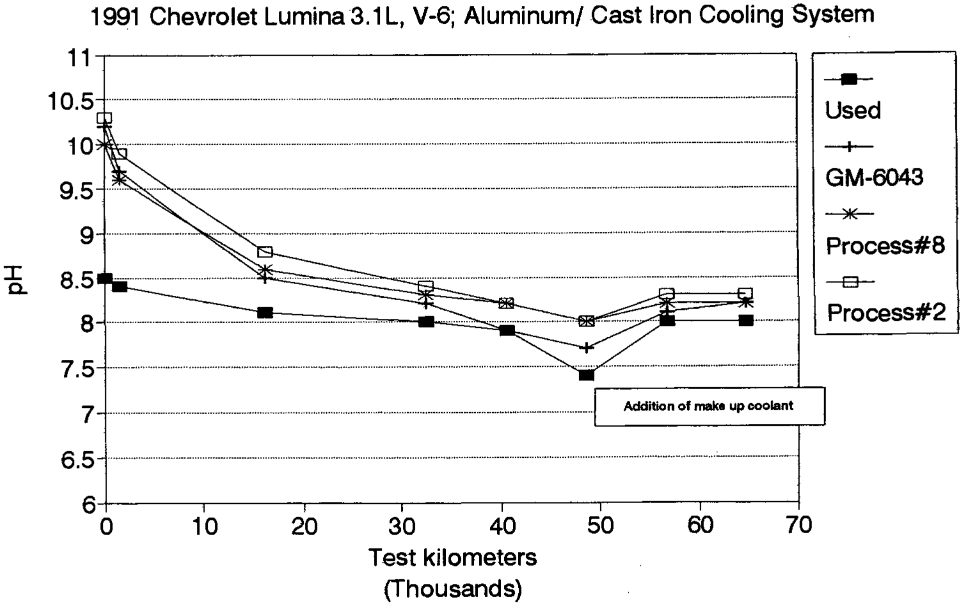

FIG. 14—*Recycled coolant fleet test: high silicate coolant/solution data.*

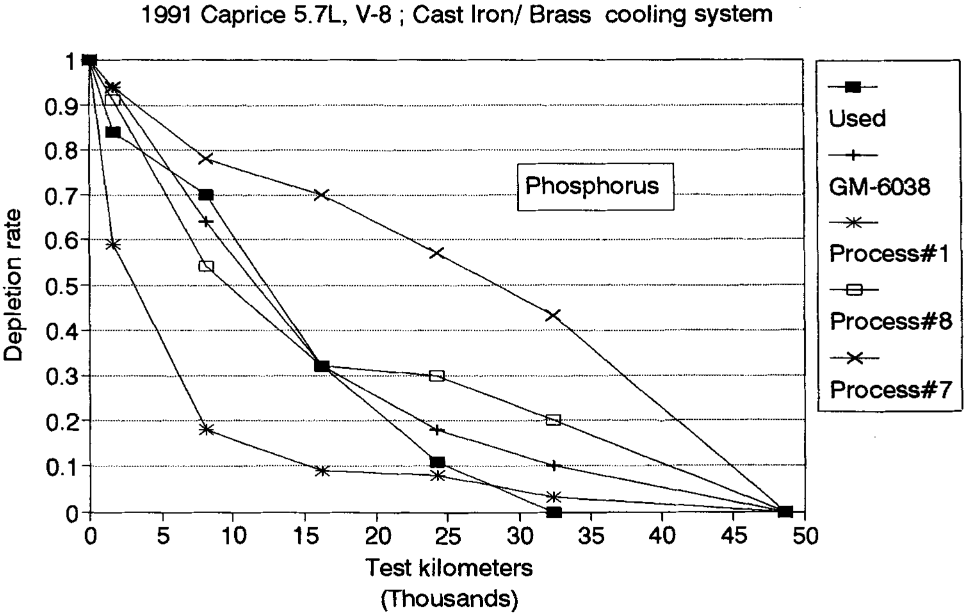

FIG. 15—*Recycled coolant fleet test: low silicate coolant/solution data.*

Conclusions

The data presented in this paper support the position for additional vehicular testing in addition to existing laboratory-oriented performance tests when evaluating used or recycled engine coolants. Several of the recycled coolants evaluated here experienced performance difficulties in fleet testing despite their acceptable performance in GM 1825/1899M (laboratory) performance testing. The virgin coolants used as controls in this study generally provided acceptable performance in both laboratory and fleet testing, which in part supports the premise that ASTM (laboratory) test procedures were developed primarily for virgin coolant applications and should not be relied upon solely in situations where used or recycled coolants are being tested. Previous (undocumented) fleet testing supports the observations made in this study and confirms the need for the addition of vehicle testing where recycled coolants are concerned.

The reference used coolant of the present study was not only representative of typical used coolant but can serve as a testimony to the robustness of the coolants used in the U.S. marketplace. This coolant demonstrated its ability to meet much of the performance criteria of GM 1825M and GM 1899M, namely the glassware, simulated service, and pump cavitation tests; however, it was not capable of meeting the requirements of the heat-rejecting aluminum protection test, the foam test, or storage and stability testing. The reference used coolant performed poorly in both the Lumina (high silicate) and Caprice (low silicate) fleet tests. Unacceptable weight losses were incurred on various metals for each vehicle operated with the reference used coolant. While no statistical inference can be drawn from the fleet data acquired in this study, it does suggest the need for conducting fleet testing in addition to laboratory testing to determine the true capabilities of both recycled and used coolants.

Once again, the *overall* effectiveness of the coolant recycling process demonstrated itself to be dependent upon the appropriate combination of process and reinhibitor formulation. Processes evaluated in this study included simple and more complex configurations of portable recycling systems as well as costly offsite processes. Throughout this and other studies [5], recycling processes managed to meet, or failed to meet, performance requirements, regardless of the cost, complexity, or level of acceptance of the process to the industry. In order for the coolant recycling process to be successful, the appropriate reinhibitor must be identified via adequate testing and then employed.

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Engine Coolant Characteristics and Quality

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Methods and Equipment for Engine Coolant Testing

REFERENCE: McCracken, S. A. and Beal, R. E., "**Methods and Equipment for Engine Coolant Testing,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 319–326.

ABSTRACT: Methods and equipment for engine coolant testing are described covering some of the newer standard procedures and proposed additions to the tests used. Methods and equipment gradually evolve according to the needs of the automotive industry. A continuous process is involved in design, safety, operator convenience and test requirements. The ASTM D 4340 test equipment with improvements is discussed. The ASTM D 3147 stop leak test has been substantially revised and updated. A new hot surface scale deposit test procedure and equipment are presented. The ASTM D 2809 test is reviewed with commentary on the current test procedure. Simulated service testing for long-life coolants requires changes to the present D 2570 standard, with consideration of including a more dynamic test similar to European approaches.

KEYWORDS: coolant test equipment, ASTM D 4340, ASTM D 3147, scale deposits, ASTM D 2809, simulated service, long-life coolant

Tests for evaluation of engine coolants and cooling system components to ASTM standards require specialized equipment to be constructed. Testing engine coolants and cooling system components often requires nonstandard or experimental approaches to achieve the desired goal. Unique test machinery and procedures developed for a specific need can lead to new or revised ASTM standards. In addition, ASTM coolant standards are dynamic, and evolve along with the needs and trends of the automotive industry. Thus it is a continuous process to design, build, operate, and update coolant testing machinery. Enhanced ASTM standard machines which are improved for safety and operator convenience have been fabricated, along with modified standard machines, and entirely unique machines which could result in revised standards and new standards. This report discusses some of these new machines and possible new standards.

ASTM D 4340 Test

An example of an existing ASTM standard which is enhanced for greater safety and higher performance is the ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions (D 4340-96) hot surface corrosion test (Fig. 1). The D 4340 apparatus simulates the hot cooling jacket surface of an aluminum engine which is in contact with engine coolant. An aluminum test coupon is heated from underneath, while engine coolant sits on its top surface. A good coolant will protect the aluminum coupon from corrosion, while a poor coolant will allow the coupon to be pitted and eroded.

Band heaters are used to heat a solid metal stem under the test coupon. Test coupon tem-

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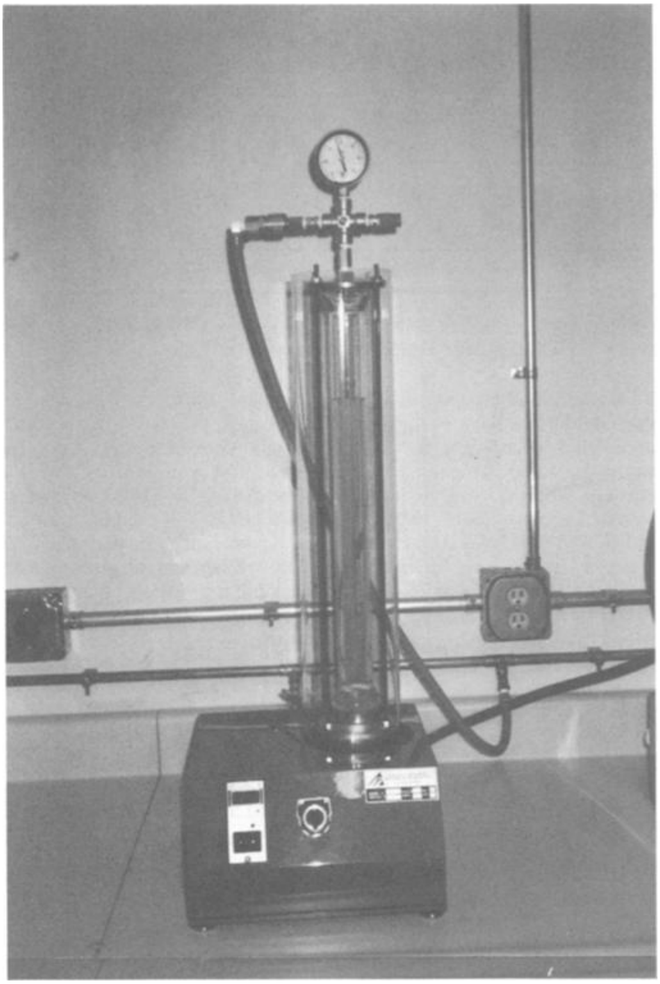

FIG. 1—*Free-standing equipment for ASTM D 4340 test with built-in safety shield and fluid containment vessel.*

perature is regulated by a digital temperature controller that monitors a thermocouple probe inserted in the coupon. The standard design uses a simple thermostatic switch for a safety cutout in case of an over-temperature condition.

A few years ago, propylene glycol coolant was being heavily tested prior to introduction, and some companies wanted to test anhydrous formulas on the D 4340 machine at temperatures as high as 400°F (204°C). The thermostat cutout of the standard design does not allow operation over 275°F (135°C), so a second digital temperature controller was added to act as an adjustable over-temperature safety. The adjustable over-temperature safety allowed the cutout temperature to vary along with the operating temperature, while maintaining a constant cutout margin, typically 100°F (37.7°C).

An over-temperature safety is important on a D 4340 machine because it is possible for the control thermocouple to slip out of the test coupon. This will fool the controller into thinking that the sample is much cooler than it really is, and turn the heaters on continuously. At best this will ruin the prepared surface of the test coupon from boiling; at worst it could lead to a test cell explosion or electrical fire.

Another enhancement of the D 4340 standard was inspired by an O-ring failure which allowed an irreplaceable coolant sample to spill out all over the workbench at 270°F (132°C). As a result, all units now incorporate an integral catch basin in the machine cabinet. This makes the machine safer to be around, and allows the possible re-use of a spilled sample. Both of these modifications have no effect on the standardized performance of the test.

ASTM D 3147 Test

An enhanced machine construction which could result in a modification of the ASTM standard is the ASTM Test Method for Testing Stop-Leak Additives for Engine Coolants (D 3147-94) test machine. After review, it was apparent the standard design was inconvenient to operate, and it lacked basic safety systems for protection in the event of low coolant level, heater overtemperature, etc. The ASTM stop-leak standard machine was moderately redesigned with more elaborate controls and greater fluid capacity (Fig. 2). This new equipment has performed more than 50 successful tests.

The test apparatus is a stainless steel enclosure that contains engine coolant and the stop-leak material under test. The coolant is electrically heated and circulated within the enclosure. Brass plates required by the standard were made with precisely EDM-machined holes and slots and mounted to the sides of the enclosure. The test solution is pressurized to force the coolant through the openings in the plates. Plates of different size openings are tried until the largest opening that can be plugged is determined according to the standard.

Experience with this test also identified some shortcomings in the test procedure. It is somewhat vague on important aspects of administering the test. The standard was rewritten to reflect the new machine design and to incorporate refinements to the operating procedure. The rewritten standard is currently in review by the ASTM D 15 Coolant Committee.

Operation of the D 3147 test revealed other important information for application of stop-leaks. Some stop-leak formulas caused tremendous foaming of the test coolant. Preventing coolant foaming is very important for efficient cooling and corrosion prevention. A reference coolant is utilized as a baseline for equipment operation and stop-leak evaluation. Some stop-leak formulas totally overpower the normal antifoaming additives used in the engine coolant.

The existing D 3147 method standard and the rewritten version do not assign a pass or fail performance requirement on tested stop-leak materials. The discovery of the poor foaming characteristics of some materials led to a proposed performance specification which includes minimum hole and slot size leak stop performance, with a specific emphasis on the need to meet ASTM foaming requirements, which is currently being adopted.

Hot Surface Scale Deposit Test

A test procedure introduced some years ago to address scale deposition in engines that has not yet been seriously considered for an ASTM engine coolant standard is the hot surface scale deposit test. This test simulates the hot walls of an engine cooling jacket that is exposed to coolant, similar in concept to the D 4340 test described before. The scale deposit test differs in that the scale surface is noncorroding, and instead tests a coolant's ability to prevent scale formation on the heated surface. The scale-forming surface is electrically heated stainless steel. A pump draws test coolant from the main tank and circulates it past the scale surface at variable

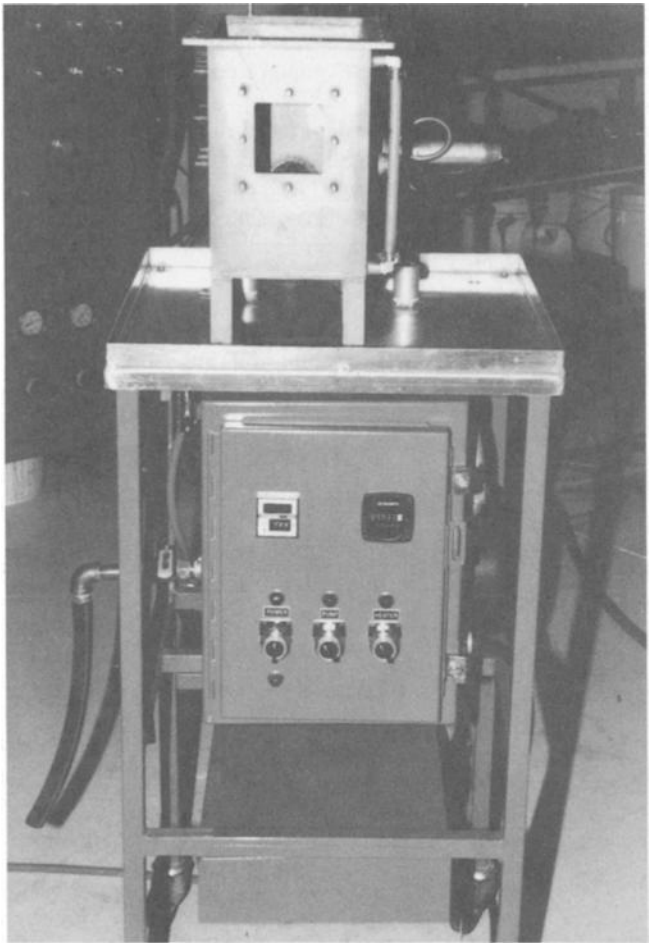

FIG. 2—*New ASTM D 3147 stop-leak test apparatus built to NEMA standards with interlocking safety devices.*

flow rates. The heater is on continuously. Test solution temperature is regulated by a digital temperature controller which occasionally activates a liquid-to-liquid heat exchanger coil in the main tank. (See Fig. 3.)

This procedure has evolved into an experimental engine coolant test from an existing test of scaling properties for cooling tower water. Engine coolant scaling experiments were performed on earlier equipment by Grace Dearborn, Fleetguard, BASF, ICI, and others. Results were encouraging, but reported as inconclusive because of the relatively low heat density available in the original design.

Fleetguard and their subsidiary, Dober of Glenwood, requested a custom hot surface scale rig with much higher heat density and greater flow rate than previously utilized. Specific test parameters were determined for the machine. The new design required about triple the heat density on the heated surface, to 90 000 btu/hr/ft^2, and a variable flow rate of 2 to 10 gal/min (7.6 to 38 L/min) past the scale surface.

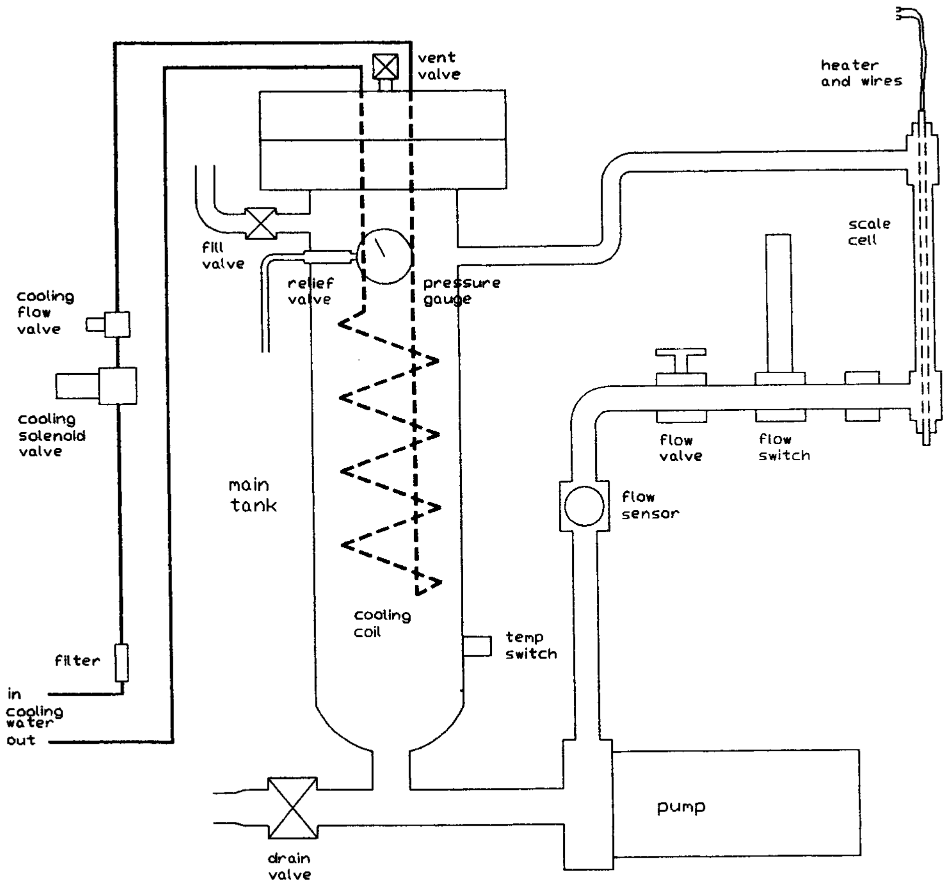

FIG. 3—*Schematic diagram of hot surface scale deposit test rig.*

The resulting machine is shown in Fig. 4. This machine is now in operation. The higher heat density was achieved by using a physically larger heater, forming scale directly on the heater sheath. Initial testing indicates rapid and consistent scale forming is now possible. Further positive results from this new design may lead to development of a scaling resistance standard for engine coolant.

ASTM D 2809 Test

There has been some speculation lately about the future of the ASTM Test Method for Cavitation Corrosion and Erosion-Corrosion Characteristics of Aluminum Pumps with Engine Coolants (D 2809-94). Changes to more modern pumps are periodically required to keep the standard up to date. An alternative standard machine is also possible with a current pump and aluminum plumbing to create an all-aluminum pump cavitation test that would more accurately simulate the majority of cars being manufactured today. This would require an additional standard to the existing D 2809 test, which should remain in service.

An important aspect of the existing D 2809 standard test procedure is unclear as written. The standard procedure at 8.4.2 calls for heating the coolant to 95 to 100°F (35 to 37.7°C),

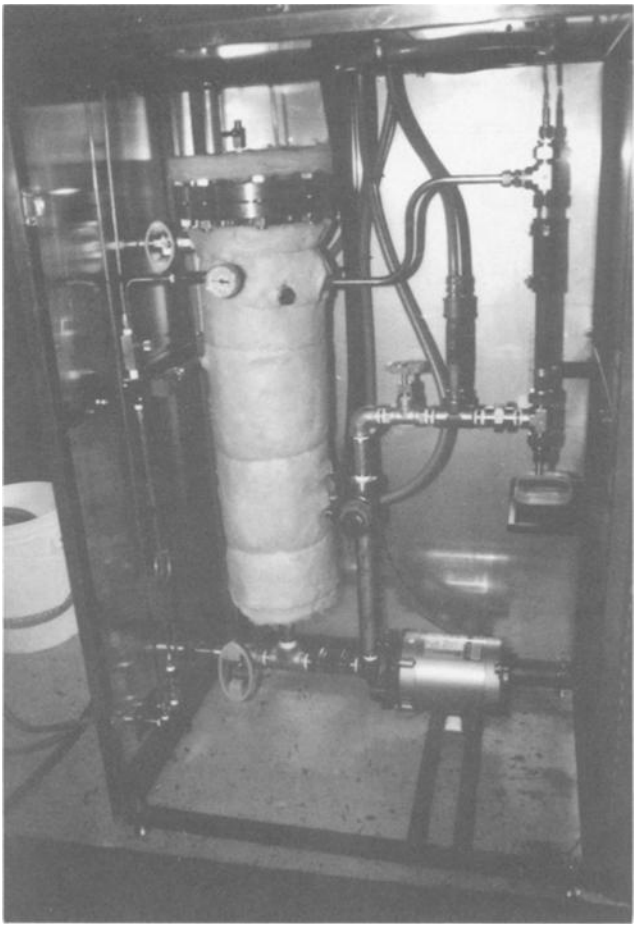

FIG. 4—*Hot surface scale deposit test machine.*

then pressurizing the system to 15 ± 0.5 psi (103.4 ± 3.4 kPa), then closing the throttling valve to provide a gage reading of 2.0 in. Hg vacuum at the pump inlet. Two inches Hg is equivalent to approximately 1 psi (6.9 kPa) of pressure (1 atm = 14.7 psia [101.3 kPa] = 29.9 in. Hg). Thus the standard is calling for a 16 psi (110.32 kPa) pressure drop across the throttling valve, 15 psig (103.4 kPa) system to 2.0 in. Hg gage vacuum.

This pressure drop condition can be achieved at a fluid temperature of 100°F (37.7°C) or less, but it requires closing the throttling valve almost entirely. The problem develops as the coolant solution heats to the operating temperature of 235°F (112.7°C). At or before this temperature, the pressure differential across the throttling valve is lost. The machine operates with the pump inlet pressure the same as the system pressure for virtually the entire duration of the test. This means there is little or no flow, and no normal pumping. This lack of pumping is easily demonstrated by monitoring the load on the drive motor: there is no load, as the pump and motor are free-wheeling. This is largely a cavitation condition with very little flow.

The standard specifies a test solution of only 16.7% glycol, yet the test operates at 235°F

(112.7°C). It is probable the hot coolant flash-boils to vapor when it enters the low-pressure area at the pump inlet. The bubble of steam would fill the pump cavity, effectively creating a loss of "prime," and minimizing flow. The nearly closed throttling valve would prevent normal flow from resuming by not passing enough fluid to flush the foam out of the pump chamber.

The low or nonexistent flow through the pump at the standard operating parameters is clearly not relevant to real vehicle operation. Of course the test is attempting to create accelerated corrosion conditions, which is the main objective. But it would make more sense if there was greater coolant flow through the pump, with a lesser, though still significant, pressure drop across the throttling valve. A more reasonable pressure drop would still allow the desired cavitation and accelerated corrosion to occur, while more accurately reproducing real flow conditions.

The vapor pressure of a 16.7% glycol/water solution at 235°F (112.7°C) is approximately 22 psi (151.6 kPa) absolute, or 7 psi (48.2 kPa) gage pressure at sea level. Below this pressure, the glycol/water mix will boil at 235°F (112.7°C). Therefore, for sea level D 2809 testing, there can be no more than an 8 psi (55 kPa) pressure drop across the throttling valve, that is, a drop from 15 psig (103.4 kPa) in the system to 7 psig (48.2 kPa) at the pump inlet. At inlet pressures below that point, the coolant will boil to some extent, and flow may stop.

The point of standardized testing is to ensure consistent results between facilities. But the D 2809 test is particularly sensitive to seemingly minor variables, such as altitude. In addition, machines made at different facilities will always contain some variations due to component quality and many other factors. The standard procedure could specify experimenting to establish the maximum pressure drop attainable at operating temperature before pumping stops on each particular machine. The test could then operate at a pressure 0.5 to 1.0 psi (3.4 to 6.9 kPa) above the cutoff point. This would neutralize significant variables like pressure gage bias and facility altitude. A modified pump test may be desirable.

Long-Life Coolant Stimulated Service Testing

Testing methods for long-life coolants are an open issue. Besides the ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light-Duty Service (D 3306-94) battery of tests, other approaches are needed to simulate long-life effects. Insight into the peculiarities of long-life coolants, and how that may lead to new test procedures and machinery, can be determined only by practical testing. It is important to continue to advance the state of the art of coolant testing.

European manufacturers have progressed further with simulated service testing than those methods generally available in the United States. An example is the FVV test, developed at Darmstadt University in Germany. This is an elaborate test that is similar in some ways to both the ASTM Test Method for Simulated Service Corrosion Testing of Engine Coolants (D 2570-96) and D 4340. It uses a dynamic fluid flow circuit that heats and cools the test fluid to greater temperature extremes than U.S. testing methods. The test fluid flows at a constant rate past corrosion coupons similar to the D 2570. The fluid flows through separate chambers for heating and cooling, and a small air bleed is included to entrain oxygen. The coolant is separately tested for cavitation corrosion before and after the FVV test period.

Another European coolant test is the MTU test for corrosion and cavitation. This test can be run independently, or directly coupled to the FVV apparatus as the modified test. A mechanically induced vibration is applied to a test fluid chamber to create cavitation corrosion. The vibration frequency is approximately four KHz, and the vibration intensity can be varied to increase or decrease the cavitation rate. Again, the approach is a more elaborate and dynamic test of materials in a flowing engine coolant circuit to better simulate actual vehicle operation.

The FVV and MTU tests have been adopted by Mercedes and some other European automobile manufacturers. MTU has also developed a flowing coolant hot surface corrosion test. Details of most of these tests were given in a paper by Liebold and Starke in *ASTM STP 887* [*1*].

The introduction of long-life coolant/antifreeze with the obvious goal of a fluid that requires no change for the life of the vehicle presents interesting and challenging demands and requirements. The total cost of testing must not be prohibitive, to prevent healthy competition between coolant suppliers, but must represent a realistic assessment for the vehicle manufacturers.

The future of engine coolant testing lies in a combination of individual simple tests that address a very specific corrosion resistance requirement, such as the ASTM D 4340 hot surface or coupon exposure in the ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384-96) or D 2570, with complex approaches adopted by the Europeans in FVV and MTU. There is a clear need for an acceptable simulated service test between the ASTM D 2570 program and a fleet evaluation for North American purposes because of the combination of cost and time involved with the latter and the inadequacy of the former for long-term testing.

A simple, effective means of gathering further information from current testing is to include the ASTM planned interval corrosion coupons, instead of identifying a corrosion condition at one point in time. This test is defined in the ASTM Practice for Laboratory Immersion Corrosion Testing of Metals (G 31-72 (1995)) on laboratory immersion, corrosion testing of metals. This expedient will greatly enhance performance data without much increase in cost. An air bleed system and doubling the time of the ASTM D 2570 test would also be beneficial as an intermediate step in addition to the planned interval coupons. Radiator pitting and corrosion analysis achieved in a progressive and overall manner by utilizing two radiators in the test can also be performed in the same test run, in a similar manner to that described by Beal and El Bourini in a paper in *ASTM STP 1192*.

A modified ASTM D 2570 with planned interval corrosion coupons and double radiators with pitting and corrosion analysis during the test can be introduced now as an advanced evaluation of long-life coolants in the United States, and for the global program in conjunction with the modified FVV test and MTU cavitation. These methods and equipment are recommended for consideration by the U.S. coolant industry to evaluate modern engine coolant with high corrosion protection and long service life.

Reference

[*1*] Liebold, G. A. and Starke, K. W., "European Test Methods for Automotive Coolants: Experience Gained in Recent Cavitation and Corrosion Tests," *Engine Coolant Testing, Second Symposium, ASTM STP 887*, R. E. Beal, Ed. American Society for Testing and Materials, Philadelphia, 9–10 April 1984.

Steven A. Schwartz[1]

Silicate Stabilization Studies in Propylene Glycol

REFERENCE: Schwartz, S. A., "**Silicate Stabilization Studies in Propylene Glycol,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing Materials, 1999, pp. 327–351.

ABSTRACT: In most North American and many European coolant formulations, the corrosion inhibition of heat-rejecting aluminum surfaces is provided by alkali metal silicates. But, their tendency towards polymerization, leading to gelation and/or precipitation, can reduce the effectiveness of a coolant. This paper presents the results of experiments which illustrate formulation-dependent behavior of inorganic silicate in propylene glycol compositions. Specific examples of the effects of glycol matrix, stabilizer type, and hard water on silicate stabilization are provided.

KEYWORDS: aluminum corrosion, alkali metal silicates, organosilicon stabilization, hard-water stability, mineral scale deposition

In most North American engine coolant formulations, the corrosion inhibition of heat-rejecting aluminum surfaces is mainly provided by alkali metal silicates. Sodium silicate inhibitors are often used for this function. The operative species is monomeric silicate (SiO_3^{2-}, $HSiO_3^-$) which complexes with aluminum to form a protective coating on the surface. However, the unstable tendency of silicate towards polymerization, leading to gelation and/or precipitation, can reduce the effectiveness of a coolant. The industry has addressed the issue of silicate instability through the incorporation of organosilicon surfactants into the coolant formulations. These materials improve the storage stability and aluminum protection capability of the coolant by interacting with soluble inorganic silicate species and preventing precipitation in the glycol matrix. They are extremely important for availing concentrations of monomeric silicate in working antifreeze solutions that are required for adequately protecting aluminum surfaces of a cooling system in service. The objective of this paper is to report results of different experiments that describe the composition-dependent behavior of silicate in propylene glycol (PG) coolant formulations.

Silicate Chemistry [*1*, *2*]

Polymerization

In aqueous solutions, solid silicate is converted to monosilicic acid (Si(OH)4) and, in the presence of base, dissolves into monomeric silicate ions

$$SiO_2(s) + 2H_2O \leftrightarrows Si(OH)4$$

$$Si(OH)4 + M^+ \leftrightarrows (HO)_3SiO^- + H_2O + M^+$$

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Polymerization of silicate leading to insoluble gelation involves two stages: (1) condensation of monomeric species into growing polymer colloids; and (2) particle agglomeration.

Condensation and Colloidal Particle Growth—Condensation of monomeric silicic acid occurs in the presence of ionized species

$$(HO)_3SiO^- + HOSi(OH)_3 \leftrightarrows (HO)_3SiOSi(OH)_3 + OH^-$$

$$m(HO)_3SiO^- + (HO)_3(SiOSi)_n(OH)_3 \leftrightarrows \text{oligomer} + nOH^-$$

$$m(HO)_3SiO^- + \text{oligomer} \leftrightarrows \text{polymer colloid}$$

Soluble colloidal particles are in equilibrium with monomeric silicate. Monomeric silicate concentration decreases with increasing particle size. The increasing ionization constants with the increasing state of coordination indicate that monomeric silicate is converted more readily as dimers, oligomers, and higher polymers are formed. Larger particles grow at the expense of smaller ones.

Particle Agglomeration and Gelation—The solubility of silica particles decreases as the concavity of their surfaces increases and approaches zero as they impinge. This occurrence is referred to as "depletion flocculation." Any monomeric silicate present deposits at the point of contact, and this results in particle coalescence.

The tendency of silica particles to grow or coalesce or both is affected by initial SiO_2 concentration, temperature, pH, and other compositional features of the host matrix. For example, hydroxyl ions catalyze dissolution of silica particles. Generally, high pH results in low-diameter silica colloids and high monomeric silicate solubility. High SiO_2 concentrations increase the probability of interparticle collisions, thereby reducing monomeric silicate solubility.

Silica has low solubility in methanol. Higher alcohols lead to even lower solubility. Ester formation is apparently involved. It is not surprising, then, that stabilizing soluble silicate in glycol-based matrices is especially challenging. These difficulties are compounded for coolant formulations, which typically also include bases, buffers, inorganic and organic corrosion inhibitors, hard-water cations, and antifoaming surfactants. The presence of corrosion metals and the production of aldehyde, ketones, and other organic acid glycol decomposition products further influence silicate solubility. Although developing a working antifreeze formulation is not contingent upon accounting completely for each of these factors, it is imperative that the silicate gelation tendency is suitably suppressed.

Stabilization

Theory—The objective of stabilization in coolants is to prevent the irreversible formation of insoluble polysilicate gel, thereby maintaining a distribution of soluble silica colloids which is in equilibrium with monomeric silicate. Key benefits from stabilization include extended storage lifetime and aluminum protection in working antifreeze solutions. It is also important to avoid heat transfer problems that may result from insoluble deposits that may restrict flow in the engine cooling system. Commonly used commercially available silicate stabilizers are based on organosilicon structures.

Stabilization in coolant concentrates involves interactions between silica colloids and the organosilicon stabilizer molecules $R\text{-}Si(OH)_3$, where R represents a large organofunctional group. The colloid particles are stabilized via adsorption of the stabilizer molecule onto their surface, thus arresting ensuing particle growth. Particle agglomeration is prevented via electrostatic and steric interactions. Stabilization yields an equilibrium distribution of soluble silica colloids whose interparticle distances exceed the value below which attractive van der Waals forces would lead to agglomeration. The equilibrium implies a reservoir of species which can be converted into monomeric silicate during hydrolysis (that is, dilution of a coolant concentrate into a working (50% aqueous) antifreeze solution) or during consumption in service.

Stabilization should occur at a rate that exceeds the rates where silica colloids can grow and become insoluble. This is dependent upon the concentration and molecular structure of the stabilizer molecules, the dispersivity of the stabilizer in the particular coolant matrix (affected by pH, blending sequence, glycol type), and the initial concentration of inorganic silicate.

Experimental Evidence—Monomeric silicate was detected by measuring the 405 nm light absorbance due to the conversion to silicomolybdic acid from silicate and ammonium molybdate at low pH. Figure 1 displays a characteristic silicate stabilization response. The concentration of monomeric silicate (expressed as ppm Si) is shown as a function of time after its introduction into the glycol matrix (ethylene glycol (EG) and other additives). The initial concentration of monomeric Si (from aqueous Na_2SiO_3) is about 400 ppm. The early-time decay of monomeric Si is due to formation of higher molecular weight colloids. In the absence of stabilizer in the formulation, this decay would proceed towards 0 ppm Si, indicating formation of insoluble gel. Stabilization results in an equilibrium distribution of soluble silica particles, some of which are monomeric. This is indicated by the flattening response to an equilibrium monomeric silicate concentration of 160 ppm.

Water dilution of the concentrate into a 50% aqueous solution hydrolyzes some of the stabilized and soluble colloids into monomeric silicate species. This is shown in Fig. 2 by a jump in the concentration of monomeric Si from 80 to 160 ppm. The system then proceeds to relax to the equilibrium solubility of stabilized monomeric silicate for the composition.

It is evident that kinetic measurements of monomeric Si in concentrates and in 50% aqueous solutions can be used to describe the stabilization behavior. The next section of this report includes specific studies of silicate characteristics as a function of compositional variations in coolants.

EG versus PG: Examples

Coolant Formulation A

Figure 3 shows monomeric Si concentration as a function of time for EG and PG versions of the same formulation. Silquest AF-1 Silane (Witco Corporation) was used as the organosilicon stabilizer. There are two main differences between EG and PG. The first is noted from the early-time behavior. While for the EG coolant, the first monomeric Si value recorded is 380 ppm, in the PG version, the monomeric Si drops almost instantly to 300 ppm. (Recall that the initial value of Si in the formulation is 400 ppm.) In PG, 25% of the monomeric Si condensed on a time scale which was faster than the measurement response time (about one minute). The data show that the polymerization of silicic acid occurs more readily in PG than in EG. Another difference between the EG and PG formulations is that the monomeric Si level equilibrates to a higher level in PG. Sample turbidity may contribute to some of this intensity.

The larger quantity of monomeric Si liberated upon hydrolysis (50% aqueous dilution) of the EG coolant (Fig. 4) signifies that the silica was stabilized into colloids with a lower particle size distribution compared with the PG coolant. The long-time response depicted in Fig. 7 shows another important contrast between EG and PG for the formulation. While the monomeric silicate concentration in the EG composition appears to have equilibrated to a constant level (80 ppm monomeric Si), the PG solution displays a monotonic decay. This suggests less efficient stabilization in the PG concentrate.

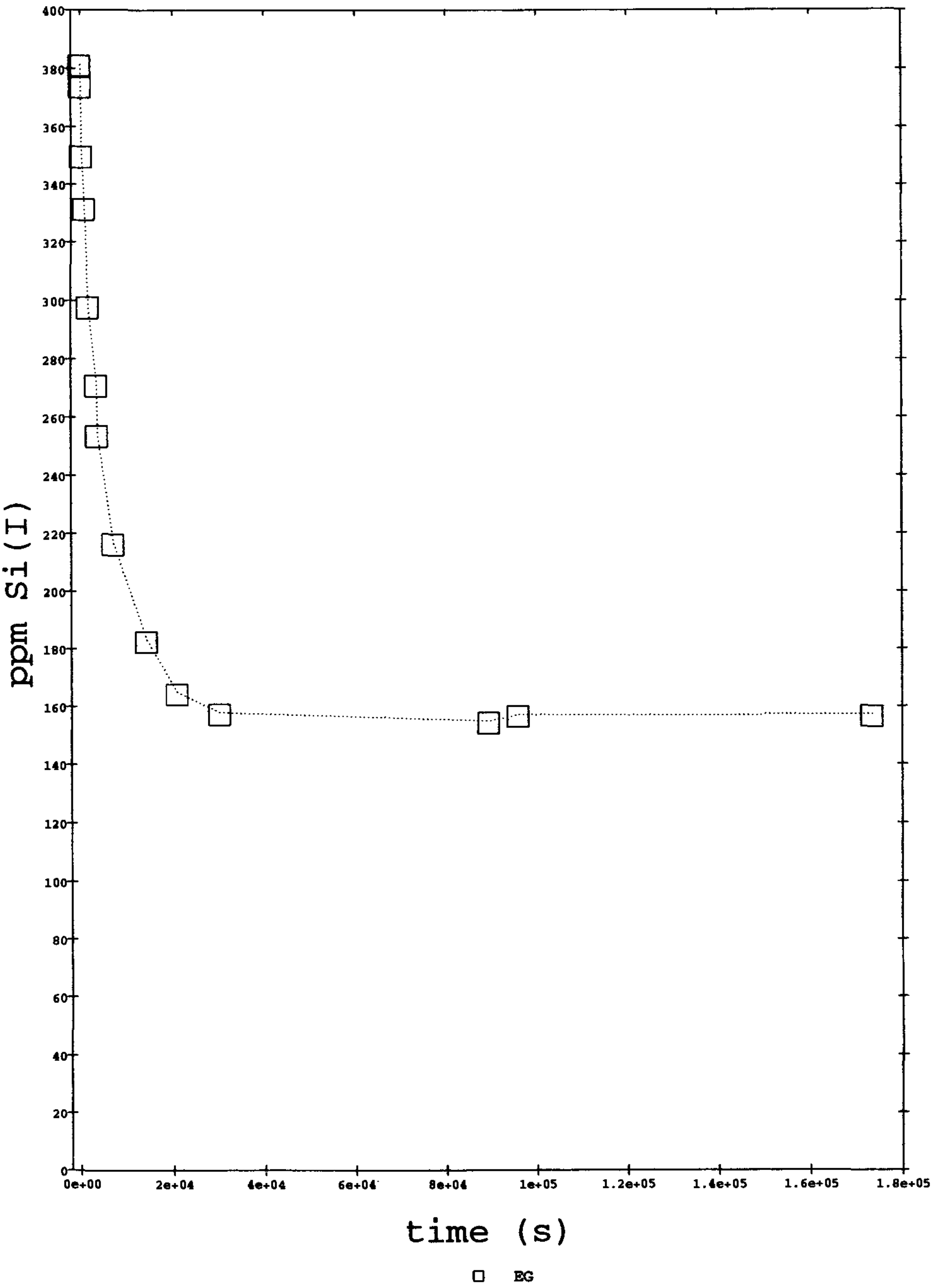

FIG. 1—*Monomeric Si versus time. EG-based coolant concentrate.*

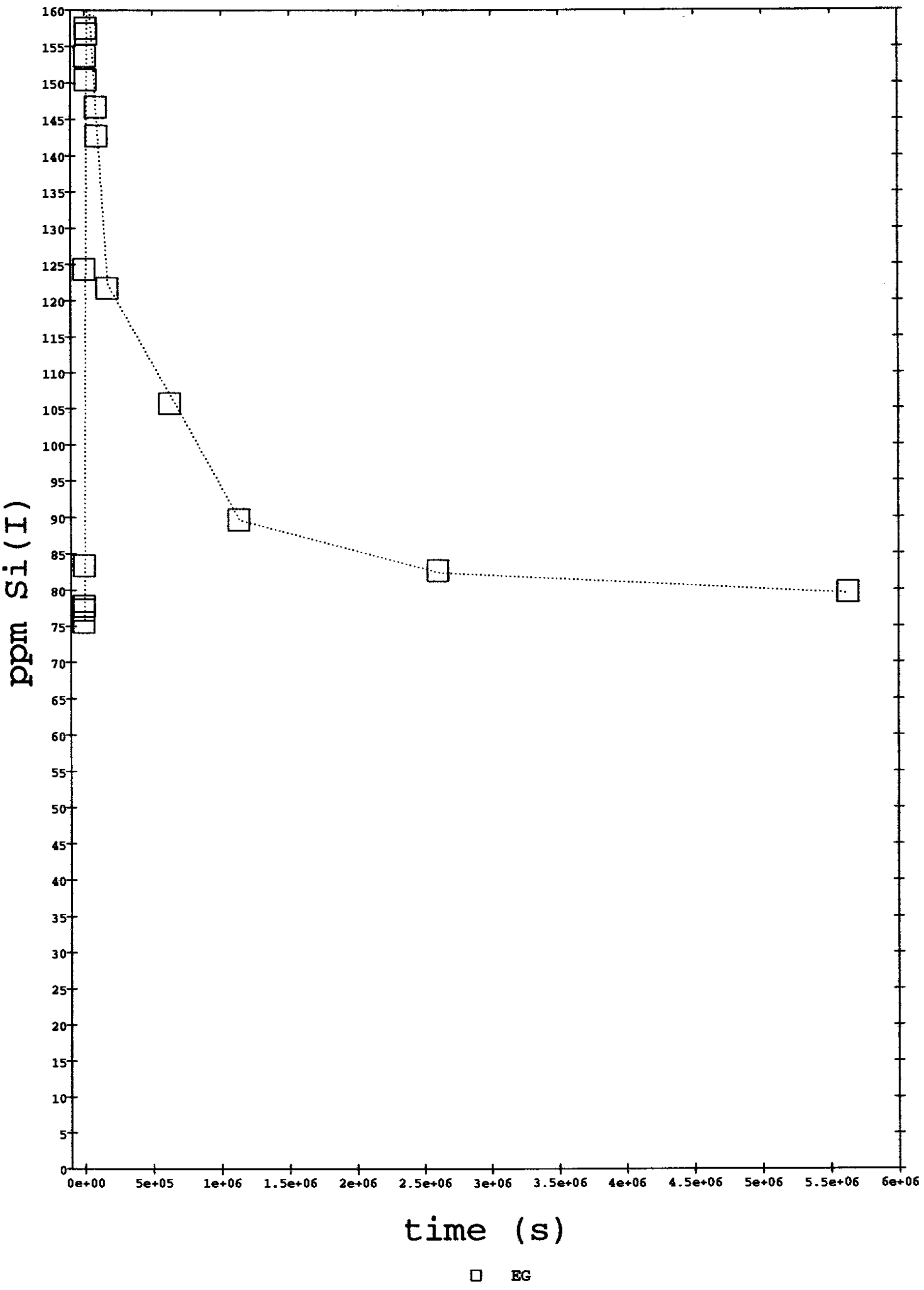

FIG. 2—*Monomeric Si versus time. EG-based coolant (50% aqueous).*

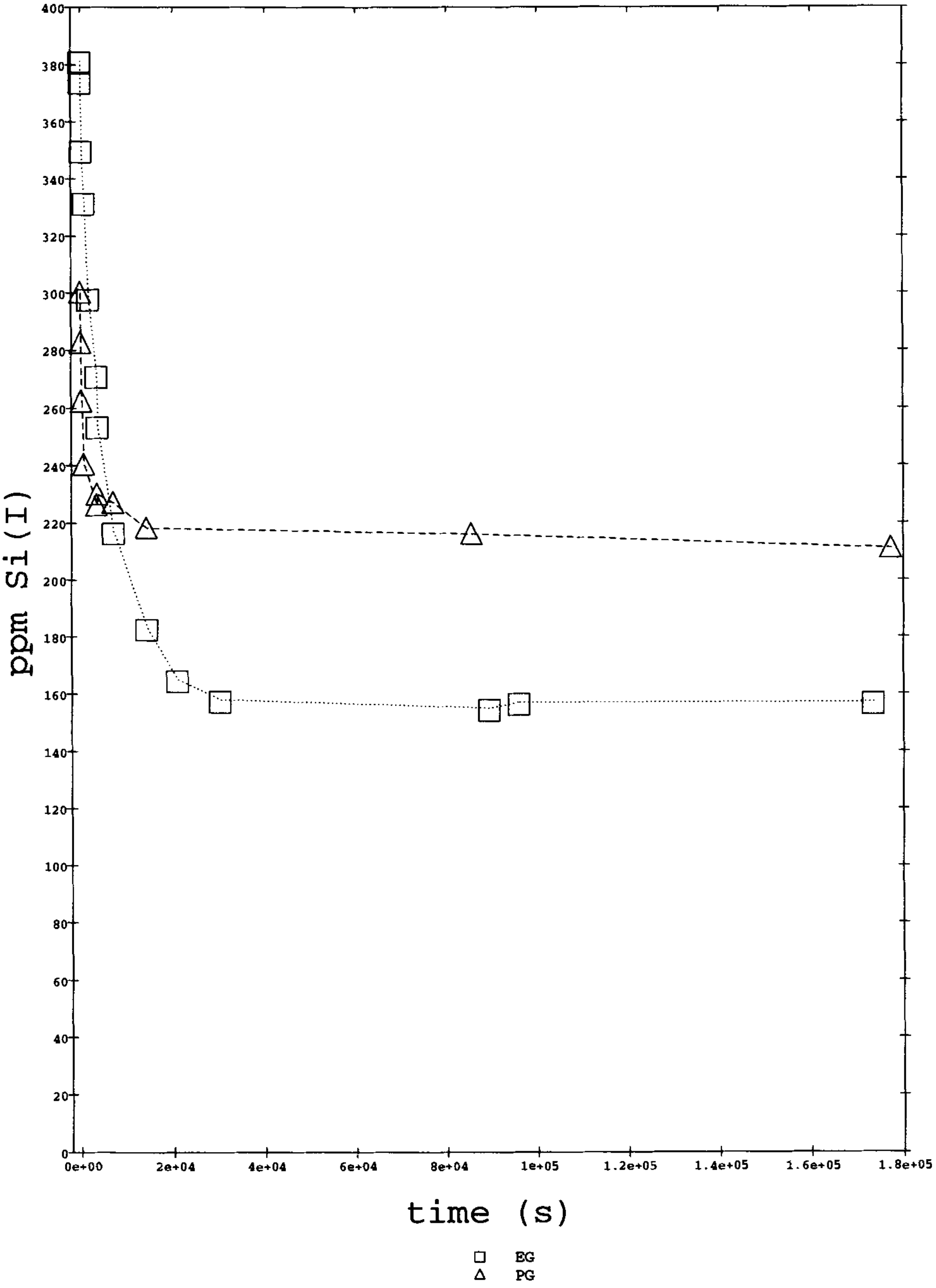

FIG. 3—*Monomeric Si versus time. EG- and PG-based coolant concentrates.*

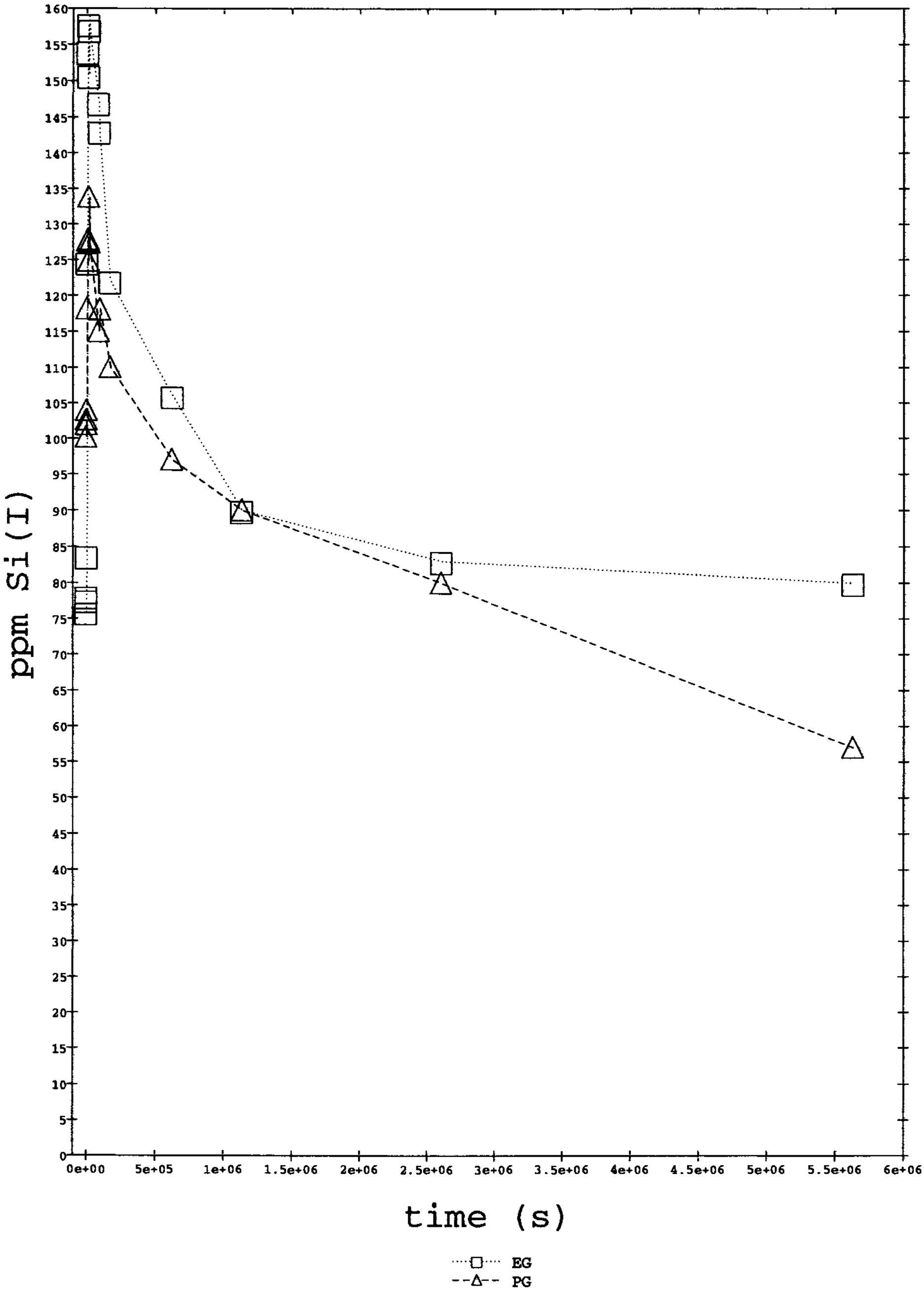

FIG. 4—*Monomeric Si versus time. EG- and PG-based coolants (50% aqueous).*

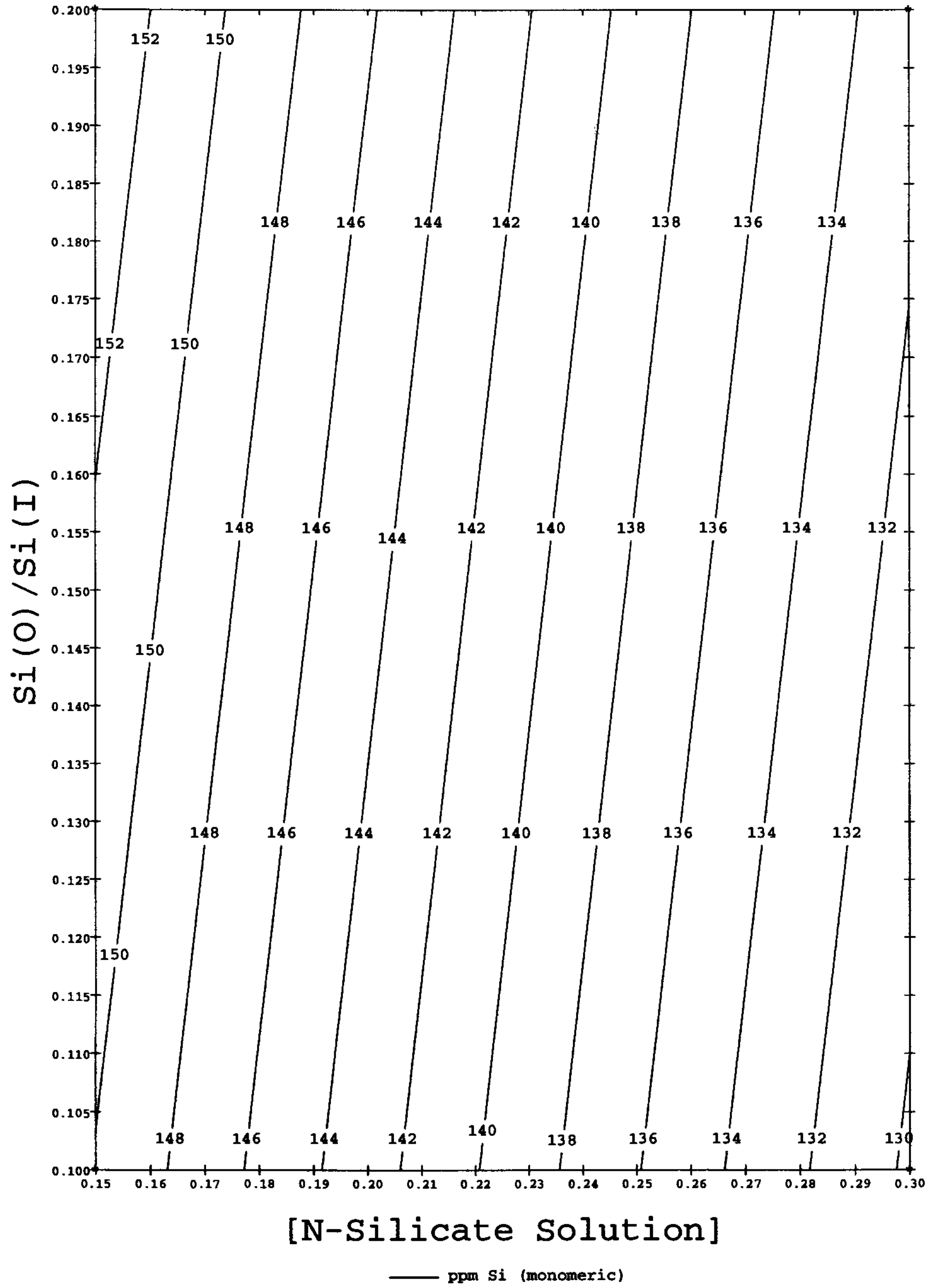

FIG. 5—*Equilibrium concentration of monomeric Si—Formulation A.*

Coolant Formulation B

Oven stability testing was performed on EG and PG versions of Formulation B. Both matrices yielded stable concentrates upon aging at $T = 55°C$ (no visible evidence of flocculation or gelation) for Si(I)/Si(O) ratios of 10. (Si(I)/Si(O) refers to the ppm "inorganic Si" (from Na_2SiO_3) divided by the ppm "organic Si" due to the level of organosilicon stabilizer.) Subsequent dilutions to 50% aqueous solutions resulted in flocculation only in the PG formulation. Doubling the quantity of stabilizer (Si(I)/Si(O) = 5) led to clear 50/50 PG solutions.

Formulation A versus Formulation B: The Effects of Coolant Matrix

Experiments were conducted to model the behavior of monomeric silicate in two separate PG coolant formulations. The glycol portions were based on Formulations A and B. The experimental variables were: (1) weight % N-Solution (sodium silicate solution from the PQ Corporation) (factor limits: 0.15 weight % to 0.30 weight %), and (2) Si(O)/Si(I) (factor limits: 0.1 to 0.2). The measured response was the equilibrium level of monomeric silicate in the concentrate following aging for seven days at $T = 55°C$.

The model that accounts for the variation is shown in Figs. 5 and 6 for Formulations A and B, respectively. Trends in the data are much different for the two formulations. In Formulation A, the solubility of monomeric Si is considerably higher than in Formulation B. Moreover, levels of monomeric Si decrease with increasing N-Solution concentration in Formulation A while they increase in Formulation B.

It is interesting to note that as the concentration of N-Solution in Formulation A increases from 0.15 to 0.30%, the solubility of monomeric Si decreases from about 150 to 130 ppm. The opposite trend is seen for Formulation B. There is no significant effect of stabilizer level for either composition.

Formulation A: Effects of Variations in Aqueous Silicate Premixes

A four-factor statistically designed experiment was performed to model the effects of varying levels of components in the "aqueous phase" of a coolant composition. The factor settings are listed in Table 1.

The measured response was the equilibrium level of monomeric Si in the coolant concentrate. Modeling of the measured responses shows that the pH, % N-Solution, and Si(O)/Si(I) are interacting variables. The large positive effect associated with pH is consistent with the known relationship between silica colloid particle size and silicate solubility in this pH region. The smaller, but significant positive effects on silicate solubility of the N-Solution concentration and stabilizer were also observed. Stabilizer X is more active than Stabilizer Y.

Three-factor interactions (pH, % N-Solution, Si(O)/Si(I)) are shown in Figs. 7*a*, 7*b*, and 7*c*, which plot monomeric Si levels as a function of % N-Solution and Si(O)/Si(I) (with Stabilizer X). The following points are evident from the data:

(1) The solubility of monomeric Si increases with increasing pH.

(2) At the highest pH (Fig. 7*c*), there is no effect of stabilizer level. This is probably due to the high solubility of monomeric Si.

(3) As the pH decreases, the stabilizer effect becomes more pronounced. Since the colloids tend to grow under these conditions, the result of higher stabilizer levels is to arrest further particle growth and preserve monomeric Si solubility.

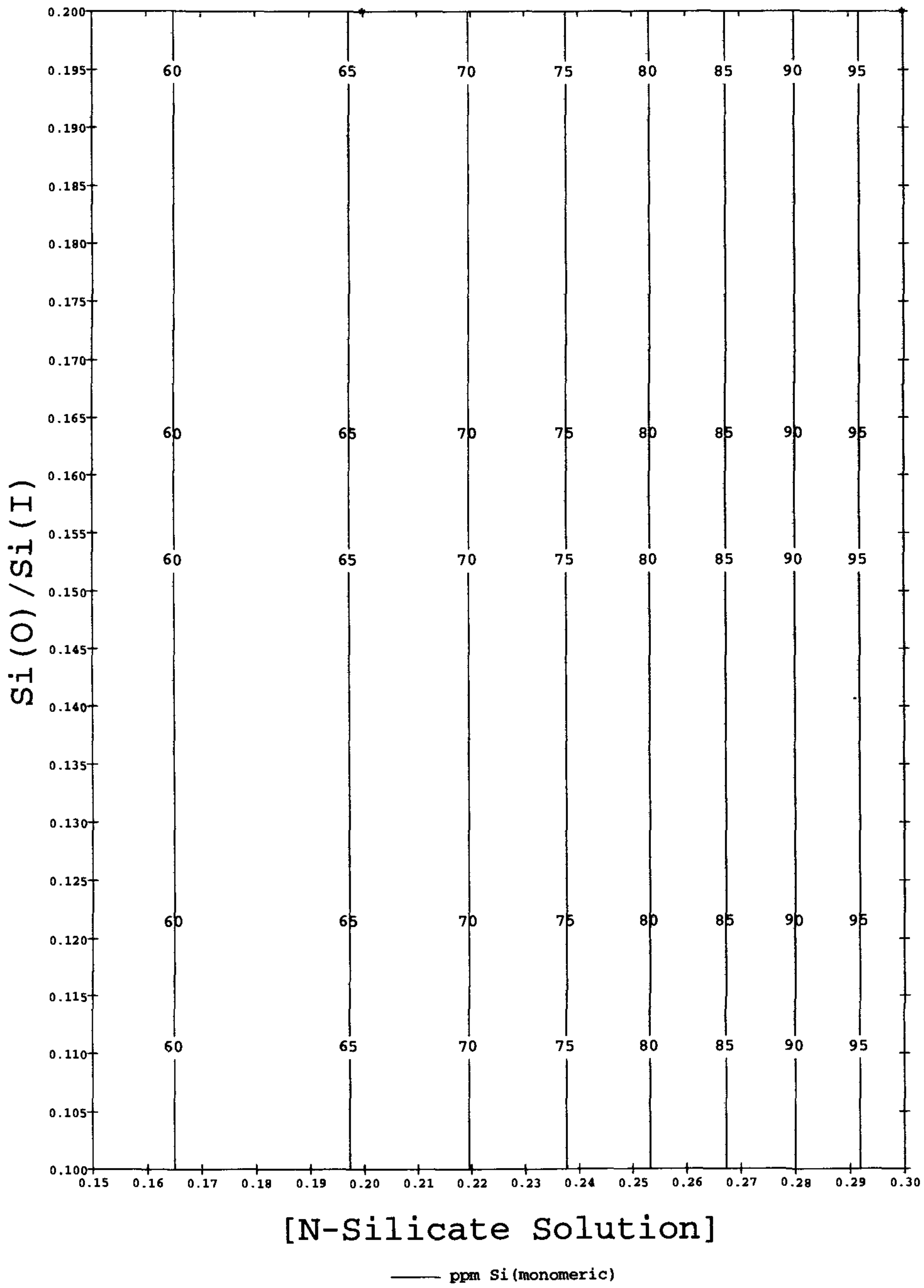

FIG. 6—*Equilibrium concentration of monomeric Si—Formulation B.*

TABLE 1—*Factors/limits.*

Factor	"–"	"+"
pH	9.8	11.2
Weight % N-Solution	0.15	0.30
Si(O)/Si(I)	0.10	0.20
Stabilizer type	X	Y

(4) At low pH values, the effect of stabilizer increases with increasing N-Solution concentration. Since the probability of colloid agglomeration grows with increasing silicate concentration, the result of raising the level of stabilizer is to reduce the effective interparticle encounters which would deplete soluble monomeric silicate.

The second example is shown in Figs. 8*a*, 8*b*, and 8*c*. In these cases, Stabilizer Y is substituted for Stabilizer X. Certain aspects of the monomeric Si behavior are quite different:

(1) Equilibrium levels of monomeric Si at low pH values are considerably lower than analogous compositions containing Stabilizer X.

(2) At high pH, there is negligible effect of stabilizer. The decreasing monomeric Si with increasing % N-Solution indicates impingement of silica particles which leads to reduced solubility.

(3) At lower pH, increasing Si(O)/Si(I) leads to increased Si solubility, but the effect is small.

Formulation C: Effects of Blending Procedure on Silicate Solubility

Blending Procedures

Silicate stability in a PG coolant formulation is sensitive to the method of component blending. A typical blend procedure may be based on separate preparations of a "water portion" premix that contains silicate and a "glycol portion" premix that contains most of the other ingredients (inhibitors, antifoams, etc.). The effect of blending sequence was studied for Formulation C. Stability of 50% aqueous solutions of the coolant was determined from the visible transparency of the solutions and from the time-evolving monomeric silicate concentrations. Five different blending procedures were investigated.

Method A—85.5% of the available H_2O was combined with Stabilizer Y and then N-Solution. This premix was added to the glycol portion. The remaining 13.5% of the H_2O (in the form of a 50% KOH solution) was added to the glycol portion.

Method B—13.5% of the H_2O (in the form of a 50% KOH solution) was added to the glycol portion. This was followed by adding a premixture of the remaining 86.5% of the available H_2O, Stabilizer Y, and N-Solution.

Method C—H_2O, 50% KOH solution, N-Solution, and Stabilizer Y were combined and added to the glycol portion. Final pH adjustment was achieved with 50% KOH.

Method D—50% of the available KOH was dissolved in 40% of the available H_2O. This solution was added to the glycol portion, followed by the addition of Stabilizer Y. The remaining 50% of the KOH was combined with the remaining 60% of the H_2O, followed by the addition of N-Solution. This mixture was then added to the glycol portion.

Method E—Similar to Method D, except that Stabilizer Y was added to the water portion instead of the glycol portion, initially.

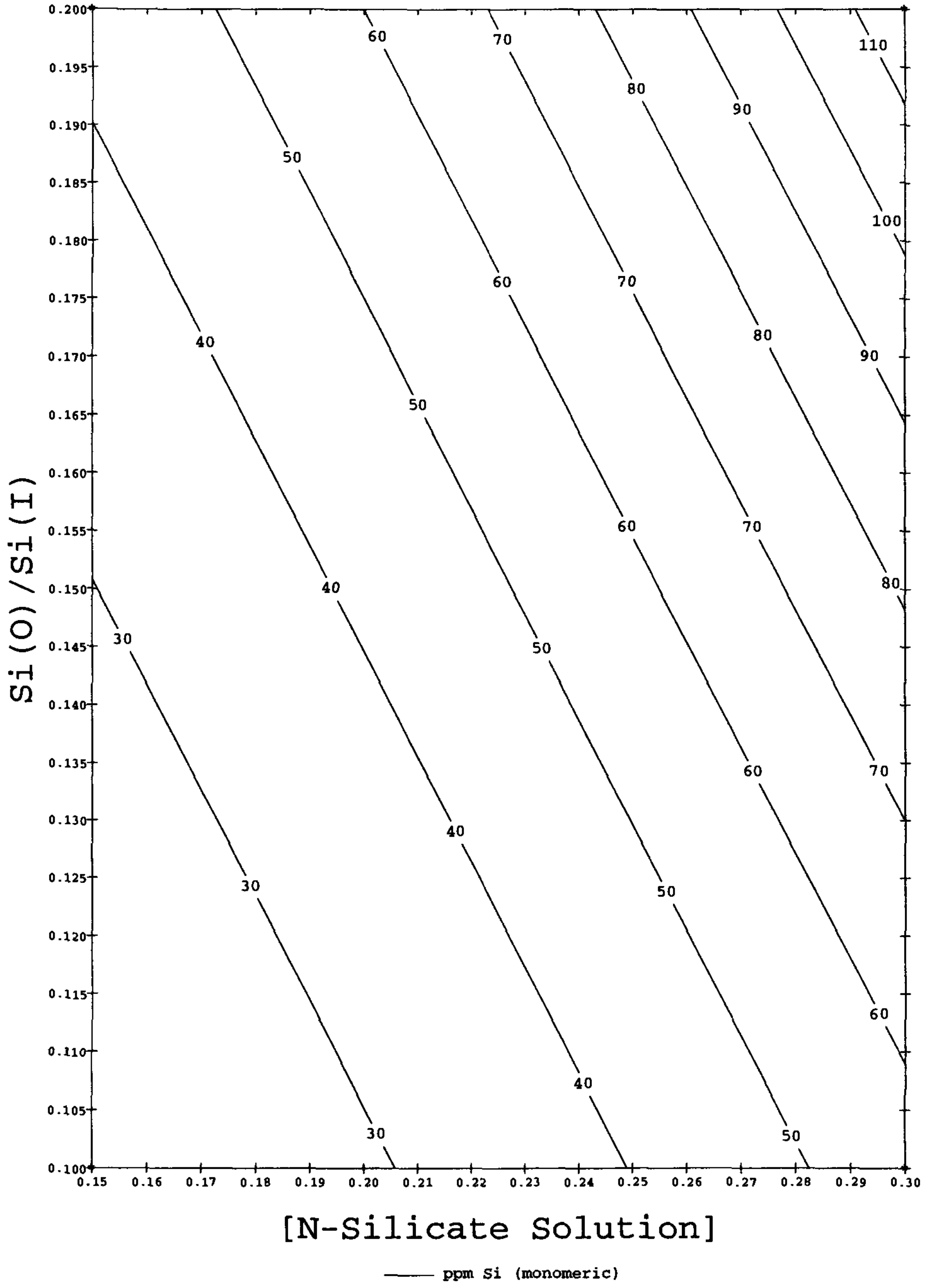

FIG. 7(*a*)—*Equilibrium concentration of monomeric Si—Formulation A (pH = 9.8; stabilizer = X).*

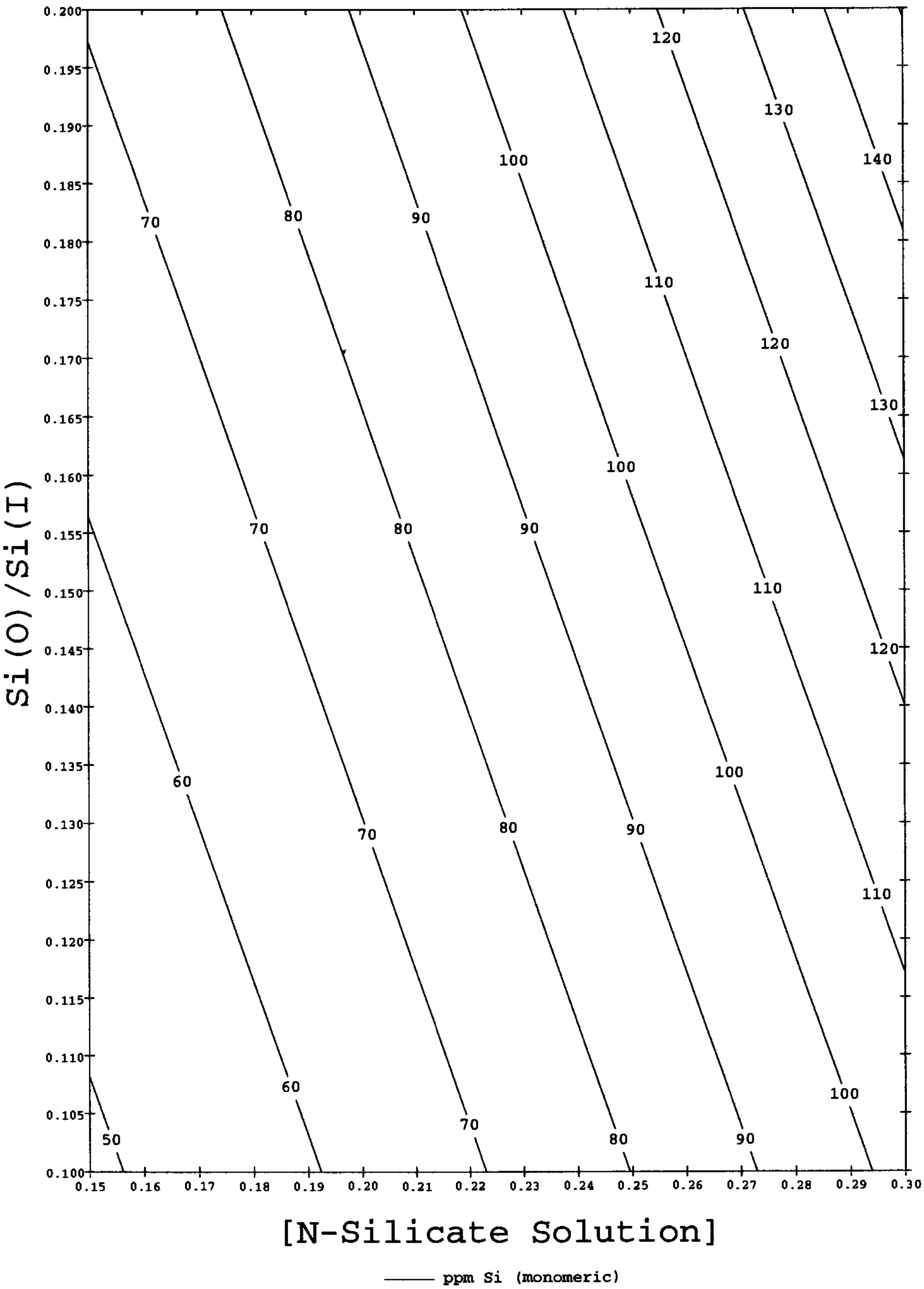

FIG. 7(*b*)—*Equilibrium concentration of monomeric Si—Formulation A (pH = 10.5; stabilizer = X).*

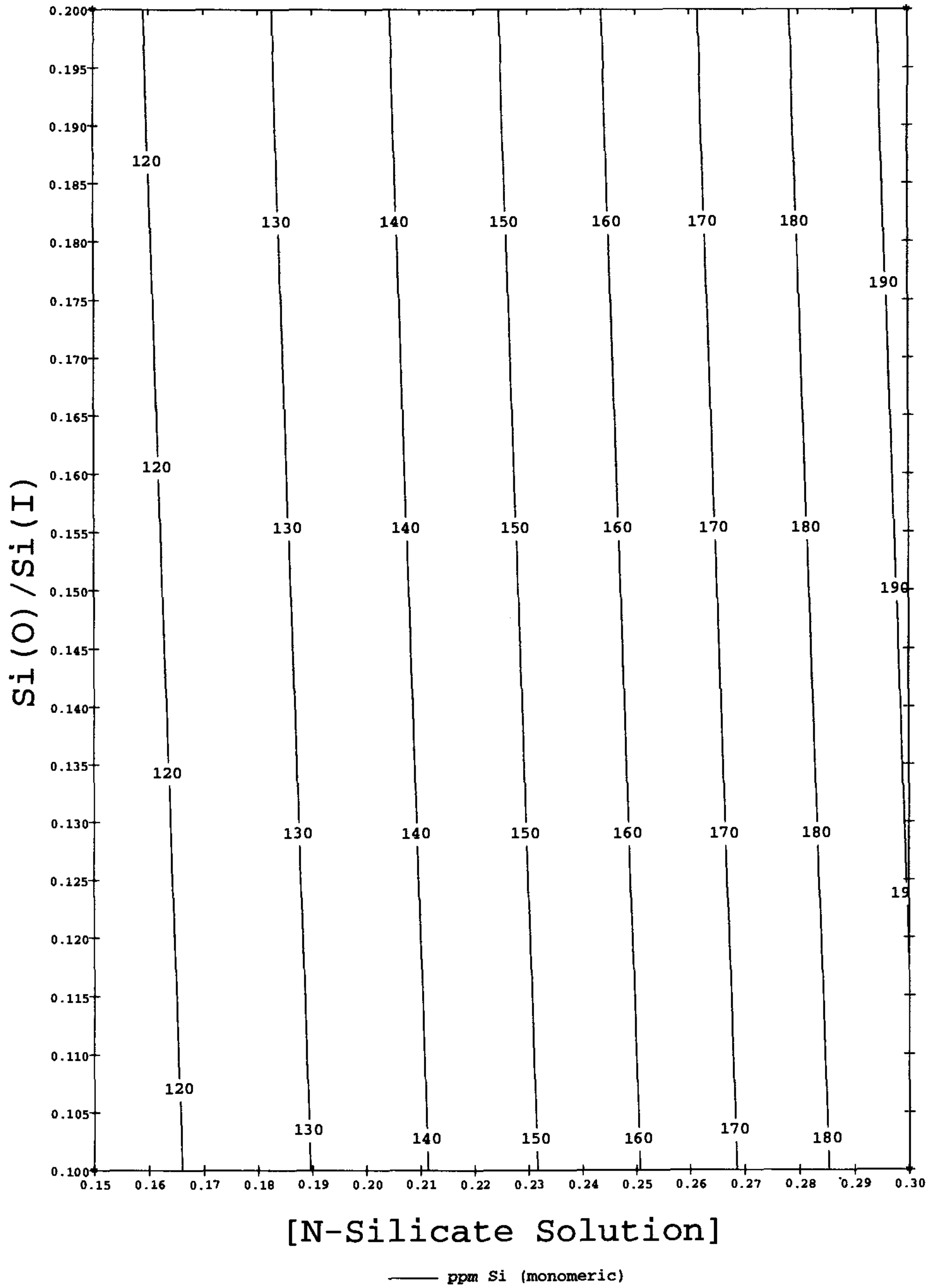

FIG. 7(*c*)—*Equilibrium concentration of monomeric Si—Formulation A (pH = 11.2; stabilizer = X).*

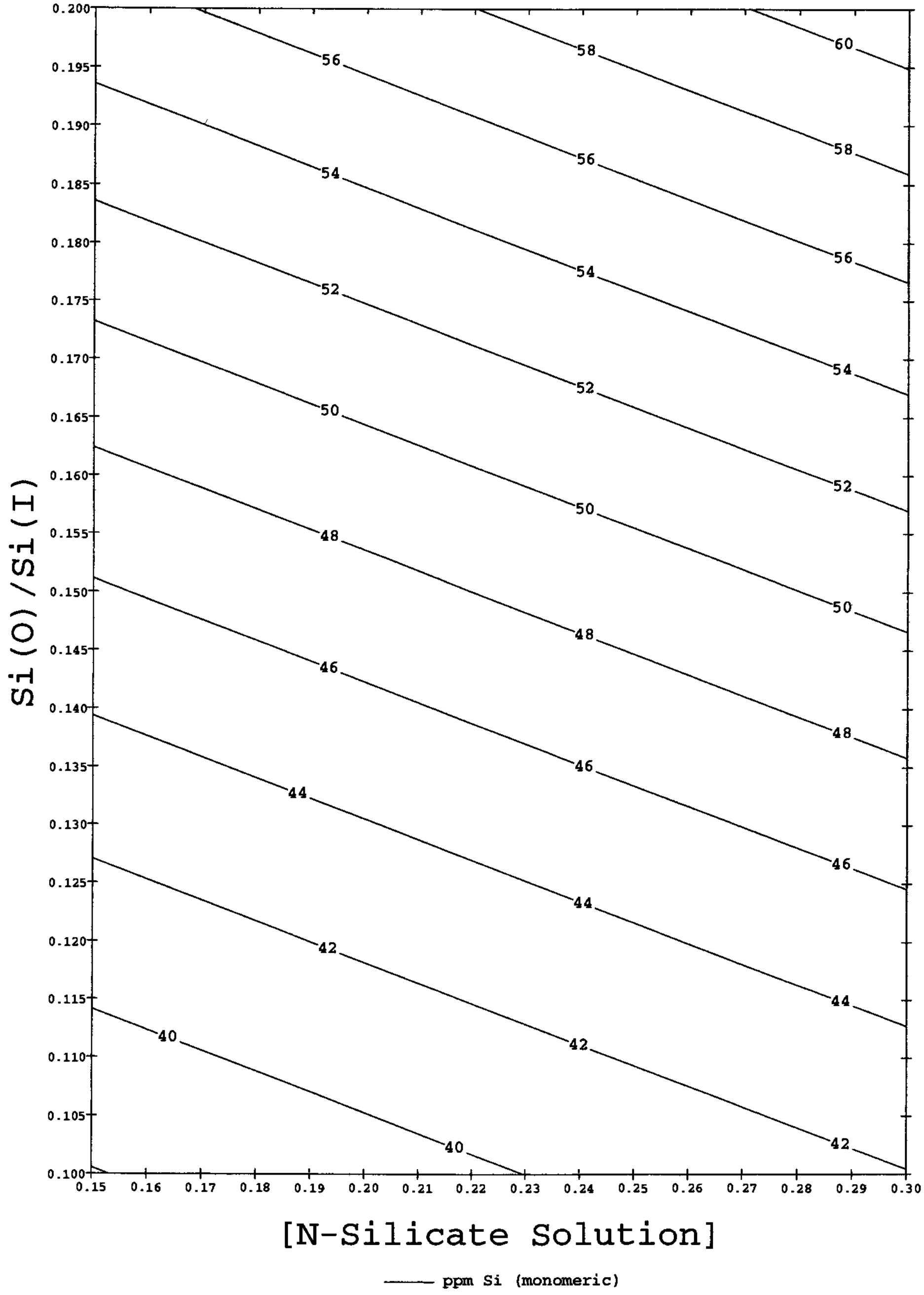

FIG. 8(*a*)—*Equilibrium concentration of monomeric Si—Formulation A (pH = 9.8; stabilizer = Y).*

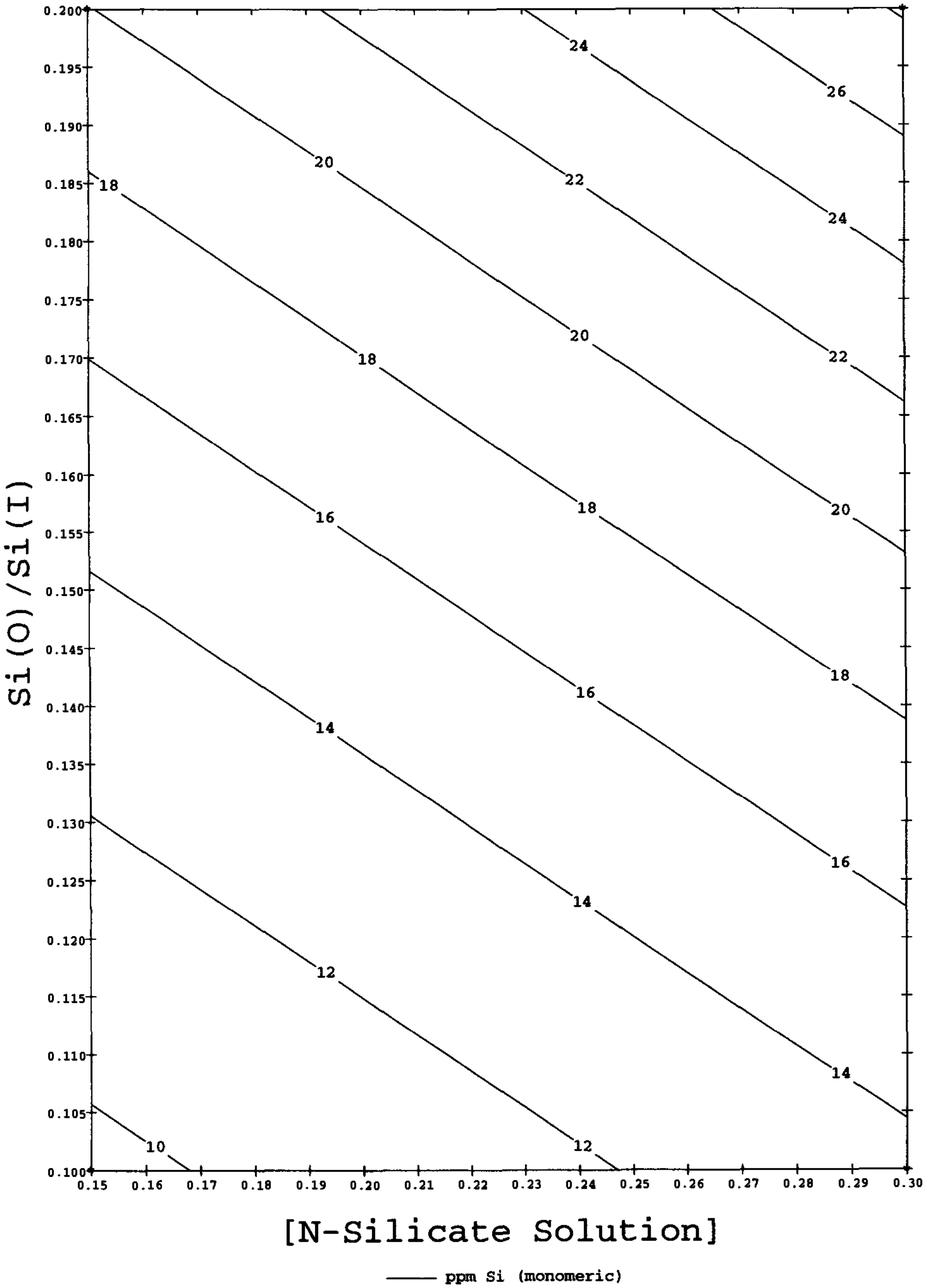

FIG. 8(*b*)—*Equilibrium concentration of monomeric Si—Formulation A (pH = 10.5; stabilizer = Y).*

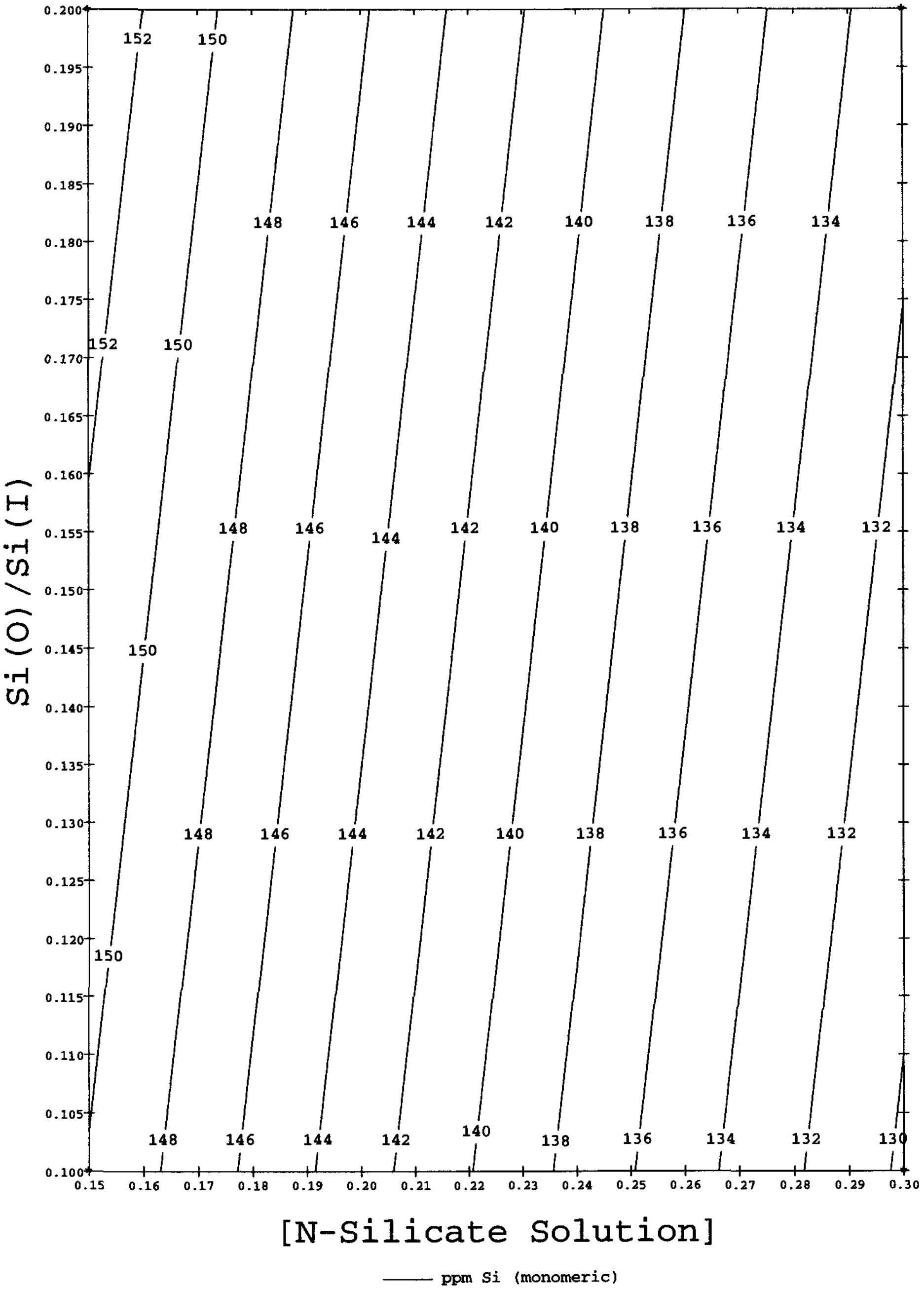

FIG. 8(*c*)—*Equilibrium concentration of monomeric Si—Formulation A (pH = 11.2; stabilizer = Y).*

TABLE 2—*Characteristic parameters of monomeric Si in 50% aqueous dilutions of Formulation C—Hydrolysis Behavior.*

Blending Procedure	''A'' (ppm Si)	''B'' (ppm Si)
A	35	65
B	35	60
C	35	80
D	45	75
E	45	80

Oven Stability

Silicate instability was evident from the visible haze observed in the samples. The UV-Visible absorbance spectra of 50% aqueous solutions that were aged for 650 h at $T = 55°C$ provided quantitative comparisons of the stability. In terms of sample transparencies, the order of merit for the five blending procedures is: C > E > D > B = A.

Monomeric Silicate

The time response of monomeric silicate in the coolants following 50% aqueous dilution was measured. Two characteristic parameters were extracted from the response: ''A'' = the instantaneous concentration, and ''B'' = the peak concentration of monomeric silicate subsequent to dilution. ''A'' reflects the silica particle size distribution that is stabilized in the concentrate. ''B'' corresponds to those colloids that are hydrolyzed to form monomeric silicate. Higher values of ''A'' and ''B'' suggest improved stabilization in the concentrate (see Table 2).

The difference between ''A'' and ''B'' relates to the amount of stabilized silicate in the formulation. It may be thought of as the ''reservoir'' of stabilized silicate that is available to unprotected aluminum surfaces in working antifreeze solutions. Thus, in terms of the quantity (''B'' − ''A''), the order of merit for the different blending procedures is: C > E > D = A > B.

Formulation C: Effects of Stabilizer Type on Performance

Oven Stability

Reducing the concentration of organosilicon stabilizer in coolant formulations can result in the formation of insoluble polysilicate species (gel/floc) in oven-aged 50% aqueous dilutions. This can occur despite oven stability ($T = 55°C$, $t = 30$ days) in the corresponding coolant concentrate. A higher concentration of stabilizer for a given coolant will produce a silica particle size distribution that favors smaller, more soluble colloids. Evidence for the tendency of the particle size distribution is provided by monomeric Si values that are shown in Table 3 for

TABLE 3—*Monomeric Si/floc observations: Formulation C.*

% Stabilizer Y	Monomeric Si in Oven-Aged Concentrate, ppm	Time to Floc for 50% Aqueous Dilutions
0.06	90	< 24 h
0.12	95	~ 3 days
0.20	105	no instability evident

oven-aged concentrates as a function of increasing Stabilizer "Y" level. All three coolant concentrates were stable.

Aluminum Corrosion Resistance: The Role of Monomeric Si

An example of the role of monomeric Si on aluminum corrosion inhibition is provided by the results obtained on an aluminum water pump cavitation test (ASTM Test Method for Cavitation Corrosion and Erosion-Corrosion Characteristics of Aluminum Pumps with Engine Coolants (D 2809-94)). Two analogs of Formulation C were run in the test. Formulation C-1 used Stabilizer "X" and Formulation C-2 used Stabilizer "Y." Each stabilizer was employed at the same concentration. A slightly different blending procedure was used for each analog based on prior optimization. Better performance on the test was determined for Formulation C-2. While Formulation C-1 caused light erosion of the edges of the impeller and on the inlet surface housing (hence, its "8" rating), no erosion was observed for the water pump tested with C-2 (score = "10").

Formulation C-2 had twice as much monomeric Si in the equilibrated concentrate as Formulation C-1. The silica hydrolysis profiles for 50% dilutions are shown in Fig. 9. Note the higher levels for C-2. This was also the situation for 16 and 33% dilutions.

Hard-Water Compatibility

Silicate stability issues are compounded when coolant concentrates are diluted with hard water (for example, containing calcium or magnesium or both). Solids formed in their presence under unstable conditions (that is, dilution factor, elevated temperature) may not only decrease a coolant's corrosion resistance, but they may reduce its heat transfer capabilities. This is due to the formation of insoluble coatings on heat-rejecting metal surfaces or restricted fluid flow. The solids can take the form of crystalline mineral scale and/or amorphous polysilicate gel.

A Closed-Loop Hot Scale Rig (a recirculation system manufactured by Amalgamated Technologies, Inc., Scottsdale, Arizona) was used to study hot surface deposits produced from PG coolant formulations mixed with water of known scaling properties (Table 4). The equipment was reconfigured (Table 5) for purposes of simulating conditions under which coolants are evaluated in the FVV Heat Test. The existing test cell was replaced with a cell that more closely resembles the heat-rejecting metal surface environment used in Darmstadt. (The FVV is a testing regimen drawn up by the "Coolant Additives" Working Party of the Combustion Engine Research Association, and it is performed at the Institute for Materials Science at the Darmstadt Technical University, Germany, to qualify coolant compositions.)

PG coolant compositions were tested at 10 and 40 volume % solutions with hard water. The composition of the hard water was: 49.7 mg/L $CaCl_2$, 91.1 mg/L CaSO4, 63.8 mg/L $MgCl_2$, 150.4 mg/L $NaHCO_3$.

Tables 6 and 7 summarize improvements in stability that were achieved for a 10 and 40 volume % dilution of the coolant concentrate (Formulation D). For the first case, instability is evident from the higher metal specimen temperatures (Fig. 10). This was due to deposits, mainly composed of Si and Ca, that reduced heat transfer. Magnesium was a minor component. X-ray diffraction identified a major component of the solids as the aragonite form of $CaCO_3$. For the 40 volume % solutions, silicate gelation contributed dramatically to inefficient heat transfer (Fig. 11). X-ray diffraction confirmed that the solids were amorphous. Improved performance (lower aluminum specimen temperatures due to the elimination of unstable solids in the forms of mineral scale deposits or silica gel; preservation of solution chemical properties during the test duration) was based on adjustments to the level of Stabilizer "Z," the sequence of component addition for the water portion, and the addition of a chelating agent.

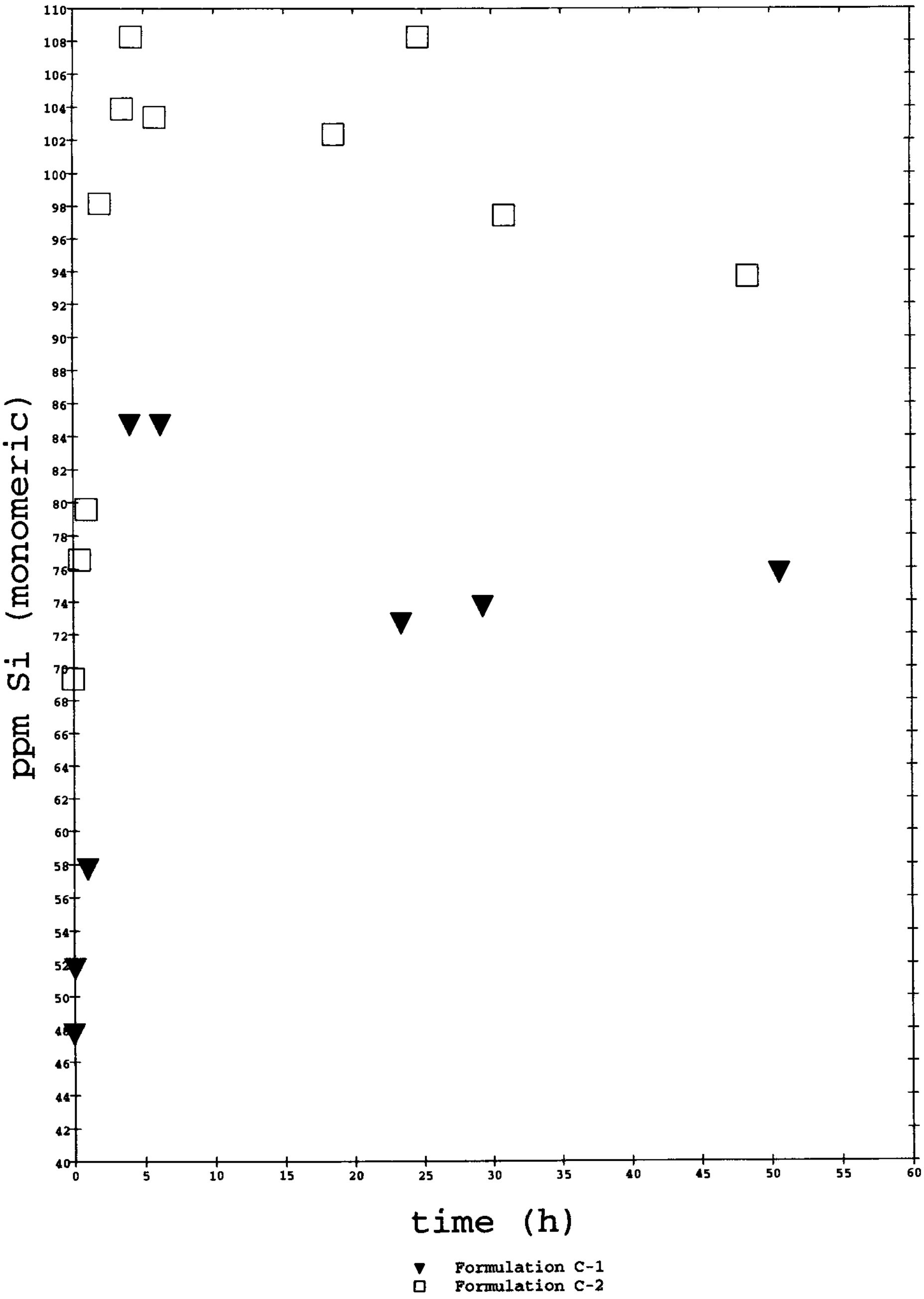

FIG. 9—*Monomeric Si versus time (50% aqueous solutions).*

TABLE 4—*Hard water composition.*

Contaminant	ppm
Ca^{2+}	44.7
Mg^{2+}	16.1
Cl^-	79.5
SO_4^{2-}	64.3
HCO_3^-	109.2

TABLE 5—*Modified closed-loop hot scale rig—experimental conditions.*

Metal Test Specimen	SAE 329 Cast Aluminum
Free test surface area	26 cm^2
Surface power density	20 W/cm^2
Test fluid volume	121
Fluid flow rate	0.06 m^3/h

TABLE 6—*10 volume % solutions of Formulation D.*

	Original Formulation D		Improved Formulation D	
Al specimen temperature range, °C	120 to 165		106 to 111	
Al specimen appearance after test	thick, white deposit		dull gray, no coating, slight erosion	
Al specimen weight gain, g	1.65		0.01	
Solution Chemistry	Before Test	After Test	Before Test	After Test
pH	8.5	8.3	8.4	8.4
B, weight %	0.011	0.011	0.017	0.017
Na, weight %	0.023	0.023	0.035	0.035
Mg, ppm	15	4	15	15
Si, ppm	48	28	40	40
K, weight %	0.076	0.076	0.076	0.076
Ca, ppm	35	4	38	38
Solid Analysis	Major: Si, Mg, Ca		None detected	
Solid Chemistry				
B, weight %	4.8	...	...	...
Na, weight %	3.3	...	...	...
Si, weight %	23	...	...	...
Ca, weight %	21	...	...	...
Mg, weight %	3.9	...	...	...

TABLE 7—*40 volume % solutions of Formulation D.*

	Original Formulation D		Improved Formulation D	
Al specimen temperature range, °C	115 to 215		113 to 120	
Al specimen appearance after test	Thin gelatinous white deposit		shiny and clean	
Al specimen weight gain, g	0.35		0.00	
Solution Chemistry	Before Test	After Test	Before Test	After Test
pH	8.0	8.0	7.7	7.8
B, weight %	0.046	0.046	0.071	0.071
Na, weight %	0.087	0.087	0.013	0.014
Mg, ppm	9.7	3.6	10	10
Si, ppm	160	140	160	160
K, weight %	0.032	0.032	0.033	0.036
Ca, ppm	21	21	24	24
Solid Analysis	Major: Si > Mg, Ca		None detected	
Solid Chemistry				
B, weight %	2.2	...	...	...
Na, weight %	1.6	...	...	...
Si, weight %	36	...	...	...
Ca, weight %	1.1	...	...	...
Mg, weight %	12	...	...	...

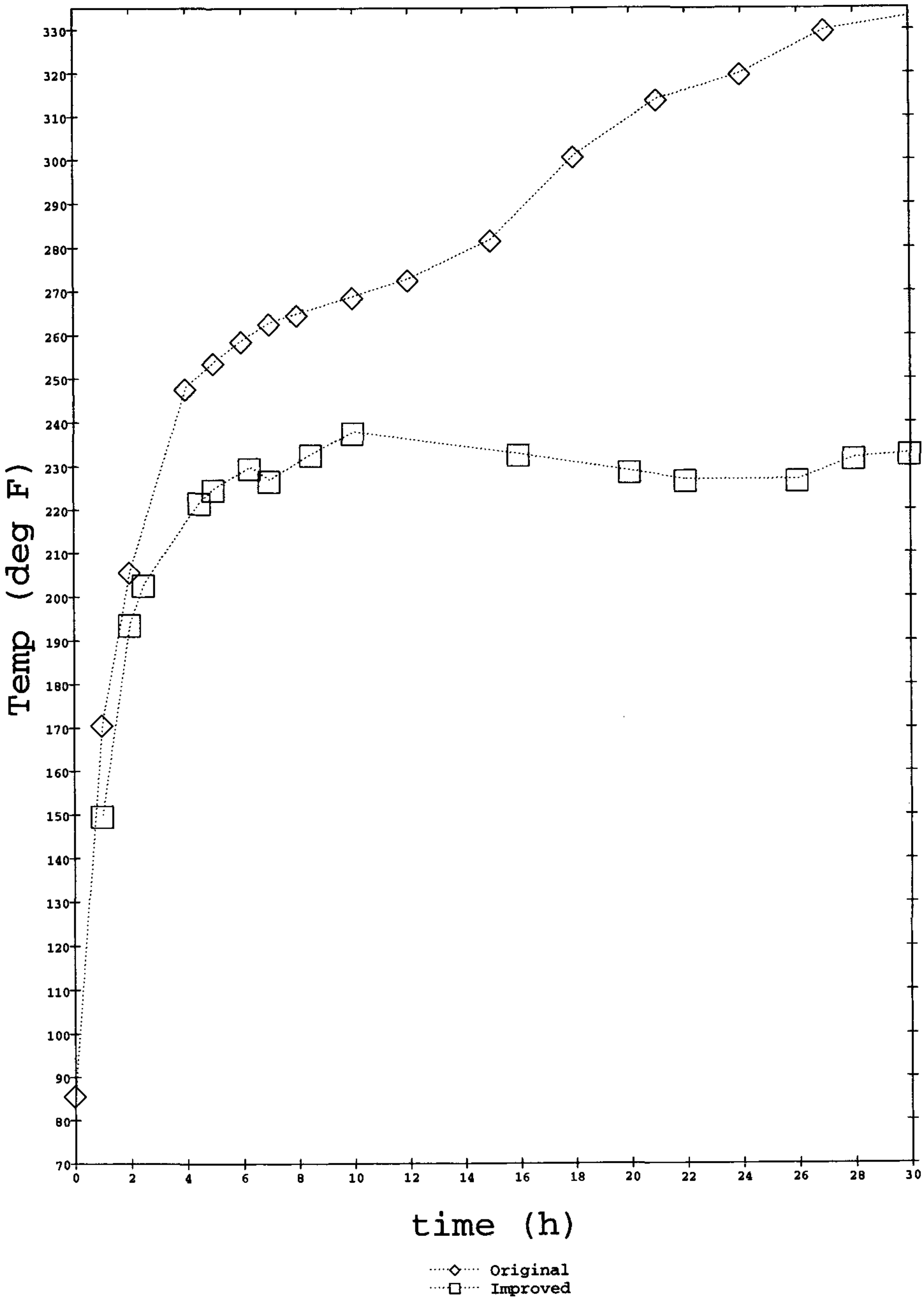

FIG. 10—*Ten percent solutions—aluminum specimen temperature versus time.*

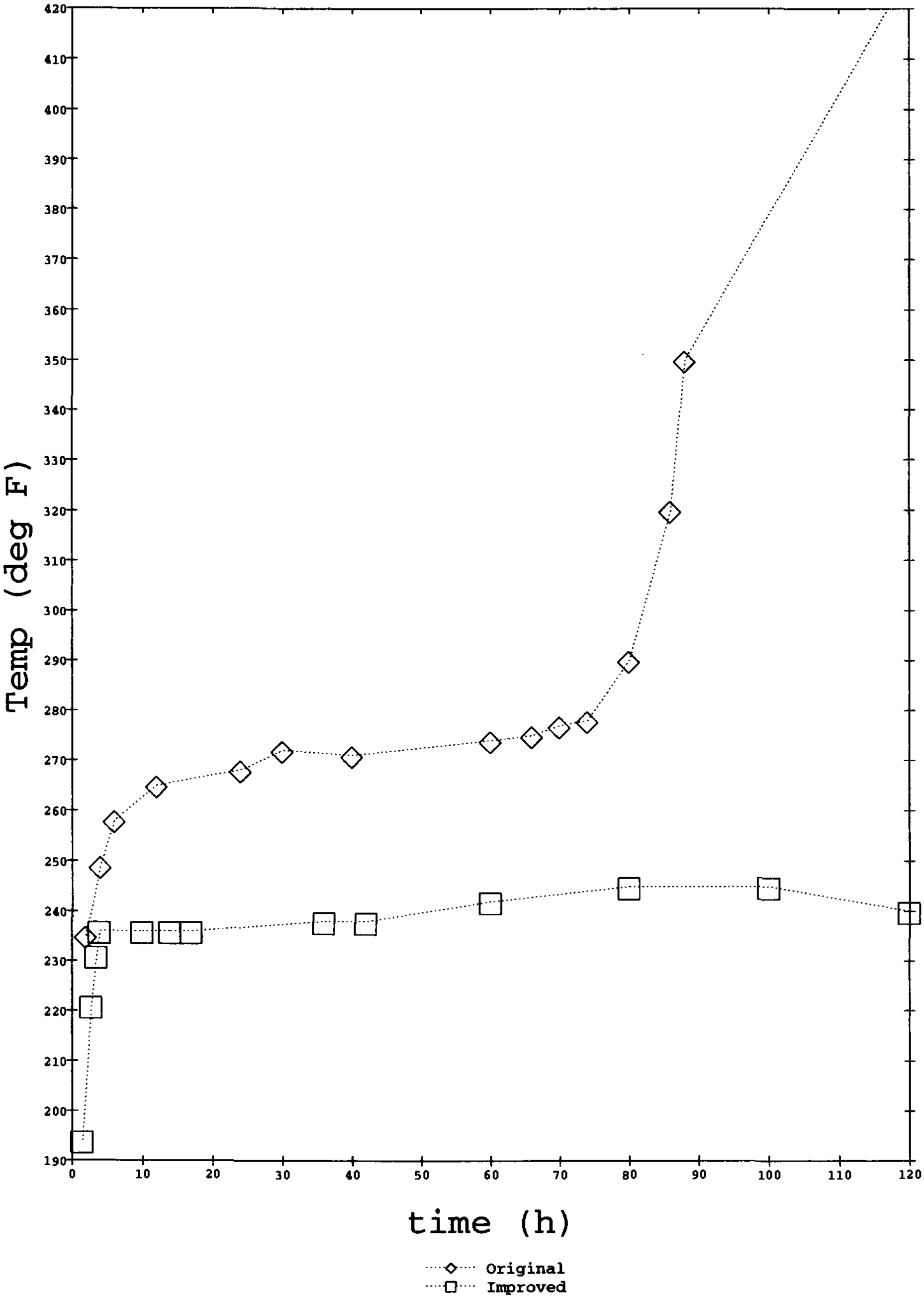

FIG. 11—*Forty percent solutions—aluminum specimen temperature versus time.*

Conclusions

Silicate is an important inhibitor for coolants. Results from experiments have been provided that show unstable silicate tendencies. It is incumbent upon a glycol-based coolant composition to provide stabilization of silicate against its conversion to insoluble products which can assume the forms of floc, gel, and scale deposits. Data were provided that demonstrated effective silicate stabilization and its related importance to performance (aluminum corrosion, heat transfer). Influences of glycol matrix, silicate concentration, stabilizer concentration, stabilizer type, and blend procedure were demonstrated.

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Jess Starkey[1] *and Margaret Couch*[2]

Antifreeze: From Glycol to a Bottle on the Shelf—Manufacturing and Quality Control Considerations

REFERENCE: Starkey, J. and Couch, M., "**Antifreeze: From Glycol to a Bottle on the Shelf—Manufacturing and Quality Control Considerations,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 352–358.

ABSTRACT: Two parties in this path to provide to the end user a quality product in a quality package will be presented. They are the coolant producer and contract blender/packager. The coolant manufacturer must establish specifications, test methods, and formulation data for the contract blender/packager. The contract blender/packager is responsible, as a minimum, to assure the coolant manufacturer's requirements are met. Major contract blender/packager programs in many cases have highly developed quality programs. ISO 9002 certifications have been issued to some organizations. This paper addresses a path from the ethylene glycol molecule to a final packaged product and quality considerations necessary to assure final product quality. Specific specifications for components are proprietary information.

KEYWORDS: antifreeze, glycol, quality control, coolants, contract blender/packager, quality programs

The Coolant Producer Program

The Outside Package Overview

A quality finished container, (drum, pail, or gallon bottle) of antifreeze on the retail shelf is the result of many manufacturing and quality considerations. The final product is a complex assembly requiring close coordination of multiple suppliers. This drum, pail, or bottle may be shipped across country, stored in multiple warehouses, and reshipped two or three times before reaching the store shelf. Specifications and quality control procedures of packaging components are vital to assure a marketable container. The product must also arrive in a bulk, drum, pail, or bottle container which prevents intransit contamination and protects its overall appearance. Federal and State laws related to markings, label layout, and legibility of required information must be assured. Finally the package must arrive in a quality state that presents to the consumer a feeling that the product is a quality product. A very clean appearance of outside packaging is known to increase sales. It can make a positive buying decision for the better looking container when two brands are side by side.

Specification Requirements

The framework for a successful final product begins with the component specifications. Specifications must be written that include testing requirements that will provide meaningful

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information as to the quality of the component item. Excessive and meaningless specifications are a waste of time and money. Examples will be provided of excessive specifications later in this paper. Once the product descriptions, specifications, testing, and reporting requirements are defined they are presented to the item manufacturers and the receiving activity. Joint meetings between the buyer, manufacturer and packaging plant are held to assure we all agree on the product programs.

Bulk Container Requirements

Physical inspection requirements include the bulk compartment, outlet valves, and pump and hoses. Additionally, proper placard information as required by regulatory activities is checked.

Quality requirements include the following areas, all accessorial equipment required by the customer is on vehicle at time of pickup, internal valves are properly closed, discharge valves, and that pump outlets and hoses are covered. Cleanliness is a simple requirement "Clean, Dry and Odor Free . . . or Reject." The quality program also assures vehicles are not shipped overweight, and a copy of the MSDS is with the driver.

Drum and Pail Container Requirements

Physical inspection includes container interior, regulatory marking, proper closures, color, label placement, and proper cap.

Quality requirements include interior cleanliness, absence or presence of lining material, dents, paint appearance, rust areas, fill volume accuracy, proper palletization, and stretch wrap turns and tightness. Retain samples identification is complete.

Carton and Divider for Gallon Container Requirements

Physical inspection requirements includes regulatory markings, copy placement and color match, delaminating board, glue flap quality, and absence of crushed or creased areas on piece part.

Quality requirements include inspection for correct scoring lines, divider is full height, carton is square when erected, and divider is scored properly. Top load or edge crush testing reports are checked to verify product meets or exceed minimum purchase requirements.

Storage and Shipping Pallet Requirements

Physical inspection requirements includes proper overall dimension, component size and spacing, nail placement and quality, four way fork lift notch size, and placement, and absence of bark.

Quality requirements include the absence of excessive cupped wood members, nail tightness and minimum splitting of boards from nailing operation, pallet size and squareness, and frequency and tightness of knots.

Cap for Gallon Bottle Requirements

Physical inspection requirements includes; cap liner materials and tightness in cap, child resistant hinge presence, inner seal properly sealed, leak test with inner seal not activated, and child resistant feature properly engaged.

Quality inspection requirements includes drop or squeeze test of innerseal without cap, and torque test of cap at time of application and one hour later.

Labels for Container Requirements

Physical inspection requirements includes copy legibility, presence of complete label, correct panel placement on bottle, and squareness and adherence to surface. Initial layout includes State and Federal regulatory markings and placement. Layout and copy for labels may be submitted to the Federal and State agencies for approval.

Gallon Bottle Requirements

Physical inspection requirements includes, verifying threads are completely filled, cap sealing surface height is correct to assure that the cap will engage child resistant features when engaged, lot number placement and legibility, and cleanliness of outside.

Quality inspection requirements include empty and filled weight control charts and statistical interpretation of data to assure legal containers are shipped, and retain sample markings.

Palletization Requirements

Physical inspection requirements include carton squareness on pallet, absence of carton overhang, number of stretch wrap turns and tightness of wrap, absence of edge crushing from wrapping, pallet squareness of second pallet in warehouse, and ability to read lot numbers on minimum of one side.

Inspection Requirements—Shipment and Storage

Physical inspection requirements includes pallets on upper level placed square on lower pallet, evidence of carton crush or bulging side carton panels, and leaking bottles. Seepage of drums and gaskets may take days or weeks to be visible. Outbound physical inspection requirements includes trailer or rail for nails protruding on floor, and proper dunnage for rail shipments.

After Market Inspection

Field inspections are made and containers are inspected for outside container appearance, regulatory marking presence and legibility, and finished container cleanliness. Samples are taken for analysis.

The Coolant

Formulation development considerations include industry specifications for antifreeze grade glycol, blending facility inhibitor specifications, and blending facilities mixing and storage equipment. Sample production blends are made at each facility and analyzed.

Manufacturing specifications must be written in ranges which represent excellent control. pH with close ranges and pH at both concentrate and dilute concentrations as each one tells a lot about inhibitor balances. The tight reserve alkalinity (RA) ranges and pH relationship tells if its made right. Freeze test is what's on the label. It must be done right and verified often. Density is run to determine fill and shipping conversions. Elemental analysis is for certain areas. If silicone is on the label it must be verified. In conclusion the total package is a lot more than the coolant inside.

The Contract Blender/Packager Program

Hi-Port, Inc. is a contract blending, packaging, and distribution facility. In addition to glycol based antifreeze and wing deicer, we produce a wide variety of other products. Blends include products for commercial agriculture; insecticides, pesticides, and cleaning products for home owners; and several different car care products. They may vary in size from a few hundred gallons to a quarter of a million gallons. We also package a variety of wet and dry products for commercial use.

Contract Packaging

Contract packaging is a very competitive business. We are successful because we consistently meet our customer's requirements for a quality product. At the core of our quality system is an ISO 9002 certificate. Almost every element of the laboratory discussed here relates to an ISO clause. The methods we have implemented to obtain this certification provide the laboratory with a strong quality assurance program.

The ultimate goal of the laboratory is to ensure the customer receives finished products that meet specifications. The testing and approval processes begin with a training program based on position descriptions. Positions are defined in terms of the tests that a technician performs. Annual training needs assessment provide a written plan for accomplishing specific goals.

Safety training is always first. This includes Right to Know information, specific material safety data sheets (MSDS) for every chemical that the employee will be working around and the Laboratory Chemical Hygiene Plan. Written procedures, one-on-one instruction, and practice testing control samples are used to develop expertise in physicochemical testing. Each technician is required to demonstrate the ability to perform the test, discuss the use of controls when appropriate, and calibrate the instrument if applicable.

The laboratory team leader and technical representatives from the instrument manufacturer provide initial training on new equipment. For some of the analytical equipment, the laboratory technicians go to seminars and formal classes offered by the equipment manufacturer. Off-site training certificates are displayed on a wall in the laboratory.

Quality training is an on going process. Laboratory technicians use team meetings to discuss specific quality incidents or concerns. At these meetings we also discuss different parts of the Quality Assurance Manual and the Quality Assurance Operating Guide.

Blending and Packaging

Blending and packaging is seasonal work, with some overlap between products. It is difficult to maintain adequately trained laboratory staff during the main seasons and not be overstaffed during the slack time. We have developed a program that gives us several advantages. Some of our blenders and line leaders have gone through an extensive training program to learn physical testing for the products they handle.

When we run two and three shifts, these people can approve their lines for start up and significantly reduce laboratory overtime. An added benefit to production is the line leader's increased knowledge of the product being packaged. Knowing how to do a specific gravity test and understanding the significance of the results has helped to reduce the amount of line flush and reduce line start up time. Changing over to a different product in the middle of the night, or resuming packaging after a pump or hose failure is more efficient when personnel are already on site to do the testing.

Testing a line start up sample is the last quality check that we make. The process actually starts with contract review. The customer provides us with a specific formulation and a set of specifications. The chemist evaluates the formula and determines whether or not we can use the specified formula to produce a blend that meets required specifications.

Laboratory hand blends are made with the same raw materials that will be used in production. Frequently these materials are very different from the analytical grades used in developing a formula. The hand blend is a small time investment compared to dealing with a full scale off-specification blend.

After the formulation and specifications are confirmed, the Antifreeze Team Leader and the blenders determine our ability to physically put the blend together according to the customer's blending procedure. When the blend formulation, specifications, and blend procedure are finalized, the chemist prepares a blend sheet report.

Each product has a unique blend sheet form. Mathematical formulas built into the blend sheet and electronic links to a raw material file calculate adjustments for changes in the concentration of raw materials such as 50% sodium hydroxide. Any changes to the formulation must be authorized in writing by the customer.

A security system is used to maintain the integrity of the original formulation as blenders, and customer support personnel generate a new blend sheet for each batch that we produce. Final calculations are electronically checked from two different sources. If the blend sheet file has been changed or corrupted, a message warns of a possible error. When the message verifies the calculations are correct, the blend sheet is ready to use.

Raw Material and Product Specifications

Raw material and product specifications are maintained in a Lotus Notes database, and a hard copy is maintained by the Laboratory Team Leader. Each specification is reviewed and electronically approved by the Laboratory Team Leader and the Antifreeze Team Leader. Technicians are trained to access the specifications and electronically generate laboratory reports for the different sets of tests that we perform.

Each specification contains a unique part number, the parameters to be tested, parameters to be verified by Certificate of Analysis, and the tests to be performed for each part of the blending and packaging process. Changes to specifications require written approval from the customer.

Nonconforming material is placed on hold through our incident reporting system. The technician finding the nonconformance initiates the report and prepares the hold sign. The material is isolated until it can be dispositioned. The disposition depends on the type of material or finished product and the nature of the nonconformance. If the material is a Hi-Port owned raw material, it is rejected and sent back to the supplier. For customer supplied raw materials and for finished blends, the customer provides the disposition.

Laboratory Testing

Laboratory testing is essential to product integrity. The physiochemical properties of the antifreeze determine its functionality, or fitness for use. We begin with raw materials that have been purchased according to specifications. Each material is purchased from an approved supplier or is customer supplied. We do not receive anything without a Certificate of Analysis. The first shipment of a new material also requires an MSDS.

After the raw material is approved, it is released for blending. Several of our formulations require in-process testing. Customers may supply written directions for making in-process adjustments or they may require notification and supply information as required. If the in-process tests indicate a problem, the blend is placed on hold until a disposition can be approved.

Finished blends are tested according to customer requirements. When the blend has been approved, a tank tag is issued. It contains a date, signature, and unique identification number. Production personnel may not connect a hose to the valve or start a production line from a tank unless the tag is in place. It is their way of knowing that the product is good and that it is the correct product for that packaging run.

Test methods may be ASTM, customer supplied, or developed internally. The specific set of tests that we do for a particular material is usually confidential. Physical testing may include pH, RA, water, specific gravity, color, odor, appearance, freeze point, foam and break, distillation range, titrations, and other customer required tests.

At the beginning of each day, laboratory control samples are tested and results plotted on a statistical control chart. If the point is not in control, the problem is identified and corrected before any materials or blends are tested. Once again later in the day the same controls are repeated.

Control Samples

Using control samples to generate data points for a control chart is one way that we verify technique, instrument calibration, and reagent purity. Reagents such as pH buffers, acids, and bases are purchased with a certificate of analysis and NIST traceability. Each bottle is labeled with an expiration date. We track these dates through our Primary Chemicals spreadsheet. As each reagent nears its expiration, it is pulled from the shelf and isolated until it can be properly disposed.

Some procedures require a known, accurate temperature. Other require routine calibration of specific instruments. Thermometers are calibrated against a certified master, and instruments are calibrated according to manufacturer's recommendations. A calibration sticker is placed on each individual thermometer. It contains the calibration due date and any correction that should be applied to the reading. A color coded piece of tape also indicates the status of the thermometer. Instrument that requires periodic calibration have calibration stickers that show the next calibration due date.

Analytical Testing

Analytical testing confirms the concentration of corrosion inhibitors and other additives. Each set of tests begins with a standard curve and a control sample. NIST traceable reagents are used when they are available. All other primary chemicals require a certificate of analysis showing the purity of the reagent. Control sample data are plotted and in control before test results are reported.

We routinely use High Performance Liquid Chromatography (HPLC), Ion Chromatography (IC), and Atomic Absorption Spectrophotometry (AA). HPLC is used for aromatic inhibitors such as tolytriazole, MBT, and other confidential ingredients. IC detects anions such as chloride, nitrite, nitrate, phosphate, sulfate and others. AA is used mainly for silicon and molybdenum.

It takes a lot of time and resources to maintain the analytical laboratory. Extensive training is provided for calibration methods, testing, interpretation of data, and routine maintenance. Training is provided both in-house and at equipment manufacturer's facilities. We have service contracts on the instruments, but we can rarely afford the down time involved with bringing in a service technician to do minor repairs. Resources invested in technicians who can make routine repairs and analyze data are time and money well spent.

All the things we do to prepare for testing and the testing itself has enhanced value when we can trace the results back to a specific sample. Our retain procedure and storage of retained samples is structured so that we have almost immediate access to any sample that is still within the retain period. Databases containing a wide variety of information related to samples provide a wealth of information. We can re-test the retain if necessary to facilitate resolution of customer concerns or complaints. The stored data provide a history of all the tests performed on the retain sample, and it provides information for tracking our blending and packaging processes.

We are working toward becoming a paperless laboratory. Ironically, the ISO 9002 system that has helped us in so many ways is a hurdle in achieving this goal. We still need controlled paper documents and procedures to use when our electronic system fails. Even with this limitation, we have greatly reduced the number of quality records that we manually file and retrieve.

Lotus Notes databases maintained by the laboratory include: the Laboratory Operating Guide, Training Records, Product and Raw Material Specifications, Preventive Maintenance, and Calibration. Other databases that we use include: Incident Report system, ISO 9002 Tier 1 and Tier 2 guides, Quality Assurance Operating Guide, and an E-Mail system for inter-departmental communication.

The Laboratory Operating Guide contains procedures and work instructions. New procedures and revisions are developed and approved by the team. Each new or revised procedure requires training. With over 100 procedures, 6 full time technicians and 10 to 12 production personnel with lab training, the Lotus Notes Training database facilitates management of our training program.

Different Types of Laboratory Analysis

Different types of laboratory analysis forms can be accessed from Lotus Notes. Each form contains specifications, required tests, and formulas to validate test results as they are entered into the form. If all of the results meet specifications, the form can be electronically approved and stored. If any parameter is out of specification, approval can only be achieved through an incident report and customer waiver.

Our incident reporting system is the tool we use to document nonconformance, describe how we will resolve nonconformance, and provide a time frame for disposition. It contains historical information that is easily sorted or grouped to show trends and repeated problems. Recurring incidents are communicated to our customers. The end result may be a change in suppliers for repeated off-specification raw materials or a change in formulation or specifications for blends that are routinely off-specification.

Lotus 1-2-3-spreadsheets are used to maintain and manage blend sheets, controlled laboratory forms, specific customer requirements, and our Primary Chemical Inventory. Other files contain replicas of certificates of analysis that we receive for each raw material receipt. The original is electronically scanned into the database and stored with a unique file name that corresponds to the file name of the test results for that material.

Conclusions

As our company grows and new customers bring intriguing challenges, we develop creative ways to fulfill requirements. This usually leads to unique spreadsheets or different databases that must be updated, stored and retrieved. We will continue to look for innovative ways to maintain an electronic system with reliable backups that are complete and readily assessible. Continuing to meet ISO 9002 requirements is our goal. The certification and recertification process provide us with tools to meet customer requirements. A paperless system makes it easier to maintain.

Engine Coolant Service and Disposal

Edward R. Eaton[1] and Heather S. Eaton[1]

Extended Service of "Fully Formulated" Heavy-Duty Antifreeze in American Cars

REFERENCE: Eaton, E. R. and Eaton, H. S. "**Extended Service of 'Fully Formulated' Heavy-Duty Antifreeze in American Cars,**" *Engine Coolant Testing, Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 361–369.

ABSTRACT: In 1995, a universal "fully formulated" antifreeze/coolant specification was published for the first time in The Maintenance Council (TMC) Recommended Practices (RP) 329 and 330. It was the intent of TMC to provide a coolant that could be used in both automotive light-duty engines and heavy-duty diesel engines. This simple, one-step coolant would allow fleet managers to decrease maintenance while complying with OEM warranty requirements. In addition, fleet managers would have only one coolant to inventory. Extensive data have been presented by various authors and are recorded in the literature regarding the application of this type of coolant in heavy-duty diesel engines. Herein are reported the positive results and documentation of the successful extended service interval (ESI) application of this coolant in light-duty automobile engines, complementing the heavy-duty performance database. Vehicles from the "Big Three" American car manufacturers were operated for a distance exceeding 100 000 km (62 000 miles) with excellent experience. This paper reports the test parameters, test methods, test data and concludes that both TMC RP-329 and RP-330 compliant, phosphate-free low-silicate coolants offer ESI performance for light-duty as well as heavy-duty applications.

The data reported in this paper are derived from a controlled ESI study. The data compare the behavior of a nitrite/borate/low-silicate, low total dissolved solids (TDS) inhibitor technology in ethylene glycol and in propylene glycol coolants. Both laboratory and fleet data from six cars, powered with different makes of light-duty gasoline engines and cooled with two different types of aqueous glycol coolants for a distance exceeding 100 000 km (62 000 miles), are reported. Data include chemical depletion rates, periodic coolant chemical analyses, coolant use and makeup statistics, and engine/cooling system reliability experience. The engines were completely disassembled both at the inception and at the conclusion of the test, allowing for thorough inspection.

KEYWORDS: fleet, extended service, delayed-release, organic acid, phosphate, nitrite, fully formulated, inhibitors, silicate, depletion, propylene glycol, aluminum radiators, water pumps

This paper supports the practice of using fully formulated, low total dissolved solids, phosphate-free, low silicate (PG or EG) coolants in light-duty vehicles for extended service intervals. Additional literature [*1*] has already supported the use thereof in medium and heavy-duty vehicles as an ESI coolant, it having been documented that the subject technology can run 800 000 to 1.6 million km (500 000 to 994 000 miles) when properly maintained with a state-of-the-art release-as-required coolant filter. Information was derived from both laboratory evaluations and a fleet test of six American cars, two each from the "Big Three" manufacturers. One member of each pair was operated with EG-based coolant, the other with PG-based coolant. The paper presents data that show that North American "fully formulated" EG and PG coolants perform well as extended-service interval (ESI) coolants in American cars. [Note: Table 1

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TABLE 1—*General terminology.*

Antifreeze	pure glycol (typically 95% min) with an inhibitor package added
Conventional coolant	coolant chemistry, usually based in ethylene glycol, that contains a corrosion inhibition package consisting of inorganic inhibitors
Coolant	heat exchange fluid consisting of water and inhibited glycol, typically at 50% each
D. I. water	deionized (purified) water
EG	ethylene glycol, the most common chemical used as a base to prepare antifreeze products
ESI	extended service interval, a maintenance interval significantly longer than the previous practice
GM-6043	GM-6043 antifreeze specification provides an actual recipe for phosphated, silicated light-duty factory-fill fluid that many antifreeze blenders have emulated to prepare ASTM D 3306 compliant antifreeze
OEM	original equipment manufacturer
Organic acid inhibitors	any of a group of carboxylic acids including sebacic, and 2-ethylhexanoic applicable as corrosion inhibitors in engine coolant
PG	propylene glycol. PG coolants are desirable in some environmentally sensitive applications, such as national parks
P.M.	preventative maintenance interval, typically defined by the oil change interval
RP	recommended practice of the TMC, often a purchasing specification
SAE	Society of Automotive Engineers
TMC	The Maintenance Council of The American Trucking Association

provides an explanation of both general and in-coolant terminologies used throughout this paper.]

Coolant serves as a heat transfer medium that allows heat to be expelled to the atmosphere. Antifreeze added to water lowers the freezing point and prevents corrosion of the cooling system. Cooling system metals may include copper, steel, cast iron, brass, lead solder, and extruded or cast aluminum. In the past, light-duty OEMs have recommended changing the coolant every two years or 38 000 to 58 000 km (24 000 to 36 000 miles), whichever came first. The data reported in this paper support the extension of the change interval of a phosphate-free, fully formulated PG or fully formulated EG coolant in light-duty vehicles beyond 112 000 km (70 000 miles).

Coolant Compositions

Two types of coolants were involved in the test:

1. Propylene glycol base, inhibited with a phosphate-free, low-silicate package compliant with TMC RP-330 mixed at 50% with deionized (DI) water.
2. Ethylene glycol type coolant inhibited with a phosphate-free, low-silicate package compliant with TMC-329 mixed at 50% with DI water.

Experimental Procedures

Laboratory Trials

The test coolants were evaluated in the laboratory for compliance with the TMC RP-329 (or RP-330) specification. The specification requires that the coolant meet both ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light Duty Service (D 3306-

TABLE 2—*General requirements.*

Property	ASTM/TMC Specification	PG Coolant Performance	EG Coolant Performance
Color	distinctive	green	green
Effect on nonmetals	no adverse effect	no adverse effect	no adverse effect

94) and ASTM Specification for Low Silicate Ethylene Glycol Base Engine Coolant for Heavy-Duty Engines Requiring a Pre-Charge of Supplemental Coolant Additive (SCA) (D 4985-94) performance criteria. The coolants were also independently analyzed before the tests. Both coolants passed the ASTM D 3306 (automotive and light-duty trucks) and D 4985 (heavy-duty trucks) performance requirements. The performance data are reported in Tables 2, 3 and 4.

Coolants Evaluated

The objective of the evaluation was to determine if a behavioral advantage observed in the laboratory for propylene glycol supercharged with an extra 50% charge of inhibitors could be observed in a fleet test in actual automobiles. Data from laboratory simulated service testing [Test Method for Simulated Service Corrosion Testing of Engine Coolants (D 2570-96)] suggested that there may be an advantage to supercharged propylene glycol as compared to a customarily inhibited ethylene glycol. "Supercharged" coolant is defined as an inhibitor level equal to 150% of that commonly used in the EG based coolant to achieve TMC RP-329 or TMC RP-330 specification requirements. The laboratory data were intriguing; if the data could be supported in the field, then it posed the possibility that such a conventionally inhibited PG based coolant may be applicable as an extended service product in both light and heavy-duty vehicles offering extended service intervals of five years or 160 000 km (99 000 miles). In an earlier comparison of conventional and organic-acid inhibition technologies in ethylene glycol, Adamowicz concluded that this might, in fact, be true. The application of propylene glycol to the system proffered the possibility of reduced solder corrosion and improved wet-sleeve liner protection, as suggested by laboratory data.

The EG coolant used in the evaluation is the type of coolant currently factory-filled at most major heavy-duty truck and bus manufacturing facilities. Its maintenance recommendation includes periodic testing and addition of SCAs either through filter or liquid methods. This served

TABLE 3—*Physical and chemical requirements.*

Specific gravity @ 15.5°C	1.110 to 1.145 EG 1.030 to 1.065 PG	1.040	1.125
Freeze point, °C	50 vol. % in water: −37 max. EG, −32.2 max. PG	−37	−39
Boiling point, (°C)	163 min. EG 151.7 min. PG	152	164
Effect on automotive finish	no effect	no effect	no effect
Ash content, mass %	5.00% max.	0.7%	0.53%
pH: 50 vol. % in distilled water:	7.5 to 11.0	10.8	10.4
Chloride, ppm	25.0 max.	21	20
Water, mass %	5 max.	3.2	2.8
Reserve alkalinity, mL	report	8.0	7.0

TABLE 4—*Performance requirements.*

			PG	EG
Corrosion in glassware	D 1384			
copper		10 max.	0	1
solder		30 max.	3	8
brass		10 max.	0	1
steel		10 max.	0	0
cast iron		10 max.	0	0
aluminum		30 max.	0	0
Simulated service	D 2570			
copper		20 max.	0	3
solder		60 max.	7	15
brass		20 max.	0	3
steel		20 max.	0	1
cast iron		20 max.	0	1
aluminum		60 max.	0	3
Corrosion of cast aluminum	D 4340	1.00 max.	0.10	0.06
foaming				
volume, mL	D 1881	150 max.	50 mL	45 mL
break time, s		5 max.	3.5 s	2.7 s
Cavitation erosion of the water pump	D 2809	8 min	10	10

as the control coolant. The experimental coolant varied from the control in two ways: It had 150% of the additive concentration and was based on propylene glycol as opposed to ethylene glycol. Propylene glycol is interesting to engine operators who are concerned about the toxicity of EG-based coolants.

Fleet Test Protocol

The test coolants were installed in the six new cars. The cooling systems were completely drained. The engines were disassembled and each component inspected to verify its compliance with the OEM initial specifications. Several engine parts were identified as out-of-spec and were replaced before the start-of-test. The engines were then reassembled and filled with coolant consisting of antifreeze (50%) with deionized water. Initial coolant and oil samples were taken.

This test was conducted as a "piggyback" test. The primary funding was provided by an unrelated lubricating oil investigation. The test was designed to accumulate mileage while providing daily cooldown cycling and a variety of driving conditions. The intended duration of the test was 160 000 km (99 000 miles). At 16 000 km (10 000 miles) inspection intervals, the glycol concentration and physical properties of the coolant were determined by laboratory analysis and recorded.

A test circuit consisting of an 80% highway and a 20% city route in the Chicago, Illinois area was developed. Highways in this area are frequently congested, offering idling and heating opportunities. Each day the vehicles were shut down for four hours to provide for a complete cooldown. During the test, the vehicles were exposed to an ambient temperature range of approximately −10 to +35°C.

The test began in March 1996 and was terminated in November 1996. The vehicles' distance accumulation averaged about 500 km (311 miles) per vehicle per day.

At the end of the test, the engines were again disassembled. All of the used test coolant was retained. The primary customer (a lubrication oil manufacturer) discontinued the test at 112 000 km (70 000 miles). The final inspections reported herein reflect that term of service. The engines were again disassembled and inspected. The radiators were also inspected and one of the aluminum radiators was sectioned. The data from the final inspection were recorded and the test was concluded.

Description of the Test Vehicles

General Motors Product—1996 Pontiac Bonneville, 3.8 L engines. These V-6 engines feature an iron block and are equipped with aluminum radiators.

Ford Motor Product—1996 Ford Thunderbird, 4.2 L engines. These V-8 engines feature a steel block and are cooled by an aluminum radiator.

Chrysler Motor Product—1996 Chrysler Concorde, 3.5 L engines. These V-6 engines feature aluminum blocks cooled with copper-brass radiators.

Coolant Performance Data

Ethylene and propylene glycol coolants in the Chrysler Concordes seem to have performed similarly (Table 5). The pH gently declined with time, but remained within acceptable ranges to prevent metal corrosion. This observation is supported by noticing that contaminants associated with component corrosion did not increase. One inhibitor that depleted significantly was silicate, which, in performing its intended function, is assumed to have formed a protective layer on aluminum surfaces. The increase in the sulfate concentration is due to the oxidation of MBT, an inhibitor added to prevent-corrosion of soft metals such as copper and brass. The authors note that it is possible to replace the MBT with TT, which will perform the same function without exhibiting the increase in sulfate concentration.

Some of the variations, such as those reported in freeze point, molybdate, phosphate and chloride content, are probably simple variations in experimental method. Inasmuch as no coolant was added to these systems, and the samples removed for analysis were small, these properties should, logically, remain constant. Nitrate concentrations increase as some of the nitrite oxidizes to nitrate. Nitrate is a desirable inhibitor, so the minor conversion of some of the nitrite to nitrate is inconsequential as manifested by the unremarkable levels of metals in the coolants.

The data from the two other makes confirm the Chrysler experience. The Thunderbird and Bonneville cooling systems generated very similar data in all of the properties measured. None of the cars experienced any cooling system problems whatsoever.

The data provide the ability to analyze the behavior of the various coolant properties and the behavior of inhibitor chemicals. The pH behavior for the group of fluids was similar. There is an initial drop in pH during the first 16 000 km (10 000 miles) period. After that initial adjustment, the rate of change of the pH value decreases dramatically. The authors note that the uniform increase in pH reported by the laboratory in the 6th and 7th samples suggests a change in the equipment or method that may have generated slightly higher results. It is unlikely that the pH actually increased.

Normally, the coolant should have been changed at about 48 000 km (30 000 miles) to comply with OEM warranty requirements. It is significant that the pH did not change dramatically during the extended service period (Fig. 1). Operation at the alkaline pH range is important to the anti-corrosive functions, and to maintaining the solubility of some inhibition chemicals in the coolant. The coolant inhibitor package contains borate buffers that appear to be successfully maintaining the appropriate and desired pH range for continued functional efficacy.

The formula used in this evaluation contains mercaptobenzothiazole (MBT) [$C_7H_5NS_2$]. The structure of MBT includes a sulfur component that is available to form sulfate compounds over

TABLE 5—*Coolant performance data.*

				1996 Chrysler Concorde, EG				
Sample	0	1	2	3	4	5	6	7
pH	9.9	8.4	8.3	8.0	7.8	7.6	9.4	8.8
FP	−38	−36	−38	−38	−36	−33	−30	−32
Cl	20	21	4	20	20	17	22	10
SO_4	140	200	220	200	270	330	460	520
Pb	0	6	1	0	0	0	0	0
Cu	0	1	0	0	1	1	0	0
Fe	0	2	1	0	1	0	0	0
Al	0	0	1	0	2	1	0	0
NO_2	1260	1030	1100	1100	930	800	1000	1000
NO_3	350	470	530	500	540	500	650	850
Si	109	62	60	70	51	64	67	96
MoO_4	13	61	50	60	50	50	0	20
P	0	56	60	0	0	0	46	44
				1996 Chrysler Concorde, PG				
pH	11.3	8.6	8.7	8.3	8.0	7.8	9.7	8.8
FP	−40	−42	−40	−40	−42	−42	−40	−40
Cl	20	14	20	20	30	20	16	10
SO_4	23	170	270	300	360	420	700	700
Pb	0	0	0	1	1	0	0	0
Cu	0	0	0	0	1	0	1	0
Fe	0	2	1	2	2	3	0	2
Al	0	0	0	0	0	0	0	0
NO_2	2000	1800	1800	1700	1450	1400	1600	1500
NO_3	700	800	850	850	900	900	1100	1400
Si	200	55	408	50	40	50	50	80
MoO_4	0	30	25	0	26	24	0	80
P	0	0	0	30	0	0	1	18
				1996 Ford Thunderbird, EG				
pH	9.9	8.6	8.3	8.1	8.0	7.9	9.4	8.8
FP	−29	−34	−35	−35	−34	−32	−30	−30
Cl	20	4	11	14	25	30	20	10
SO_4	140	70	120	130	150	200	230	300
Pb	0	0	0	1	0	0	0	0
Cu	0	0	0	0	0	0	0	0
Fe	0	1	1	0	0	1	0	1
Al	0	0	1	0	0	0	0	0
NO_2	1260	1150	1200	1100	940	900	1200	1300
NO_3	350	420	470	450	410	400	500	600
Si	109	60	60	61	65	60	45	80
MoO_4	13	17	0	22	13	20	0	6
P	0	0	17	0	0	0	1	2

time in the coolant (Fig. 2). This behavior is made manifest in the gently increasing sulfate concentrations. Sulfate is of interest because it is thought to contribute to aluminum corrosion. Such corrosion would be evidenced by aluminum in the coolant analyses. The authors refer to the above tables, which report no significant aluminum presence in the coolant samples. It appears that any corrosive propensity developed through the accumulation of sulfates is coun-

TABLE 5—*Continued.*

1996 Ford Thunderbird, PG

pH	11.3	9.3	8.9	8.5	8.5	8.2	9.7	8.9
FP	−56	−55	−60	−39	−42	−32	−56	−52
Cl	20	20	10	10	40	30	27	10
SO_4	12	70	130	200	260	300	410	450
Pb	0	0	1	0	0	0	0	0
Cu	0	0	0	0	0	0	0	0
Fe	0	1	1	0	1	2	0	1
Al	0	0	0	1	0	2	0	0
NO_2	1900	1900	2000	1700	1600	1500	1900	1900
NO_3	700	800	800	800	850	800	1000	1100
Si	200	44	44	40	50	45	44	66
MoO_4	0	2	45	20	17	18	0	5
P	0	0	0	0	0	0	1	7

1996 Pontiac Bonneville, EG

pH	9.9	8.6	8.7	7.8	8.4	8.2	9.4	9.1
FP	−29	−32	−34	−37	−35	−35	−35	−35
Cl	20	14	0	14	25	11	23	10
SO_4	140	50	100	100	130	170	230	300
Pb	0	0	0	0	1	0	0	0
Cu	0	0	0	0	1	0	0	0
Fe	0	1	0	1	0	1	0	0
Al	0	0	1	1	0	1	0	0
NO_2	1260	1100	1000	900	810	750	1000	1100
NO_3	350	400	460	500	520	500	500	700
Si	109	61	53	70	60	50	42	60
MoO_4	1	0	0	0	0	0	0	0
P	0	0	0	0	0	0	1	1

1996 Pontiac Bonneville, PG

pH	11.3	9.1	9.1	9	8.8	8.7	9.8	9.2
FP	−58	−52	−55	−40	−46	−40	−58	−56
Cl	20	20	20	20	20	7	24	10
SO_4	23	80	140	140	200	250	340	400
Pb	0	0	0	0	1	0	0	0
Cu	0	0	0	1	0	0	0	0
Fe	0	2	0	1	1	1	0	0
Al	0	0	3	0	0	1	0	0
NO_2	190	180	170	150	140	138	160	170
NO_3	70	80	80	80	85	80	90	110
Si	200	48	41	35	40	30	40	50
MoO_4	0	0	0	0	0	0	0	0
P	0	0	0	0	0	0	1	10

tered by the inhibition action of the coolant chemistry, in particular the silicate, relative to aluminum corrosion.

Silicate is the inorganic inhibitor of choice for aluminum corrosion inhibition. The silicon concentration in the coolant reflects an initial surface coating activity when the engine metals are new, followed by a stable period (Fig. 3). The absence of aluminum in the analysis reports verifies that the quantities of silicate, in combination with the other inhibitors that constitute the package in these coolants, adequately protected all three engines' aluminum components

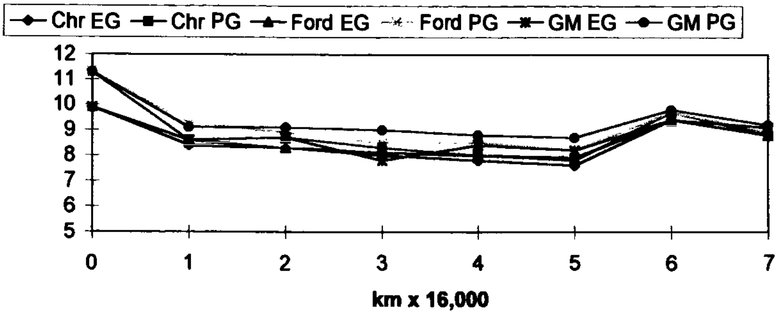

FIG. 1—*pH behavior.*

against corrosion. This finding is further supported by careful visual inspection of the disassembled engines and aluminum radiators after the conclusion of the test.

Overall, the behaviors of the additives were consistent with previous experience and expectations. Initially the fresh metals in the engine deplete some of the additives. The mechanism is generally acknowledged as a film-forming process, reducing the concentration of additives. After this initial period, the rate of depletion slows.

Summary

The test data generated in the bench tests which suggested that a supercharged PG (SPG) would perform better than the phosphate-free TMC RP-329 specification, normally inhibited EG, were not confirmed. Instead, both coolants completed the test protocol successfully. If the SPG has a longer term of service, it is beyond the 112 000 km (70 000 miles) duration of this fleet evaluation.

Examination of the data reveals no negative behavior in any of the three types of vehicles involved in the test. No components were lost, and there was no indication of corrosion in the system. The properties of the coolant remained adequate to continue to protect the system at three times the previously recommended change interval for conventional coolant technology.

There were no traces of deposits found on any components in the cooling system. The water pumps, engine coolant passages and radiators were all closely examined and photographed. The condition of the components in all of the engines could easily be compared to new components.

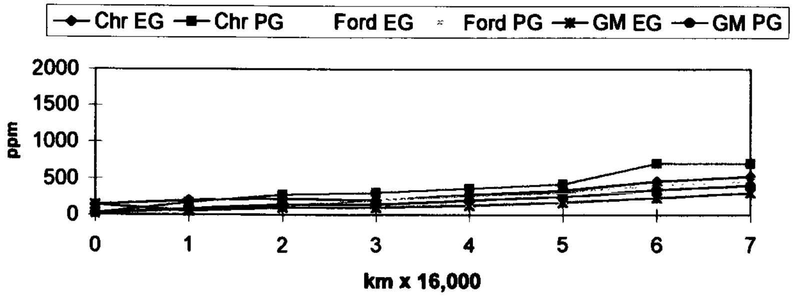

FIG. 2—*Sulfate concentration.*

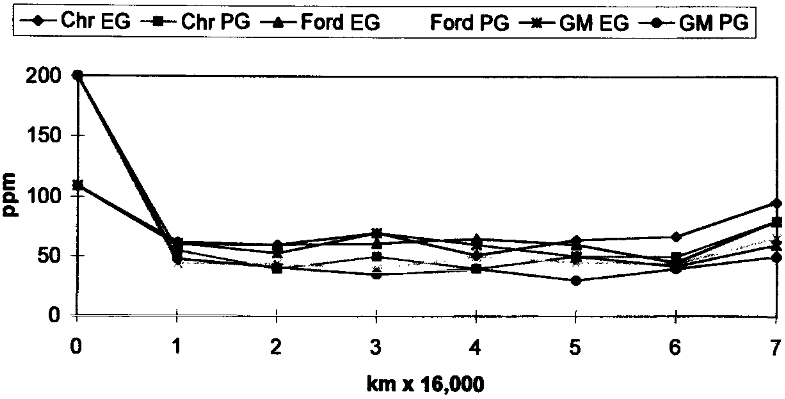

FIG. 3—*Silicon behavior.*

Conclusions

Each of the six cars operated satisfactorily on "fully formulated" antifreeze.

Propylene glycol base and ethylene glycol base coolants with this "fully formulated" inhibitor package performed similarly in terms of corrosion protection.

Light-duty, aluminum-containing engines may be operated for periods of at least 112 000 km (70 000 miles) on phosphate-free, low-silicate coolants meeting TMC RP-329 (EG) or TMC RP-330 (PG) specifications with excellent performance expectations.

Reference

[1] SAE Technical Papers 969642 (Eaton, Carr), 961039 (Scott, Weir), 961819 (Eaton), 962239 (Eaton): Aroyan, S. S. and Eaton, E. R., "Fleet Test Evaluation of Fully-Formulated Heavy-Duty Coolant Technology Maintained with a Delayed-Release Filter Compared with Coolant Inhibited with a Nitrited Organic Acid Technology: An Interim Report," *Engine Coolant Testing, Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, West Conshohocken, PA, 1999, pp. 43–51.

Allen B. Wright[1]

Fleet Test Evaluations of an Automotive and Medium-Duty Truck Coolant Filter Conditioner

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REFERENCE: Wright, A. B., "**Fleet Test Evaluations of an Automotive and Medium-Duty Truck Coolant Filter / Conditioner,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 370–391.

ABSTRACT: The use of coolant filtration and supplemental coolant additives (SCA) to replenish depleted protective chemistry has been applied in the heavy duty diesel arena for many years. Some filtration of coolant and SCA usage in light gasoline engine and automotive diesel engine vehicles has taken place using off-board equipment to filter and recondition coolant. As concerns about the environment have increased, disposal of spent coolant that is replaced on a scheduled basis is a burden on fleets as well as individuals. In addition, as the efforts by vehicle manufacturers to extend or eliminate routine service intervals of vehicle systems increase, the use of an on-board system has become more attractive.

A number of filtration/conditioning designs have been developed for light and medium duty use and have been on field tests for over a year. These field tests are described and reported, along with background on the filter design and chemistry package used. Field testing included: low and high mileage vehicles; newer and older vehicles; well and poorly maintained vehicles; and an assessment of the possibility of overcharging of the coolant chemistry.

KEYWORDS: coolant, filtration, supplemental coolant additives, diesel, automotive, medium duty, gasoline, filter/conditioner

Background

The use of supplemental coolant additives (SCAs) to replenish depleted chemistry and filtration of coolant fluids is well known and widely used in the heavy-duty diesel engine field. The wet sleeve construction of these engines and the long service life of the coolant requires that the cavitation-corrosion chemistry, buffers and other corrosion or scale inhibitors or both be refreshed periodically. Dry and wet additives have been developed and techniques of introducing these additives are common shop maintenance practices with heavy-duty diesel fleets [*1*].

Use of additives or filtration in lighter duty automotive and even in medium-duty applications such as delivery fleets has not been approached in nearly as wide spread a manner as that of heavy duty [2]. The length of time the engine/vehicle manufacturers recommend between drain/flush/refill is short in comparison to heavy duty [25 000 to 35 000 miles (40 233 to 56 326 km) versus 200 000 to 500 000 miles (321 860 to 804 650 km)]. The need for wet sleeve cavitation corrosion protection is not an issue with gasoline engines. Automotive antifreeze coolant is easy to use, inexpensive, and can even be purchased as a pre-mixed product. Since following

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the change recommendations of the vehicle manufacturer replenished the chemistry while removing much of the solid contaminants, there was no incentive to develop, manufacture, or market a coolant additive or filter package for this market segment.

Several factors have emerged over the past decade that are changing the concept that filtration of coolants and SCAs are not for automotive and medium duty applications. First is the increasing use of aluminum and other metals/alloys in what was traditionally a cast iron engine [*3*]. This increase in materials diversity has created the need for specialized chemistry targeting these metals for corrosion protection. These chemicals will deplete as they are deposited on the wet surfaces, and combine chemically with other compounds. The need to make up for this depletion is bringing the use of a chemical additive into the automotive and medium duty realm. The second driver toward development of coolant additives and filtration for nonheavy duty vehicles is the growing environmental concern and cost of disposal. Some filtering/reconditioning devices have been developed recently, but are of an off-vehicle style that, while lending themselves to the garage or large shop environment, are not easy to use, or affordable to own, by individuals and small fleets [*4*]. Extending the life of the coolant and keeping the cooling system clean has been the impetus behind our effort to develop a simple to service device that will clean the solids from the cooling systems of automotive and medium duty engines while acting as a delivery system for makeup chemistry for those compounds normally depleted over time.

Objective

The purpose of this study was to evaluate the effectiveness of transferring proven heavy-duty truck technology to a coolant filter/conditioner applied to automotive and medium-duty vehicles. Vehicles chosen were passenger automobiles (used primarily for owner conveyance), medium sized sport-utility vehicles (SUVs) (used for both personal transportation and towing of trailers), and larger pickup trucks/large vans (used for towing and some farm use). The effort to acquire data was due to questions raised by the first fleet owners approached in our initial marketing study. These questions included; Does the product deliver what it claims? Is it safe and easy to use? Will we experience the chemical drop out problems that plagued the heavy-duty (HD) industry in the early years of SCA use? How will it affect the chemical balance of the coolant?

Early Prototypes

The first prototype samples utilized an existing metal in-line filter body with barb style fittings on the ends for attachment to the heater hose. The cartridge inside contained the same media used in HD truck coolant filters. An SCA that would replenish the most commonly depleted additives in automotive antifreeze was developed. This SCA package was made into a water soluble pellet that was inserted into the cartridge during manufacture. Also included in the design of these prototypes was a relief valve set to open at 6.9 to 20.7 kPa (1 to 3 psi) differential across the cartridge. This valve was included to allow coolant to flow to the heater core after the filter element had plugged. Later prototypes utilized the same metal body and cartridge but were made with beaded tube ends versus barbed fittings.

Test Fleet

The vehicles used for prototype testing of the filter/conditioner were pulled from an existing pool used for evaluation of oil and fuel filters. Those chosen were of varying age, mileage,

TABLE 1—*Test fleet vehicle list.*

Vehicle Number	Make	Model	Year	Displacement	Start Mileage	End Mileage	Test Miles	Number of Filter Changes
1	Ford	F 150	1992	5.0 L	42 248	60 578	18 330	1
2	Ford	F 150	1994	5.0 L	19 136	52 394	33 258	2
3	Ford	F 150	1992	5.8 L	68 921	103 566	34 645	3
4	Ford	Aerostar	1986	3.0 L	153 125	163 492	10 367	8[a]
5	Chrysler	Cherokee	1990	5.0 L	132 242	168 079	35 837	4
6	Ford	F 150	1995	5.0 L	18 458	29 995	11 537	1
7	Mercury	Gr. Marquis	1987	5.0 L	91 475	107 862	16 405	1
8	Mercury	Gr. Marquis	1987	5.0 L	78 055	88 317	10 262	1
9	Mercury	Gr. Marquis	1989	5.0 L	91 122	108 268	17 146	1
10	Mercury	Gr. Marquis	1987	5.0 L	130 039	139 284	9 245	1
11	Mercury	Town Car	1987	5.0 L	72 337	107 862	16 405	1
12	GM	Suburban	1989	5.7 L	106 117	117 586	11 469	1
13	Ford	F 150	1988	5.0 L	66 906	69 957	3 051	1

[a] This vehicle had several filter/conditioners installed to evaluate the effect of "overcharging" the coolant system.

NOTE—1 mile = 1.61 km.

past coolant system maintenance practice, and all were from 3.0 to 5.8 L in displacement. Age ranged from 8 months to 10 years old. Mileage at the start of the test program ranged from 18 500 to over 153 000 miles (29 772 to 246 223 km) (Table 1).

Test Procedure

Once the test fleet had been chosen, each vehicle was examined for placement of the first generation prototype filter/conditioner. Placement should be easy, safe, and as nonvehicle specific as practical in order to reach the largest percentage of the current vehicle population as possible. The filter/conditioner was placed in-line in either heater hose (inlet or outlet) for the convenience of the shop/fleet mechanic or do-it-yourself'er. This has been the choice of flush kits for many years, and is accepted widely in the marketplace.

The procedure for sampling of the coolant was to have the engine warm, but not hot, removing the radiator cap, starting the engine to heat and circulate the coolant until the thermostat opened to allow flow throughout the engine and heating system. The engine was allowed to run for 10 min after the thermostat opened. Using a clean sampling syringe and plastic hose, a 226.8 g (8 oz) sample was withdrawn from 15.29 to 25.4 cm (6 to 10 in.) below the water level in the radiator. One exception was the Jeep Cherokee (Vehicle No. 5), which had a system without a radiator cap. The coolant fill/recovery tanks are accessible, but act as a settling tank without a great deal of fluid exchange. For this vehicle, we installed a sampling valve downstream of the filter/conditioner and analysis samples were drawn from this point after the stabilization period as described previously.

During the test, technicians replaced the sample coolant volume with a 50/50 mixture of distilled water and a commercial antifreeze. Analysis of this makeup mixture was also done. Vehicles were generally returned to the garage for any makeup coolant needs. Except for one vehicle that had a hose leak that required about half of its coolant to be replaced (Vehicle No. 3), and two others that added a late winter top off (Vehicle No. 2 and Vehicle No. 12). This was done and volumes of makeup fluid recorded.

Each sample was divided into clean glass lab sample bottles of 56.7 and 170.1 g (2 and 6 oz) size. The small sample was retained as a control/backup, and the larger sample sent directly to the analysis lab for testing/chemical analysis.

Concerns had been raised about the possibility of over-servicing this product, causing an "overcharged" condition of chemical additives. These concerns have roots in the early heavy-duty usage of SCAs where a dropout of the chemicals resulted in what now is referred to as "green goo." In an effort to evaluate such a possibility, one vehicle (Vehicle No. 4) was chosen to have the filter/conditioner replaced at least 6 times in a one year period versus 12 000 to 15 000 mile (19 312 to 24 140 km) intervals.

Analysis and Sampling

Analysis

Analysis of the coolant samples were tabulated and tracked for each vehicle, and charting was done on suspended solids, tolyltriazole, nitrate, molybdenum, silica, and orthophosphate. We tracked the suspended solids parameter to evaluate the effectiveness of the filter in cleaning the system, and tracked the other items since they were part of the chemical SCA package used. All values were reported in parts per million (ppm).

In addition, the analysis lab provided information on dissolved solids (%), pH, freeze point (°F), mercaptobenzothiazole (ppm), and chloride (ppm). Although the numbers from analysis of these were monitored, the SCA was not formulated to change pH or freeze point, and contained no mercaptobenzothiazole or chloride. The amount [7 g (¼ oz)] of chemicals in our SCA did not have any noted effect on dissolved solids levels, including that of the purposely over-serviced vehicle (Vehicle No. 4). Dissolved solids ranged from 1.1 to 2.6%, with most near the 1.3% baseline of our 50/50 makeup mix.

Raw data from the analysis done for each field test sample, by vehicle and variable charted are listed in Table 2. The data were graphed showing the levels of the charted variables for each vehicle (Figs. 1–13). These graphs show the baseline analysis of the 50/50 makeup mix as a straight line.

Samples

Samples were withdrawn from each vehicle prior to installation of the filter/conditioner to obtain a base datum for each. Subsequent samples were taken as the vehicles were brought in either for: replacement of the filter/conditioner, makeup coolant, and in the case of the purposely over-serviced vehicle (Vehicle No. 4), when the employee was requested to do so.

Results

Suspended Solids

Data shown graphically (Figs. 1 to 13) show that the suspended solids were indeed reduced dramatically. With each vehicle in the study, the opacity of the coolant was visibly reduced between the first and second samples. Some of the vehicles had very few miles between these samples. The range of visible improvement was from a milky green initial sample changing to one where print could be read clearly through the next sample, to the worst case where the initial sample was an almost black muddy fluid changing to a light brown-but-still-opaque green tinged sample. Ppm data show this improvement, even on vehicles that had but one filter/conditioner installed during the year long field test. The question of whether the filter part of the filter/conditioner worked has certainly been answered.

TABLE 2—*Fleet test raw data summary.*

Miles Between Samples	Total Miles Driven	Tolyltriazole	Nitrate	Orthophosphate	Molybdenum	Suspended Solids	Silica	Filter Installed
Vehicle No. 1								
0	0	340	970	1 340	0.7	30	51	Y
566	566	440	1 050	1 520	8.8	75	77	
12 457	13 023	395	1 000	1 136	30.0	23	51	
5 307	18 330	380	890	940	40.0	18	54	Y
Vehicle No. 2								
0	0	530	800	2 180	0.5	70	113	Y
781	781	620	900	2 400	9.7	170	131	
23 483	24 264	485	920	1 606	11.0	214	98	Y
8 994	33 258	495	1 000	1 870	30.0	10	107	
Vehicle No. 3								
0	0	360	930	1 700	0.5	100	113	Y
483	483	450	1 030	1 920	9.7	200	101	
2 309	2 792	450	1 040	2 000	9.1	80	83	Y
3 784	6 576	600	1 100	2 210	25	9	98	Y
28 069	34 645	860	1 300	5 500	20	10	36	Y
Vehicle No. 4								
0	0	190	1 000	2 700	9	100	62	Y
210	210	310	1 080	2 760	20	200	86	Y
719	1 757	450	1 400	3 200	38	50	111	Y
656	2 413	585	1 300	3 370	62	9	113	Y
1 665	4 078	670	1 400	3 850	60	9	94	Y
2 767	6 845	610	1 400	3 753	63	9	103	Y
3 522	10 367	510	1 100	3 250	70	16	64	Y
Vehicle No. 5								
0	0	410	1 080	1 270	270	3700	88	Y
1 234	1 234	530	1 180	1 600	330	4480	109	
905	2 139	510	1 230	1 560	280	4400	86	
3 730	5 869	520	1 200	1 800	270	1080	73	Y
943	6 812	720	1 600	2 300	288	125	96	Y
18 152	24 964	850	1 800	2 971	241	385	92	Y
10 512	35 476	920	1 600	3 500	185	120	64	Y
Vehicle No. 6								
0	0	490	800	1 800	2	12	126	Y
1 256	1 256	600	920	2 300	12	16	116	
5 464	11 537	540	910	2 034	11	9	124	
Vehicle No. 7								
0	0	210	1 200	2 900	5	312	98	Y
892	892	290	1 300	2 900	17	24	90	
1 960	2 852	315	1 200	2 730	20	16	90	
3 841	6 693	290	1 300	2 997	14	31	124	
4 466	16 405	316	1 140	3 330	8	20	36	

TABLE 2—*Continued.*

Miles Between Samples	Total Miles Driven	Tolyltriazole	Nitrate	Orthophosphate	Molybdenum	Suspended Solids	Silica	Filter Installed
VEHICLE NO. 8								
0	0	230	2 500	3 400	36	88	135	Y
810	810	340	2 300	3 300	41	96	118	
2 421	3 231	350	2 600	3 380	46	10	116	
7 031	10 262	480	2 000	3 100	60	18	117	
VEHICLE NO. 9								
0	0	360	950	2 200	1.2	104	90	Y
1 344	1 344	480	1 200	2 600	12.0	40	86	
1 853	3 197	465	1 000	2 450	15.0	9	83	
13 949	17 146	400	1 064	1 780	4.6	9	53	
VEHICLE 10								
0	0	340	750	6	93	510	18	Y
897	897	440	860	10	100	112	18	
2 172	3 069	580	880	15	123	72	18	
2 959	6 028	520	730	30	95	38	23	
3 217	9 245	480	600	30	95	34	14	
VEHICLE NO. 11								
0	0	340	1 500	2 400	83	747	71	Y
133	133	450	1 600	2 800	90	180	193	
3 760	3 893	410	1 800	2 249	84	144	62	
2 042	5 935	393	1 440	2 490	72	144	21	
VEHICLE 12								
0	0	280	1 500	600	6.8	457	56	Y
7 083	8 083	340	1 500	1 383	11.0	47	62	
4 386	12 469	335	1 000	1 600	25.0	16	64	
VEHICLE 13								
0	0	80	340	50	1.9	640	39	Y
1 394	1 694	190	470	810	13	140	156	
1 657	3 351	168	470	516	12	196	105	
PPM ANALYSIS OF 50%-50% MAKE UP ANTIFREEZE MIX								
		540.00	765.00	3820.00	18.00	10.00	255.90	

NOTE—1 mile = 1.61 km.

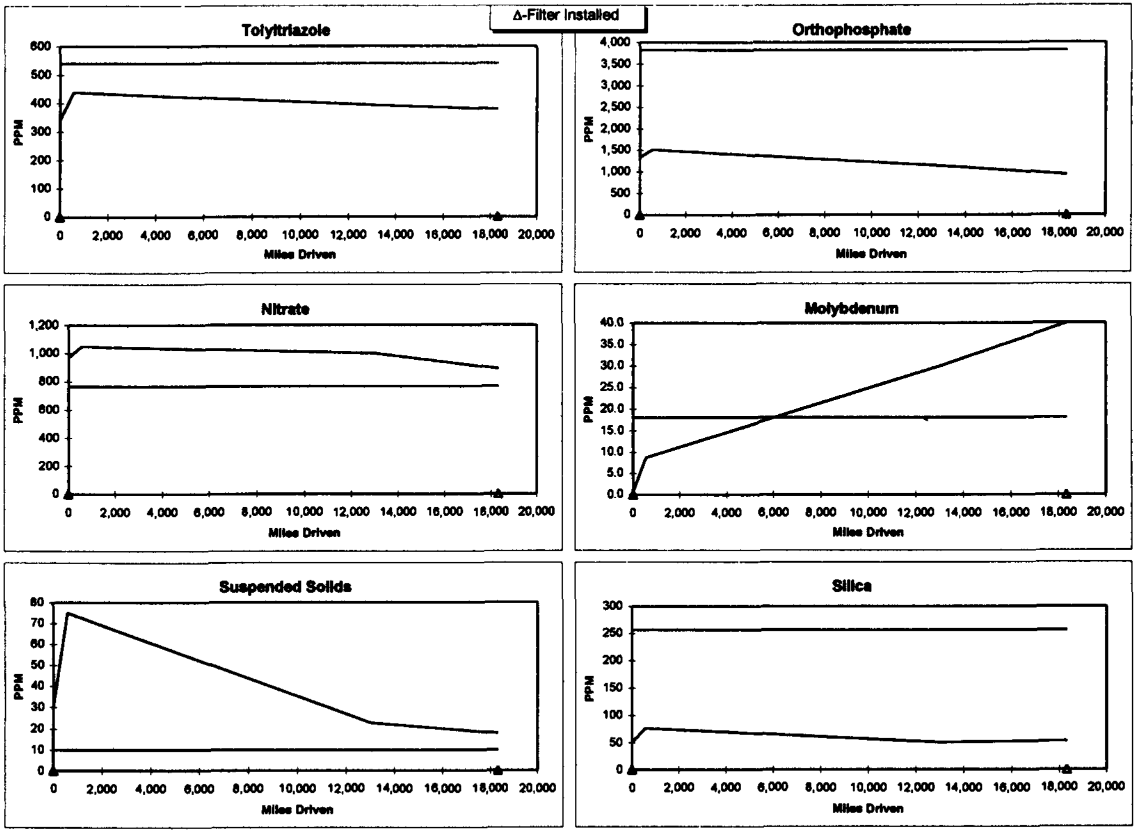

FIG. 1—*Analysis data charted versus mileage for Vehicle No. 1.*

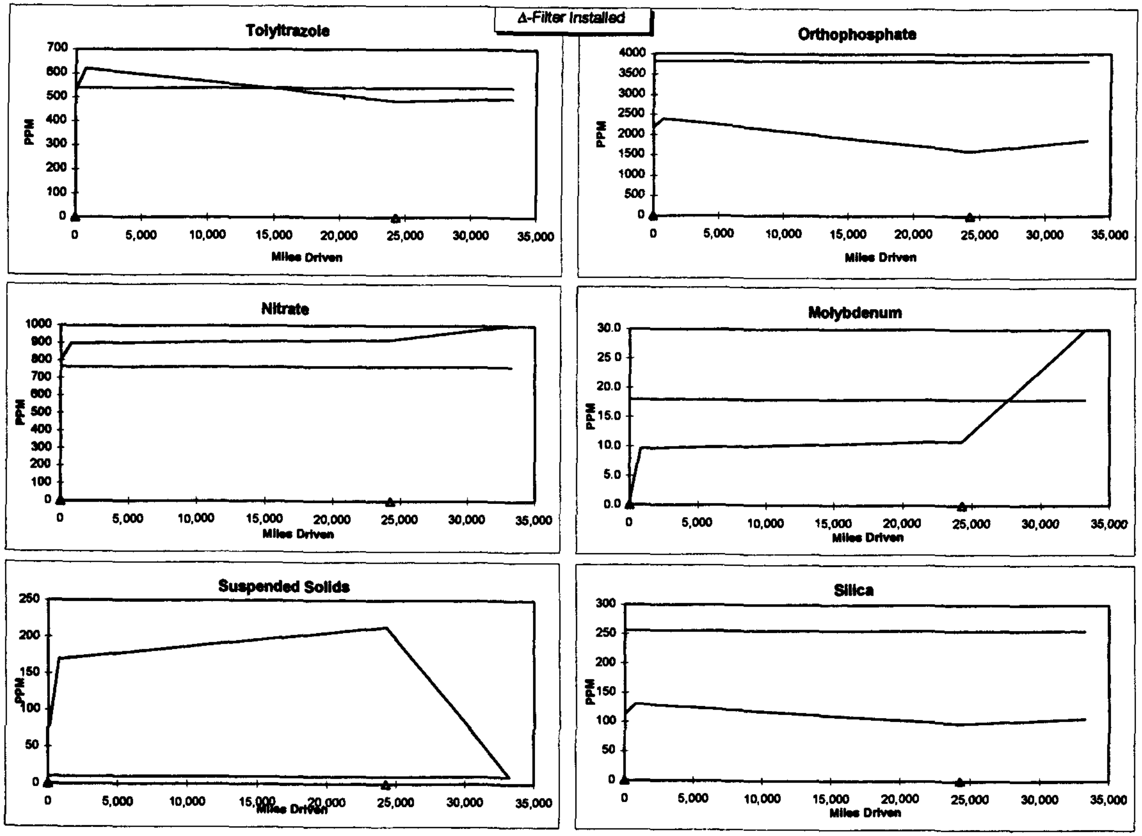

FIG. 2—*Analysis data charted versus mileage for Vehicle No. 2.*

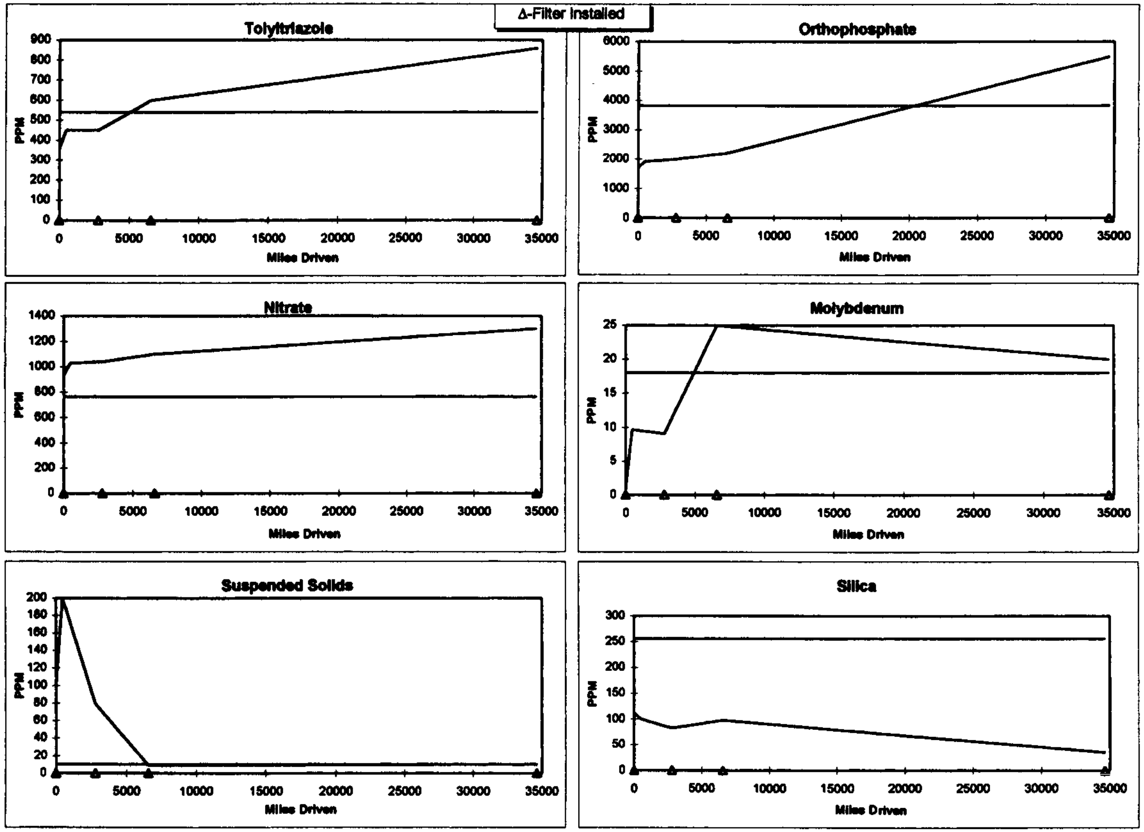

FIG. 3—*Analysis data charted versus mileage for Vehicle No. 3.*

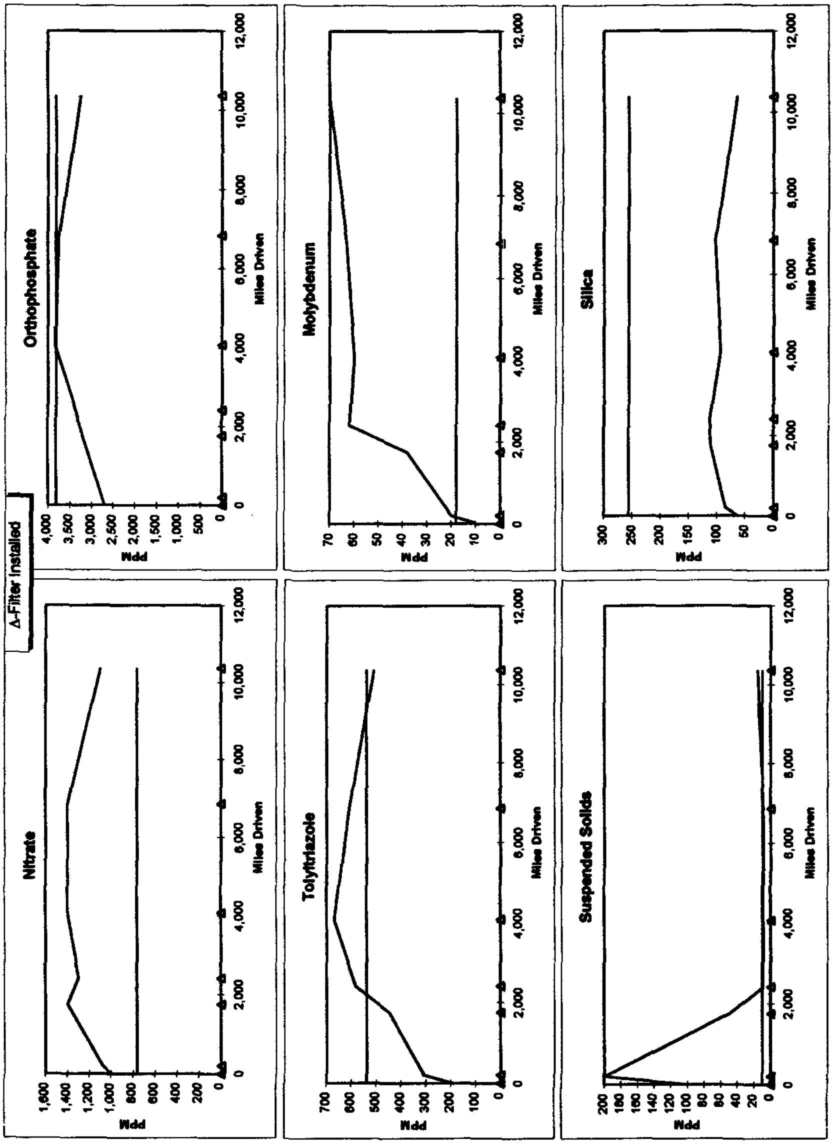

FIG. 4—*Analysis data charted versus mileage for Vehicle No. 4.*

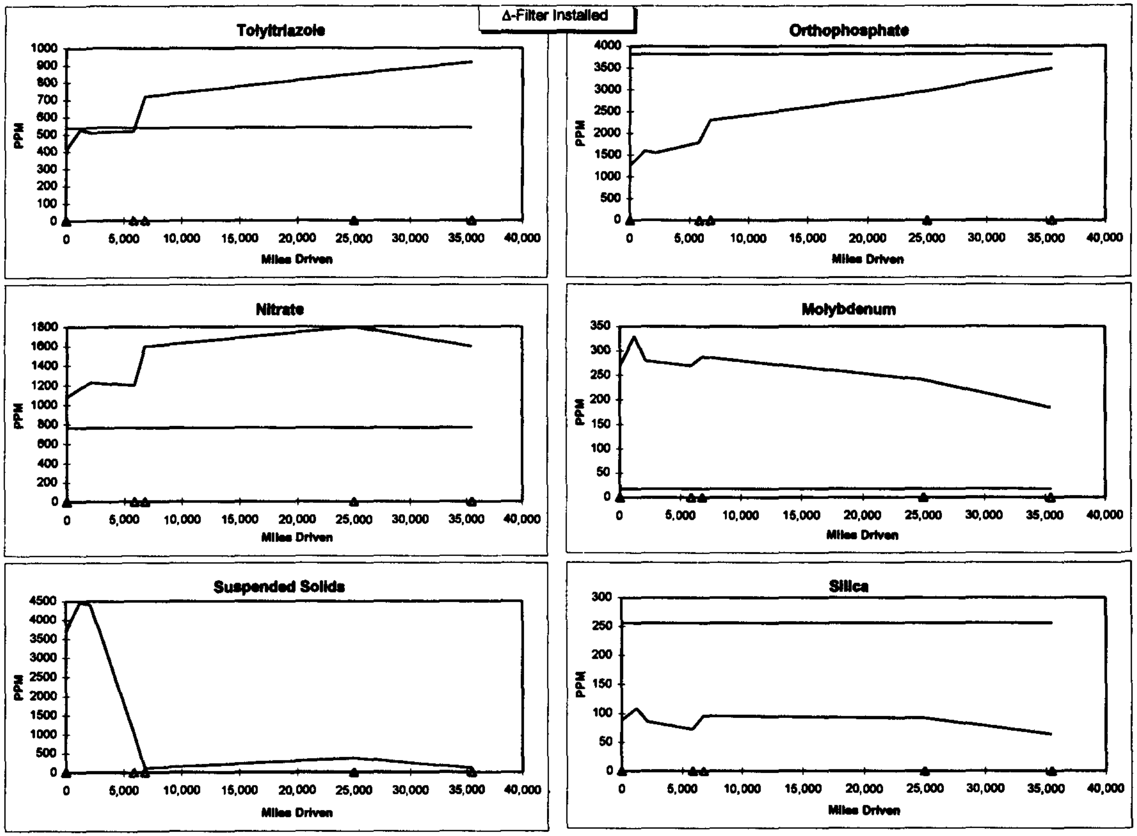

FIG. 5—*Analysis data charted versus mileage for Vehicle No. 5.*

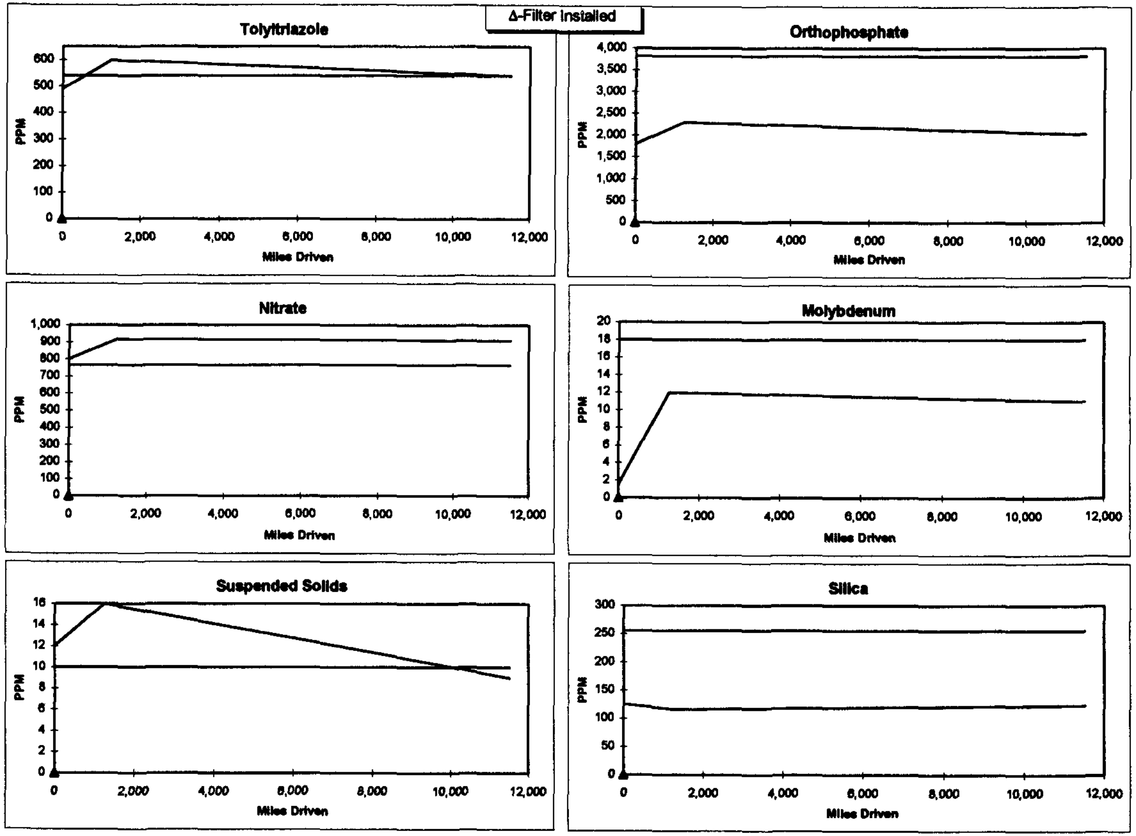

FIG. 6—*Analysis data charted versus mileage for Vehicle No. 6*

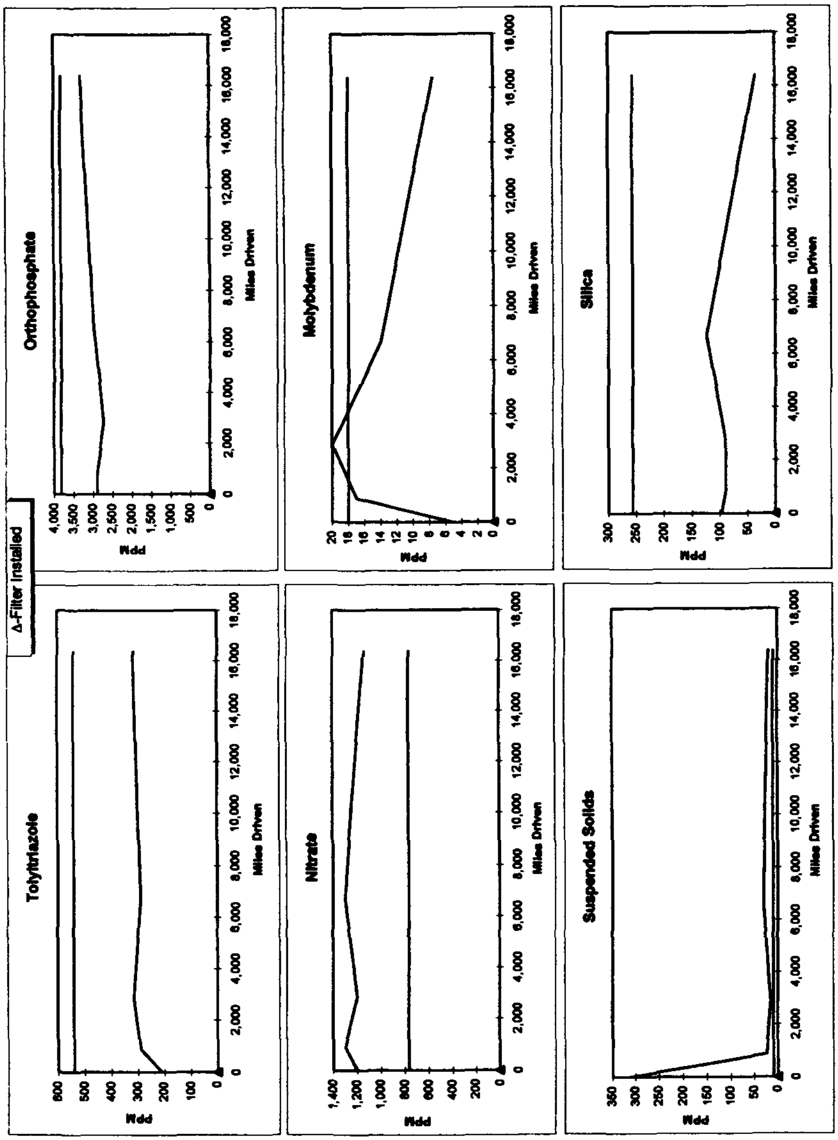

FIG. 7—*Analysis data charted versus mileage for Vehicle No. 7.*

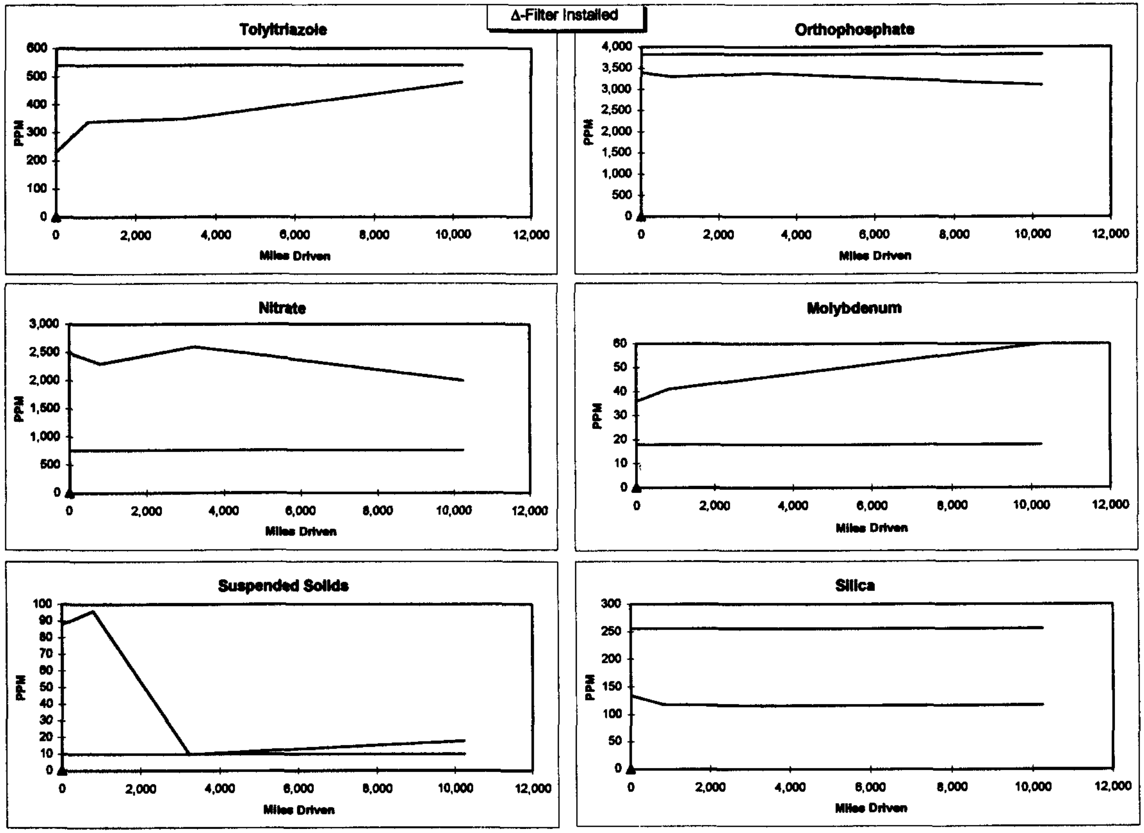

FIG. 8—*Analysis data charted versus mileage for Vehicle No. 8.*

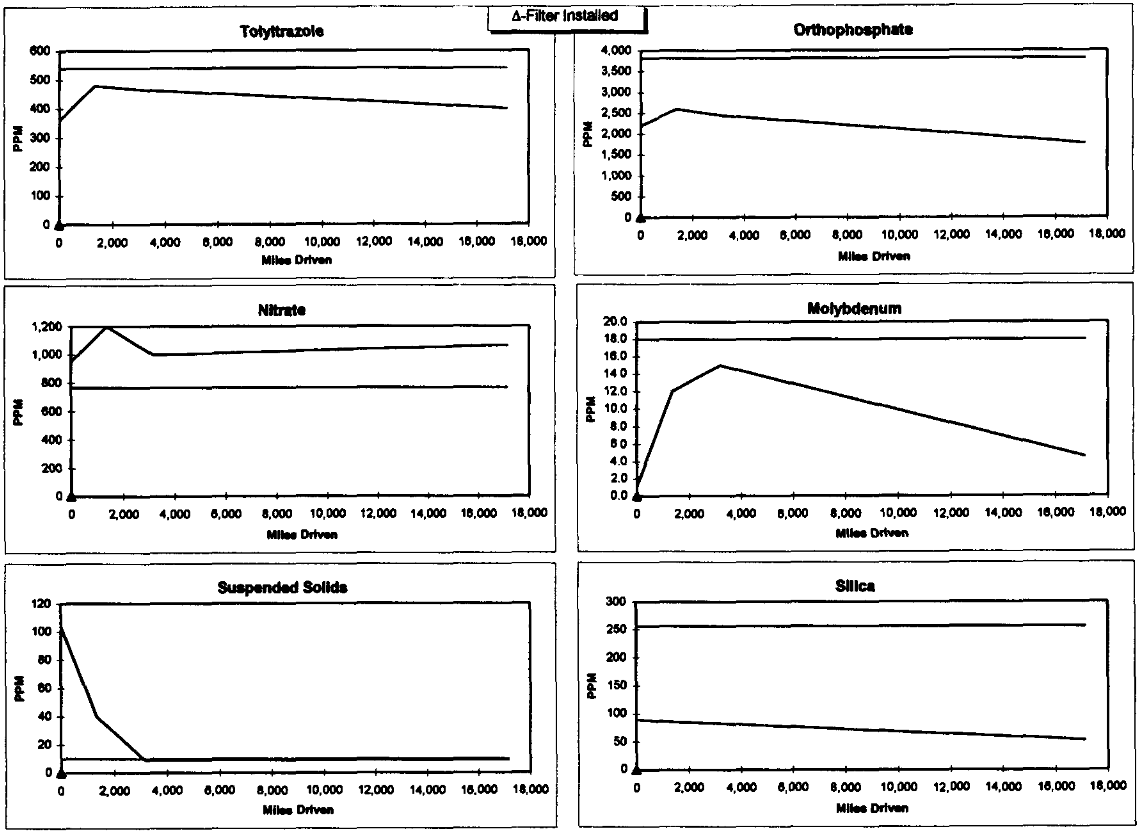

FIG. 9—*Analysis data charted versus mileage for Vehicle No. 9.*

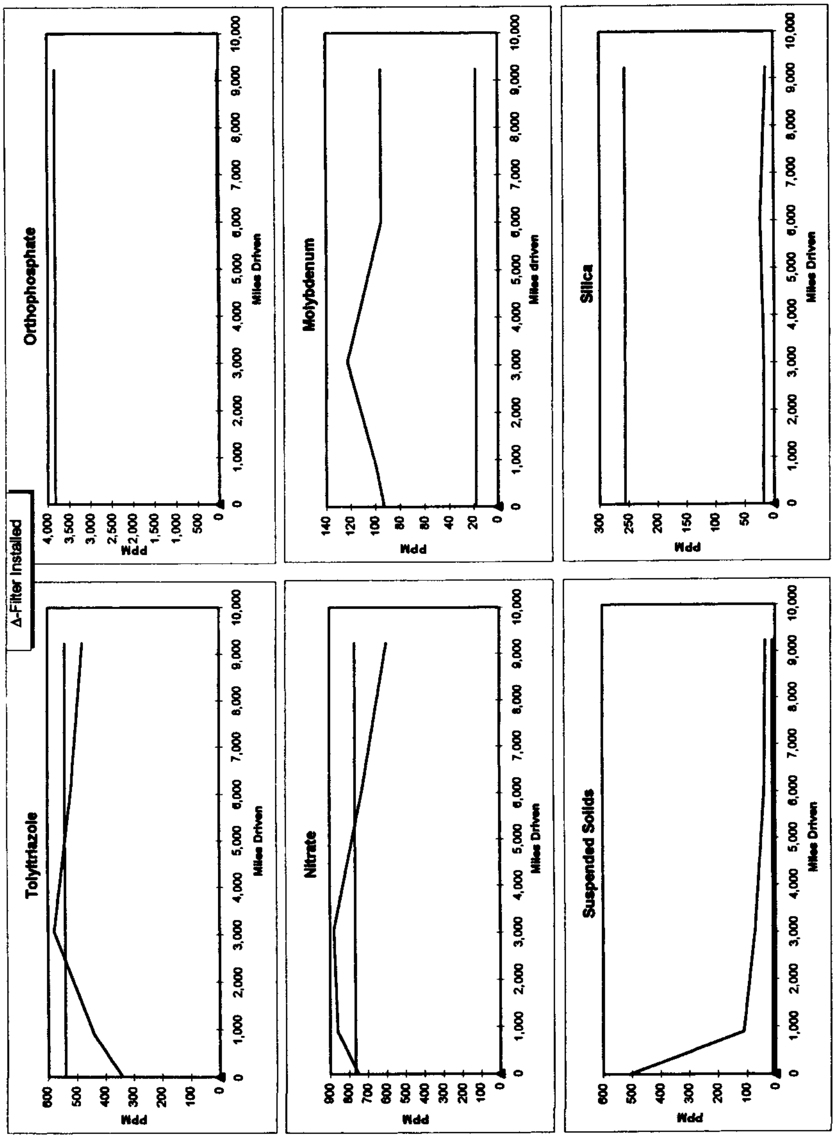

FIG. 10—*Analysis data charged versus mileage for Vehicle No. 10.*

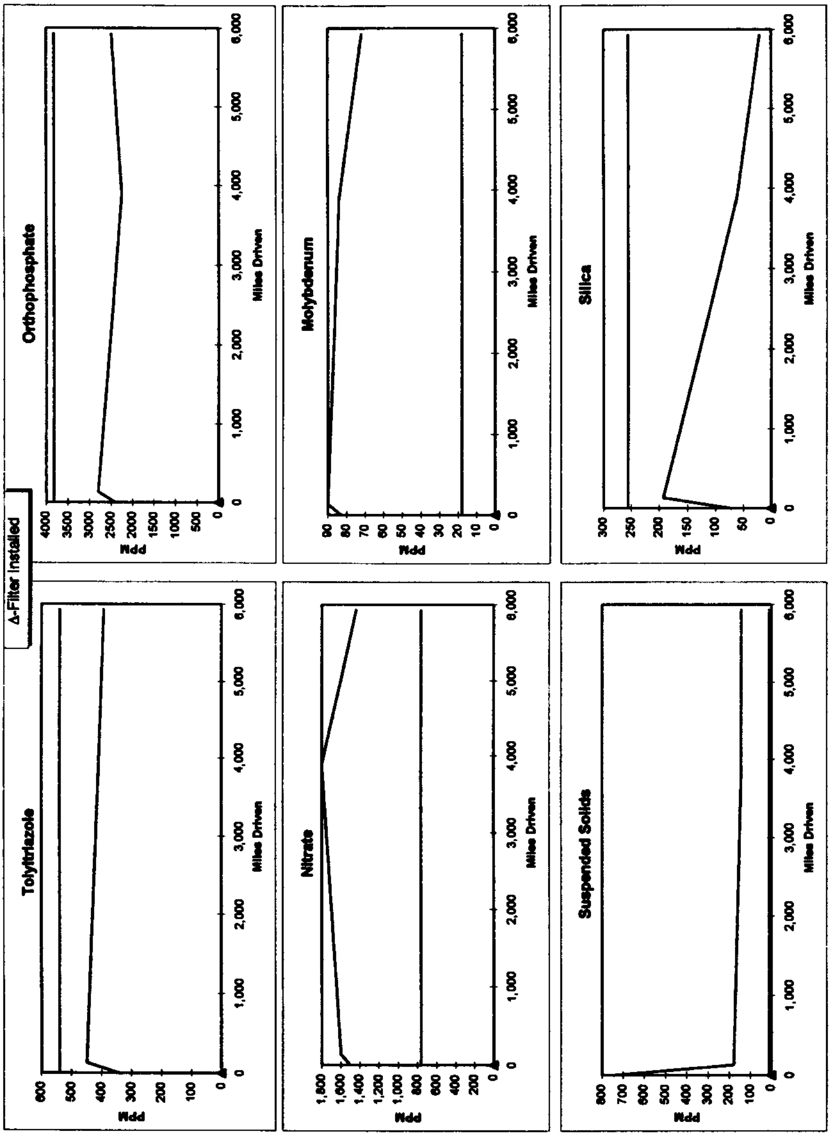

FIG. 11—*Analysis data charted versus mileage for Vehicle No. 11.*

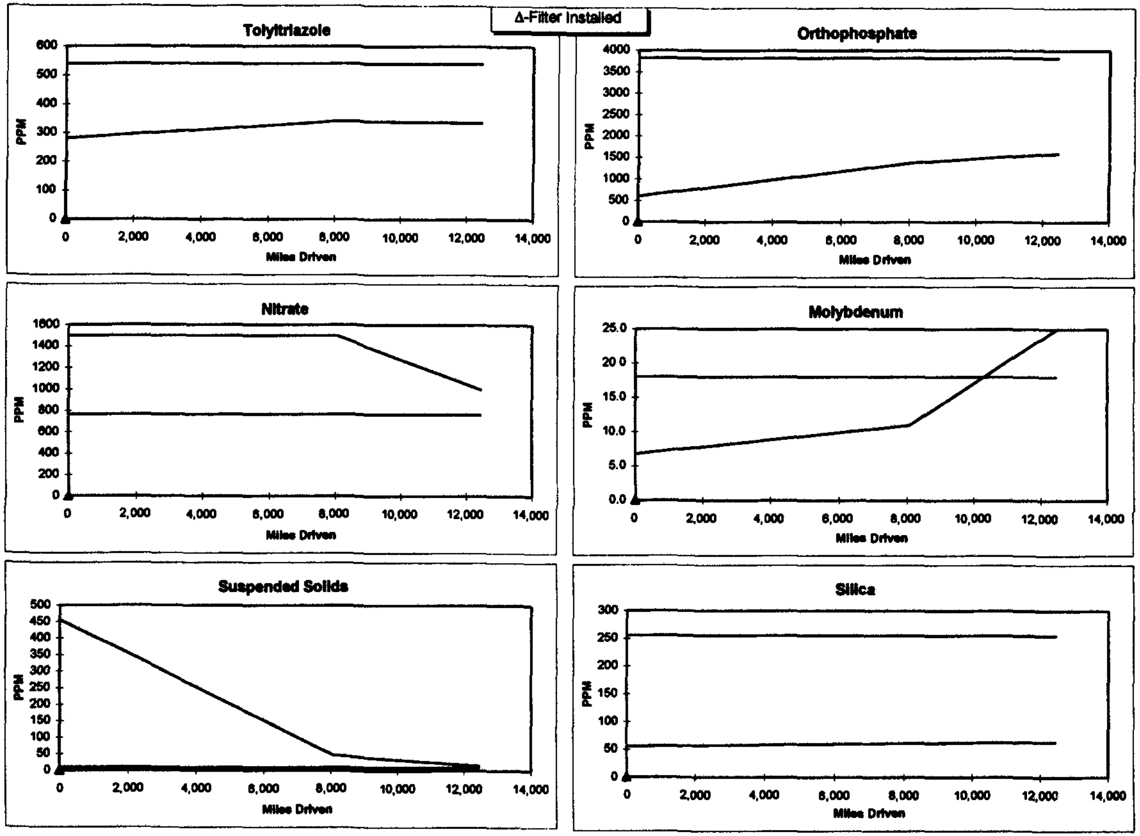

FIG. 12—*Analysis data charted versus mileage for Vehicle No. 12.*

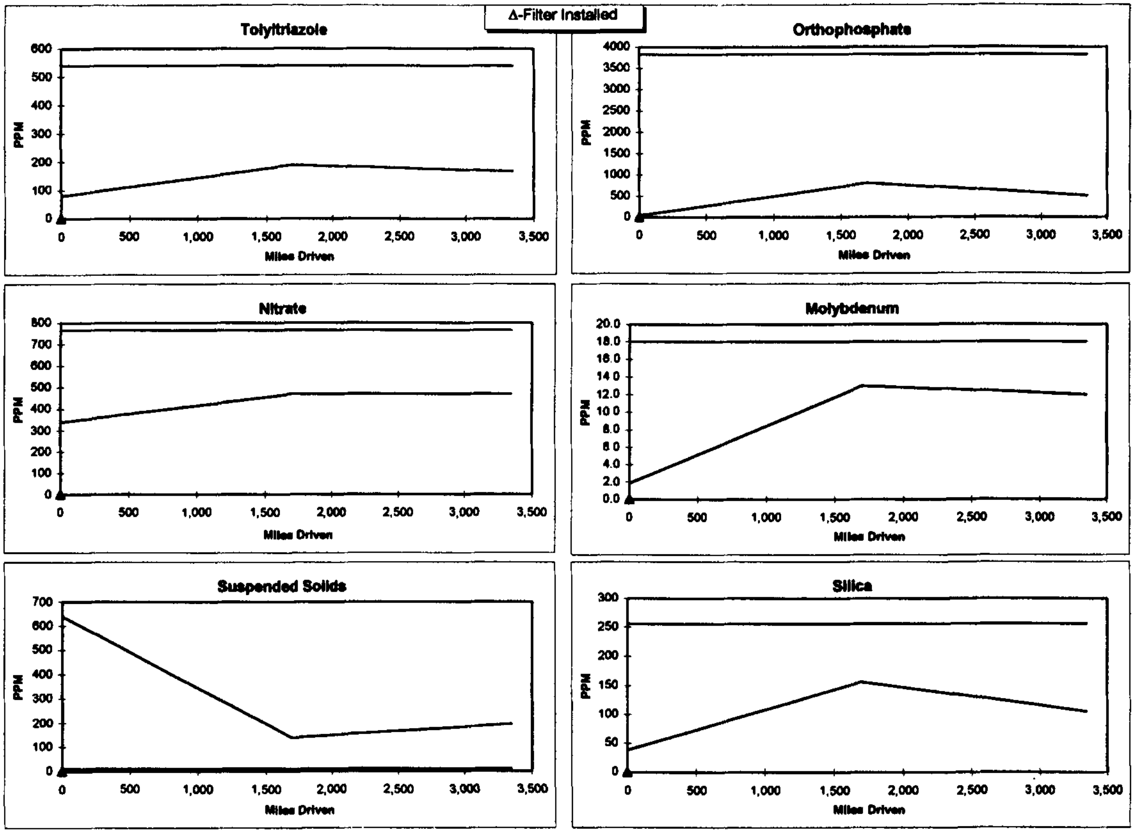

FIG. 13—*Analysis data charted versus mileage for Vehicle No. 13.*

Chemical Additives and Depletion

Each of the samples taken from vehicles that did not have outside antifreeze added exhibits a slight increase in ppm of chemicals known to be in our SCA after installation of the filter/conditioner. A general gradual dropoff or leveling out occurs after that, as would be expected of this group of additives. Some larger jumps in levels are found in those vehicles that had the uncontrolled antifreeze additions. There were two vehicles that had increased levels of molybdenum where a depletion curve was expected. These increases were on the order of 20 to 30 ppm out of 40 to 60 ppm total, and although unexplained, were not felt to invalidate the test or analysis in any way.

Vehicle No. 10 had measured levels of orthophosphate of 6 to 30 ppm, where all other vehicles had measurements at or well above 1000 ppm. This vehicle also had somewhat higher molybdenum levels than most, and could therefore have started the test with an antifreeze based on different chemistry and buffers. The owner started the test with over 130 000 miles (209 209 km) on his vehicle, and stated he could not remember ever doing anything with the antifreeze.

The graphs for the vehicles that had more than one filter/conditioner installed during the test have quite different curves, as do the vehicles that had significant outside makeup antifreeze. In the cases where outside makeup antifreeze was added to the system (Vehicle No. 2, Vehicle No. 3, and Vehicle No. 12), we see a small jump in ppm levels of tolyltriazole, orthophosphate, and molybdenum, with a less notable effect on nitrate and silicate.

The vehicles that had more than one prototype installed during this year long test had increases in each compound's ppm levels at each filter/conditioner installation, with some depletion in between (where there was enough time between installations to measure the depletion).

The purposely over-serviced vehicle (Vehicle No. 4) had eight filter/conditioners installed in its cooling system during the year long test. The initial unit, and those thereafter, were changed out with the following mileage on each: 210, 39, 789, 719, 656, 1665, 2767, and 3522 miles (338, 63, 1270, 1157, 1056, 2679, 4453, and 5668 km), with this last unit still on the vehicle, but no coolant samples yet taken. As would be expected, the levels of each compound rose at each new filter/conditioner installation. Even with seven times the chemistry added than would be seen at a recommended once-a-year change period, these levels were not the highest noted in this test fleet. No dropout or sedimentation of the chemical package in the antifreeze was noted. Suspended solids rapidly decreased to the level in the clean 50/50 make up mix and stayed there. This vehicle had more than 153 000 miles (246 223 km) on the engine at the start of the test, and put on almost 10 400 miles (16 737 km) during the field test.

Operator Input

From the outset of the field test, the vehicle operators were encouraged to inform us of any problems or difficulties they may experience with the vehicle, the filter/conditioner, or the heating system. We also solicited comments at the half-year point of the test and had a debriefing after one year of trials.

Installation was performed on all vehicles by one of two test technicians, so these are the only opinions we have as to the installation of the units. The only comment from these technicians on actual installation was that, in some situations, a section of hose had to be cut out to fit the prototypes into the heater hose. This would require replacement of the hose if the vehicle were to be returned to the condition of not having a filter/conditioner installed. We initially looked at smaller displacement engines as well and concluded our initial prototypes were too large for most midsize and smaller automobiles. The fact that many of the newer automobiles have molded hoses with little room for installation was also noted.

Of all of the operator comments, we had only two negative experiences, both of which are related to the bypass capability of the relief valve at idle with a plugged filter.

These complaints were that, after the filter/conditioner had been on the vehicle for several thousand miles, long periods at idle condition could draw all of the heat out of the heater core, and the air being received into the passenger compartment would cool off. In both of these reported situations, the idle time was relatively long, one being at a railroad crossing waiting for a train to clear the road, and the other one was where the occupant was idling at curbside waiting for a passenger to arrive. In both cases, the operators reported normal warm air from the heating system once the vehicle began moving again.

These units were removed and replaced once the comments were received. The restriction was measured and the units disassembled for examination. We found that the filter elements were fully plugged, and, even though the relief valves were operable, the idle flow pressure in the vehicle heating hoses was not enough to fully overcome the spring load of the valve to allow sufficient hot coolant to the core.

Second Generation Prototypes

Interviews with the operators and technicians involved in this test, information gathered from fit-try examinations of most current passenger car, van, pickup truck, and SUV platforms, and focus group meetings with potential consumers gave direction for further design improvements and styles. After several iterations, a design style was chosen to be used for next generation prototypes and market studies. This design is expected to be that which goes to market, with only minor performance/manufacturing improvements incorporated as they are identified. The changes and benefits of this design over the earlier prototypes are:

1. Can be installed without removal of hose sections, in most cases
2. Tooling will accommodate more than one hose diameter.
3. Adaptable to different sizes for smaller or larger system needs.
4. Is a true bypass design where only a portion of the heater flow is diverted through the filter element. This eliminates the slowdown of hot coolant to the heater when the relief valve did not see sufficient flow pressure to open.
5. Utilizes an engineering thermoplastic in housing construction. This thermoplastic is specifically blended for use in cooling systems, and integrates the seven metal parts found in the first prototypes into two plastic parts.

These new prototypes are undergoing laboratory and on-vehicle tests.

Summary

The purpose of this field test was to gather information on the installation, use, effectiveness, and design features needed to introduce the coolant filter/conditioner technology used in the heavy-duty truck industry to the medium-duty and automotive vehicle population. Several questions were asked and answered by this study.

- The prototypes filtered suspended solids from the coolant while acting as a delivery system for replenishing chemical additives.
- The early prototypes had some drawbacks to installation that have been addressed by later redesigns.
- Over-servicing up to eight times the recommended intervals did not produce adverse chemical balances nor did the chemical package drop out of suspension.

Testing has led to a viable and consumer acceptable filter/conditioner design that can be utilized to: extend the useful life of automotive antifreeze; reduce the labor and the cost of periodic draining/flushing/refilling the coolant, even if not eliminating it; and aid in reducing the expense and environmental impact of spent coolant disposal.

Acknowledgments

The author would like to thank Mr. David Little, senior group leader, and Mr. Wayne A. Mitchell, senior research associate, of Grace Dearborn Company for their analytical and SCA development work, and Mr. George Beck, sales consultant for Grace Dearborn Company for his encouragement to write this paper and his patience in explaining SCA chemistry to a filter engineer. Additionally, the technical and research assistance of Mr. Jerry Bolser, AlliedSignal is principal engineering technician, has been much appreciated. I would also like to thank the management at AlliedSignal Filters and Spark Plugs for their support and permission to present this paper.

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Markus B. Brösel[1]

Overview of Engine Coolant Testing in Europe with Particular Regard to Its Development in Germany

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REFERENCE: Brösel, M. B., "**Overview of Engine Coolant Testing in Europe with Particular Regard to Its Development in Germany,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335*, R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 392–408.

ABSTRACT: Many procedures exist worldwide to develop and to approve coolants for internal combustion engines. This paper discusses the aspects and types of coolant testing in general and the recent development of new test procedures in Europe. The work of the German coolant group is discussed in detail because they are completely revising the well known FVV Test R443/1986, which is the most important test for German car manufacturers.

KEYWORDS: engine coolant systems, test requirements, coolant testing, test standards, corrosion, cavitation, heat transfer, inhibitor technology

A paper on coolants for combustion engines cooled by liquid presents a difficult topic due to the many aspects to be taken into consideration. Many laymen would claim that coolants are merely a matter of "water mixed with a little chemistry." In fact, engine coolants are just as critical to the performance of an engine as lubricants. Failure of either will result in costly engine damage.

In order to obtain an overview of the complex topic of coolant testing the many aspects generally taken into account are summarized first, and the second part gives an insight into the situation in Europe, concentrating particularly on the new German FVV procedures.

Table 1 gives a brief overview of the aspects for a discussion of coolant testing. A deep look into all aspects would exceed the size of this paper. Therefore, the aspects are partly condensed by tables and figures.

European Coolant Testing

Due to the large number of specific research and development methods, this paper describes primarily the test procedures developed for coolant approval.

In Europe, with a coolant market one-third that of the United States [2], the test standards and statutory regulations may vary from country to country, added to which is the existence of "in-house tests" developed by engine or car manufacturers.

In spite of the progressive attempts for development of the European Community towards one economic region and political forum, many areas are still dealt with on a national level.

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TABLE 1—*Aspects for a discussion of coolant testing.*

Which Stress Is Simulated?	What Purpose Do the Tests Have?	Which Parameters Are Tested?	Who Develops and Performs the Tests?	Classification of the Test Methods	What Acceptance Do the Test Methods Have?
Figure 1 shows the conditions which must be met by the coolant and which must be simulated by the coolant test methods. In addition, new aspects in coolant development (long-life coolant, world coolant) and new materials (magnesium) influenced the test method development.	Coolant test methods are used for research and development of coolants or for approval of the automobile producers.	The parameters that are tested can be classified in: (1) chemical/physical parameters; (2) (cavitation) corrosion protection; (3) compatibility with elastomers (hoses), synthetics, dynamic and static seals as well as organic coating; and (4) handling criteria, toxicological and ecological parameters.	Four groups can be distinguished: (1) national committees (Table 2); (2) international committees (Coordinating European Council (CEC)); (3) engine manufacturers ("in-house" test procedures); and (4) coolant manufacturers.	Following a classification by Rowe [*1*] for (cavitation) corrosion tests the following classification can be used: (1) glassware tests (static or dynamic); (2) recirculation tests (with or without temperature/time cycles); and (3) engine tests (*laboratory or engine fleet* tests) (Fig. 2).	Most important is the acceptance of the car manufacturers which give the approvals for coolants. In general, coolant tests are accepted if they have good statistical quality in: (1) variability, *(2) repeatability and* reproducibility, (3) discrimination power, and (4) correlation.

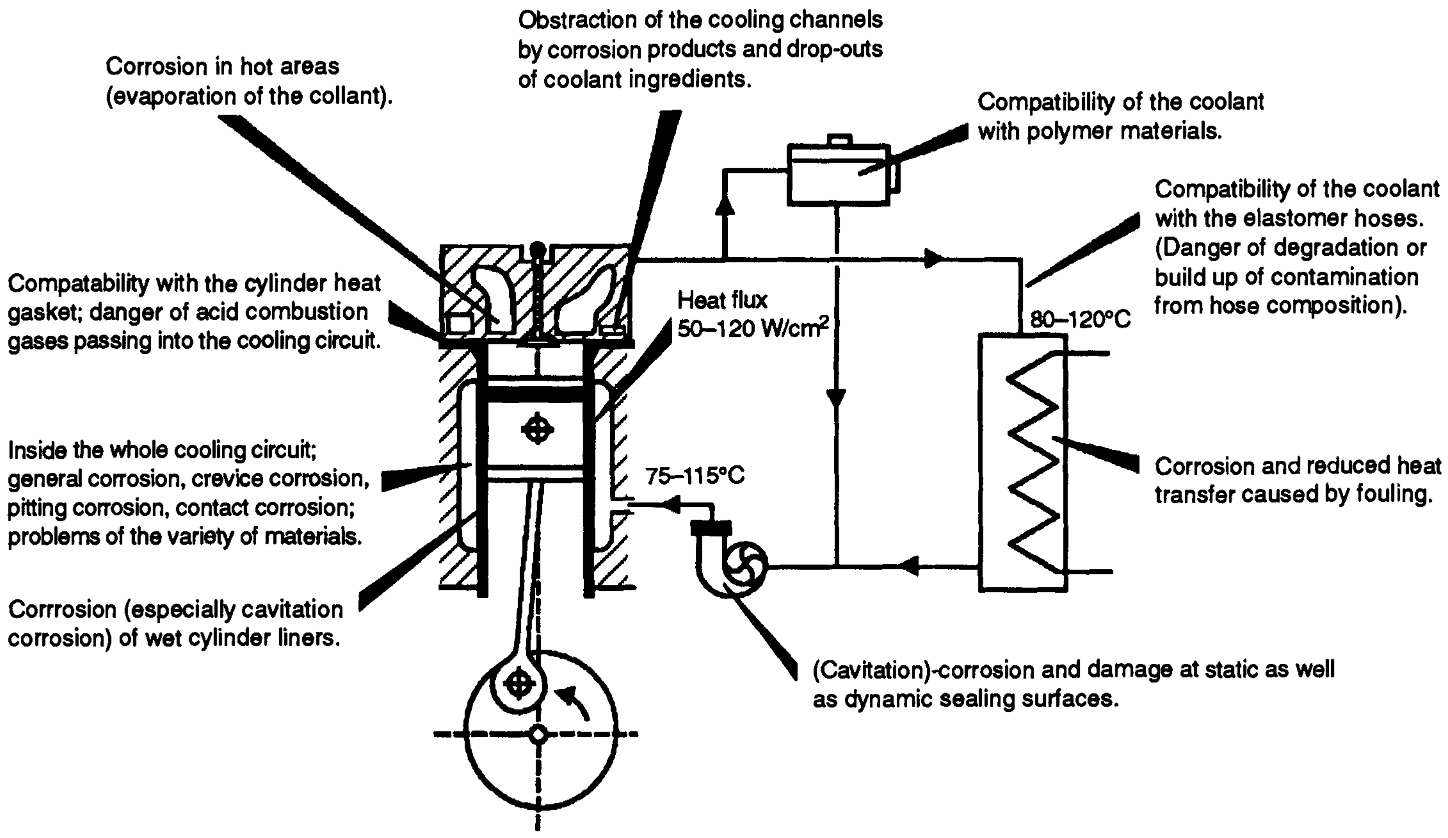
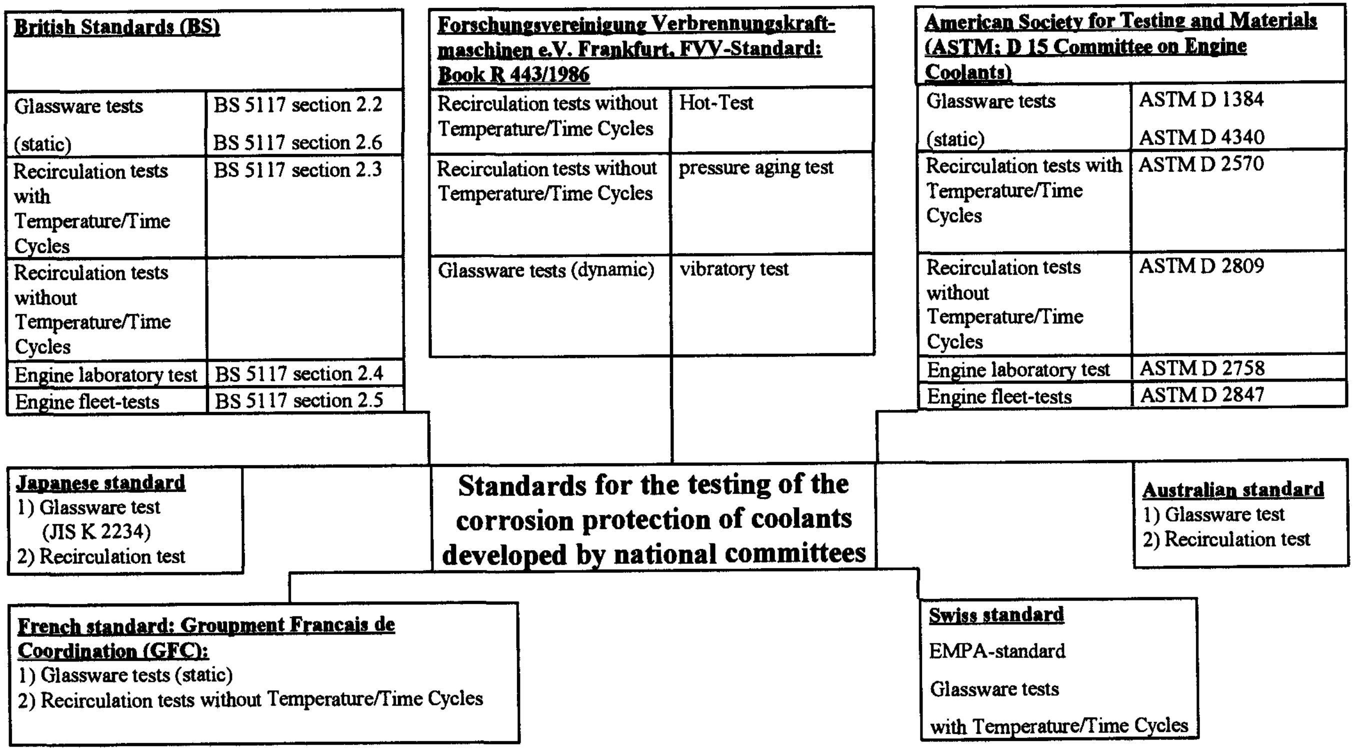


FIG. 1—*Overview of conditions in cooling system.*



Standards for the testing of the corrosion protection of coolants developed by national committees

British Standards (BS)	
Glassware tests (static)	BS 5117 section 2.2 BS 5117 section 2.6
Recirculation tests with Temperature/Time Cycles	BS 5117 section 2.3
Recirculation tests without Temperature/Time Cycles	
Engine laboratory test	BS 5117 section 2.4
Engine fleet-tests	BS 5117 section 2.5

Forschungsvereinigung Verbrennungskraftmaschinen e.V. Frankfurt, FVV-Standard: Book R 443/1986	
Recirculation tests without Temperature/Time Cycles	Hot-Test
Recirculation tests without Temperature/Time Cycles	pressure aging test
Glassware tests (dynamic)	vibratory test

American Society for Testing and Materials (ASTM: D 15 Committee on Engine Coolants)	
Glassware tests (static)	ASTM D 1384 ASTM D 4340
Recirculation tests with Temperature/Time Cycles	ASTM D 2570
Recirculation tests without Temperature/Time Cycles	ASTM D 2809
Engine laboratory test	ASTM D 2758
Engine fleet-tests	ASTM D 2847

Japanese standard
1) Glassware test
(JIS K 2234)
2) Recirculation test

Australian standard
1) Glassware test
2) Recirculation test

French standard: Groupment Francais de Coordination (GFC):
1) Glassware tests (static)
2) Recirculation tests without Temperature/Time Cycles

Swiss standard
EMPA-standard
Glassware tests
with Temperature/Time Cycles

FIG. 2—*Examples of coolant test methods of national committees.*

TABLE 2—*Selection of national committees which publish the standards for coolant tests (without military standards).*

Name	Abbr.	Country
British Standards	BS	United Kingdom
Forschungsvereinigung Verbrennungskraftmaschinen e.V., Frankfurt	FVV	Germany
Deutsche Industrie-Norm(en)	DIN	Germany
Österreichisches Norminstitut	ÖNORM	Austria
Eidgenössische Materialprüfungs- und Versuchsanstalt	EMPA	Switzerland
Groupement Française de Coordination	GFC	France
Association Française de Normalisation	AFNOR	France
Commissione Tecnica di Unificazione Nell' Autoveicolo	CUNA	Italy
Una Norma Española	UNE	Spain
Polski Komitet Normalizacji, Miar i Jakosci	PN	Poland
Magyar Szabvány	MSZ	Hungary
Czeska Statni Norma	CSN	Czechoslovakia
Jugoslovenski Standard	JUS	Yugoslavia
Standard Association of Australia (Australian Standard)	AS	Australia
Japanese Industrial Standard	JIS	Japan
Society of Automotive Engineers	SAE	USA
Engine Manufacturers Association	EMA	USA
Truck Maintenance Council	TMC	USA
American Society for Testing and Materials	ASTM	USA

Furthermore, there are still some European countries which are currently not members of the European Union (EU). Table 3 shows the European situation with respect to coolant testing.

In summary it can be said that current European coolant tests are in the majority influenced by ASTM D 15 standards. Although national standards are applied in the area of chemical/physical tests, many countries apply the ASTM D 15 tests as well.

The ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384-96) is standardized as the most important corrosion test in virtually all countries. Germany with its dynamic tests is the exception in this respect. The FVV (Forschungsvereinigung Verbrennungskraftmaschinen e. V., Frankfurt) test, for instance, included by Mercedes-Benz and VW in their delivery specifications as a compulsory test to be passed, is, however, not comparable to ASTM D 15 tests. Similarly, the structure of the EMPA (Eidgenössische Materialprüfungs- und Versuchsanstalt) test, where the test samples are attached to an agitator, are not directly comparable to D 1384. On the other hand, this test is not as important as the FVV test.

Apart from BS based on ASTM, no country has standardized the direct engine test. On the one hand, a perfect simulation of the costly engine tests via recirculation tests is striven for; on the other hand, the test procedure is left up to the specific technical requirements by the engine manufacturers for approval. Integrated tests, which exceed the safety regulations for identification and are combined with environmental protection tests, have to date not been standardized for coolant testing. Efforts are made in this direction in Germany, the priority of which will significantly increase in the future (coolant tests by the company DEKRA-Umwelt).

In spite of the strong influence exercised by ASTM standards, a large number of different standards exists. Thus a committee has been established that is aiming at a coolant test standardization on a pan-European level.

CEC

The objective of the Coordinating European Council (CEC) is to standardize technical tests on a European level. Currently, the CEC is represented by 14 European countries and 300

TABLE 3—*Standards of coolant testing in some European countries.*

Country	Comments*
Austria	Austria has ÖNORM V 5123, which is partly based on the coolant requirements of Mercedes-Benz delivery specifications DBL 7700. The test specifications for the chemical/physical tests are based on ASTM, ÖNORM and DIN. ASTM D 1384 is recommended for corrosion tests.
Belgium	No standards for coolants specified.
Czechoslovakia	The test specifications for the chemical/physical tests are based on ASTM and CSN. ASTM D 1384 is recommended for corrosion tests.
Denmark	No standards for coolants specified.
Finland	No standards for coolants specified.
France	The GFC and AFNOR standards exist side-by-side. The GFC standards were developed in preparation for a European standard and are partially of the same content as AFNOR, and partially include further developments. In respect to most chemical/physical, electrochemical and static glassware tests, they are mostly equal. The chemical/physical tests are in the majority in accordance with ASTM; the static glassware tests are similar to ASTM D 1384 and ASTM D 4340; they are, however, subjected to more severe conditions. The GFC has also standardized costly tests (recirculation tests, bomb tests).
Germany	In contrast to other countries, there is no DIN system in Germany for chemical/physical and corrosion tests for coolant testing. With the cooperation of private institutions of the FVV, dynamic corrosion tests were developed that were standardized in a test directive (FVV R443/1986). This directive is generally accepted in Germany. Statistical glassware tests and chemical/physical tests were not incorporated in the standard.
Great Britain	Britain has a system of coolant tests and specifications, BS 6580 and BS 5117, which is mainly in line with ASTM.
Hungary	A restrictive standard, MSZ 924-82 of 1987, is in existence which is still in line with Russian standards. The standard describes chemical/physical tests and a static glassware test similar to ASTM D 1384.
Italy	The Numero CUNA (NC) standards for coolant tests are currently being revised. With two exceptions, the standards strongly resemble those of ASTM. With respect to the chemical/physical tests the standards are comparable to ASTM D 1384 and the ASTM Test Method for Simulated Service Corrosion Testing of Engine Coolants (D 2570-96).
The Netherlands	No standards for coolants specified.
Norway	No standards for coolants specified.
Poland	The coolant testing standards are summarized in WT-ITS/3/94/ZLG. With a few exceptions, the chemical/physical tests and the two corrosion tests are in accordance with ASTM standards. ASTM D 1384 and D 2570 have been adopted.
Spain	UNE 26361-88 provides the basis of Spanish coolant testing. The chemical/physical tests are similar to those of ASTM or BS. ASTM D 1384 and D 2570 have been adopted for corrosion testing.
Sweden	No standards for coolants specified.
Switzerland	For corrosion testing Switzerland carries out so-called EMPA tests. This dynamic glassware test is not directly comparable to ASTM D 1384.
Yugoslavia	Yugoslavia operates a test system, JUS H.Z.2010, which is based on ASTM standards.

*Abbreviations are explained in Table 2.

enterprises. Figure 3 shows the current five committees dealing with the test standardization in four areas. Each committee evaluates tests existing in the respective countries for their technical and statistical quality. Different tests from different countries are also acceptable as CEC standards provided they have the same statistical quality. In this connection each test is subjected to development phases from x = experimental via t = tentative/final to a = approval. The test is adapted to a CEC format. It is the CEC's aim to standardize so-called performance tests that

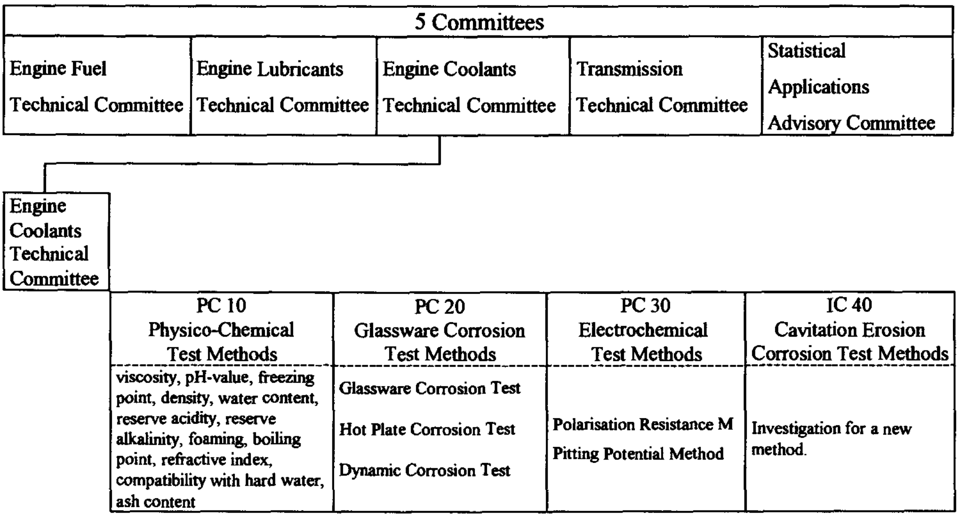


FIG. 3—*The Engine Coolants Technical Committee in the structure of the CEC.*

conform to the requirements of the current engine development. In respect to statistical quality and field experience the test requirements are extremely high. In contrast to national standardization committees, CEC standards aim to incorporate developments into the standards more speedily. The tests are evaluated annually for their quality. Predominantly costly simulation tests (that is, performance tests) were standardized. Simple analysis tests (pH value, etc.) are normally not standardized; the tests by national committees are considered to be adequate. If chemical/physical tests are nevertheless standardized, they must pass through all CEC approval levels. So far, CEC does not object to the acceptance of tests on an international level, for example, by the International Standardisation Organisation (ISO).

The "Engine Coolants Technical Committee (ECTC)" standardized coolant test is subdivided into four areas. Under PC10 the physico-chemical test methods are standardized. Table 4 shows the methods of the parameters which are transformed into the CEC format with the relevant standards that form the basis of the CEC standards. This group also includes the so-called "bomb test" for coolant testing. During this test aluminum and cast iron materials are exposed to the heated coolant. The pH value is recorded over time. To date the test has not been recommended as a European CEC standard by the ECTC Committee. PC20 summarizes the static glassware corrosion tests as well as the dynamic test. The glassware corrosion test is based on ASTM D 1384 and the hot plate corrosion test on the ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants under Heat-Rejecting Conditions (D 4340-96). Table 5 compares the test parameters of D 1384 with those of the CEC test "Measurement of Corrosion-Inhibitive Properties of Engine Coolants" (CEC C-03-X-97). It is observed that the CEC has intensified test conditions.

As different countries apply different material standards, a compatibility table for the test bundles was created (Fig. 4). In the hot plate test higher test metal temperatures were used by the ECTC Committee (150°C ± 2°C). A comparison of the two types of test equipment is not made at this point, as the American and European committees plan to make changes to the tests. One important change envisaged for the CEC test will be the cleansing of the sample. Sample cleansing with chromium and phosphoric acid is to give way to a cleansing method that complements the other protection mechanisms of the organic acid technology (OAT) cool-

TABLE 4—*Physico/chemical tests.*

Parameter	Method	Comments
Viscosity	ASTM Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity) (D 445-96)	ASTM will be used. No need to transform into CEC format.
pH Value	ASTM Test Method for pH of Engine Coolants and Antirusts (D 1287-91)	The ASTM test will be used. AFNOR, ISO, DIN are similar.
Freezing point	ASTM Test Method for Freezing Point of Aqueous Engine Coolants (D 1177-94)	No need to transform into CEC format.
Density	ASTM Test Method for Density and Relative Density of Liquids by Digital Density Meter (D 4052-96)	No need to transform into CEC format.
Water content	ASTM Test Method for Water in Engine Coolant Concentrate by the Karl Fischer Reagent Method (D 1123-93) (or DIN 51777)	Both are similar. No need to write CEC format.
Reserve acidity	DN 505343 (Peugeot Method)	No need for a European standard, no further work.
Reserve alkalinity	ASTM Test Method for Reserve Alkalinity of Engine Coolants and Antirusts (D 1121-93)	Data are established at a pH value of 5.5 and to an inflexion point to have titration curves.
Foaming tendency	GFC Pr-L-113-02 with apparatus of ELF	Change to CEC C-10-X-97.
Boiling point	ASTM D 1120 or GFC-L-104-A-90	No need to transform into CEC format.
Refractive index	GFC-L-102-A-90 or DIN 51423	CEC format not yet decided.
Compatibility with hard water	GFC-L-106-A-90 or BS 5117, 1.5	Change to CEC C-06-X-95.
Ash content	GFC-L-103-A	Change to CEC C-02-X-95.

ants. During the current cleansing process, using extremely harsh chromium and phosphoric acid distorted the coupon. Deep abrasions were observed. Investigations as to the use of formic acid or nitric acid are currently ongoing.

During the ECTC Spring Conference in 1997, it was decided that the French double chamber test as a dynamic corrosion test should be investigated for its quality by various companies which own the necessary test equipment. At a later stage, the German new hot test apparatus,

TABLE 5—*Comparison between ASTM D 1384 and CEC C-03-X-97.*

	ASTM D 1384		CEC C-03-X-97
Equipment		similar	
Airflow	100 ± 10 mL/min		100 ± 8 mL/min
Temperature	88 ± 2°C		100 ± 1°C
Duration		similar	
Concentration		similar	
Water		similar	

METALS	COPPER	SOLDER	BRASS	STEEL	CAST IRON	ALUMINIUM
STANDARDS (CEC C-03-T-97)	UNS C11000 or UNS C11300	ASTM B 32 Alloy Grade 30A or 30B	UNS C26000	UNS G10200	NF A 32-101 FGL 200	NF A 57-702-Feb 81 A-S5U3 Y30
GERMANY standard name/number	DIN E - Cu 57 2.0060	DIN L - Pb Sn 30	DIN Cu Sn 30 2.0265	DIN C 15 1.0401	DIN GG 20 0.6020	DIN Al Si 6 Cu 4 3.2151
FRANCE standard name/number	NF Cu - al	NF	NF Cu Zn 30	NF XC 12	NF FGL 200	NF A - S5 U3
UK standard name/number	BS C 101	BS	BS Cz 106	BS 080 M15	BS Grade 220	BS LM 21
ITALY standard name/number	UNI Cu - ETP	UNI	UNI P - Cu Zn 30	UNI C 15 (CK 15)	UNI G 20	UNI 3052
SPAIN standard name/number	UNE Cu - ETP C1110	UNE	UNE Cu Zn 30 C6130	UNE F 15 M (CK15)	UNE FG 20	UNE L - 2620
USA standard name/number	UNS C11000	UNS Alloy Grade 30B	UNS C26000	UNS G 10200	UNS Class 30B	UNS AA 319.0
INTERNATIONAL standard name/number	ISO Cu - ETP	ISO S - Pb 70 Sn 30	ISO Cu Zn 30	ISO C15 E4 (CK15)	ISO Grade 200	ISO Al - Si 6 Cu 4

FIG. 4—*Compatibility of the materials for test bundles.*

which is described in the final section of this paper, will also be subject of this investigation. The main point of the French double chamber test are two test chambers; the first chamber contains a round cast iron sample and the second chamber contains a round aluminum sample. Both are heated from the bottom. The coolant circulates in the steel tube circuit and is heated via the heat exchanger in the two test chambers from 115°C to approximately 130°C. Such high temperatures are in accordance with current specifications of the engine manufacturers. The test duration is 72 h.

Within the PC30 attempts are made to standardize electrochemical corrosion tests. The polarization resistance methods and pitting potential methods applied to date did not produce adequate results for standardization in respect to organic acid technology (OAT) coolants.

The Project Committee (PC) 40, renamed to Investigation Committee (IC) in the spring of 1997, shows that a cavitation-erosion-corrosion test, currently recommended, does not meet the test requirements. Investigations are therefore carried out as to whether the cavitation test according to FVV R443/1986 or the knocking chamber test meet the requirements of the MTU or whether a new cavitation test needs to be developed.

German Coolant Testing

As shown in Fig. 2, there is no test system in place in Germany that could be compared to that of ASTM D 15. Test standards of DIN for chemical/physical parameters are in existence. However, such standards have not been developed specifically for coolant testing. There are also standards for coolant hoses, but they are not incorporated in a coolant testing system. The currently valid and recognized test directive in Germany recommends ''performance testing of coolant additives in combustion engines,'' and is stipulated in directive R443/1986. According to this directive, only the (cavitation) corrosion protection for various metals and the heat transfer ability are to be tested. This directive was put forward by the working group ''Coolant Additives'' of the Forschungsvereinigung Verbrennungskraftmaschinen e. V. (Research Association for Combustion Engines) Frankfurt (FVV) (Fig. 5) in cooperation with manufacturers on the basis of research work by the Institute of Material Science of the Technical University of Darmstadt (IfW). The State Testing Laboratory (MPA), associated with the IfW, is conducting the tests exclusively in Germany. Engine manufacturers, such as VW and Mercedes-Benz, stipulate in their delivery specifications for coolant additives the implementation of this test before they test the product under their own test procedure (in-house test). It is clearly evident from the structure of the working group that there is no demand for a test system. German engine manufacturers use ASTM and DIN regulations in their coolant specifications for chemical/physical tests and do not see the need for determining their own standards for such parameters in respect of coolant test systems. A standardization of the laboratory recirculation tests that simulate the engine stress is in this context much more important as well as difficult. That is why the working group never included static glassware tests in the test standards. They do not meet the simulation requirements but can at most be used as initial screening tests.

The structure of the individual tests is described in various publications [*4–6*]; therefore, only the most important features of the tests are summarized in this paper. In the vibratory test (Fig. 6), the cavitation-corrosion protection efficiency of the coolant vis-a-vis aluminum and cast iron materials is tested. In the hot test (Fig. 7), the heat transfer through the hot cylinder wall is simulated and the corrosion protection for aluminum and cast iron materials as well as the heat transfer are evaluated. By means of the pressure aging test (Fig. 8), the coolant is artificially aged over 120 h at temperatures ranging from 115 to 135°C. After the test period, two test bundles are examined for corrosion. Using the pressure aged fluid in addition to the

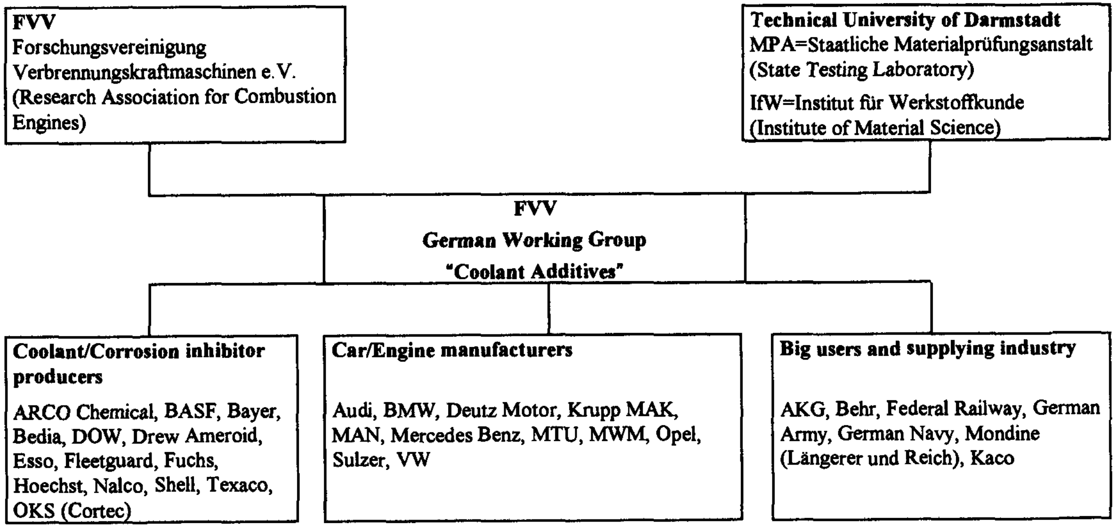
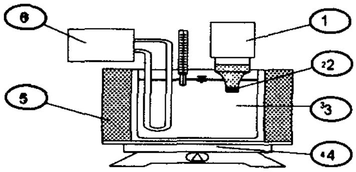


FIG. 5—*Representatives of the FVV German working group "Coolant Additives."*



Frequency:	20 ± 1 kHz
Amplitude:	0.020 ± 0.001 mm
Temperature:	80 ± 1°C
Pressure:	atmospheric pressure
Gasing:	none
Liquid volume:	3.5...4.0 L
Test time:	10 x 30 min for cast iron 8 x 10 min for aluminium

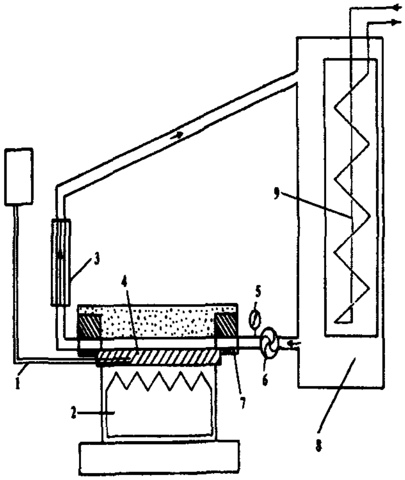
FIG. 6—*Vibratory test (cavitation test).*

test coolant mixtures (40 and 20 volume % in deionized water and in water with hardness of 10°dGH), hot tests and cavitation tests are carried out.

As mentioned above, the requirements on the coolant have increased due to the progressive engine technology. Thus, the working group has worked at the IfW on a development of a new FVV test directive during the past three years.

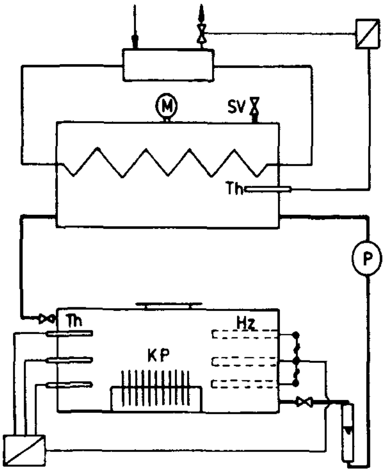
The New FVV Test Directive

The new test directive is similar to FVV R443/1986. It is not extended to a test system as is that of ASTM, but it remains as the directive according to which complex recirculation tests with field experience are standardized.



Free scanning zone:	30 cm^2
Electric power:	1500W
Surface power density:	50 W/cm^2
Solution volume:	2.3 ± 0.1 L
Chamber inlet temperature:	80 ± 1 °C
Flow rate:	0.26 ± 0.02 m^3 / h
System pressure:	150 ± 10 kPa
Test time:	30 h

FIG. 7—*Hot test.*



Pressure (primary loop):	350 ± 10 kPa
Pressure (secondary loop):	250 ± 10 kPa
Flow rate:	0.18 ± 0.01 m³ / h
Electric power:	5 x 1840 W
Energy density:	20 ± 1 W / cm²
Liquid temp. (after heating):	135 ± 3 °C
Liquid temp. (after cooling):	115 ± 3 °C
Test time:	120 h

P	**pump**	**KP**	**test bundle**
Hz	**heater**	**TH**	**temp. sensor**
M	**pressure sensor**		
HT	**heat exchanger**		
SV	**saftey valve**		

FIG. 8—*Pressure aging test.*

On the one hand, the new test directive is meant to take into account technological progress. On the other hand, meaningful tests are to be facilitated. It is specifically a question of adapting the tests to the engine technologies, adapting to the evaluation under the OAT technology and reducing the test costs. Simultaneously, the statistical test qualities are to be improved and state-of-the-art control, measuring, and documentation technology are to be applied. If required, studies of influence parameters must be conducted, which had not been possible with a standardized test. The tests need to be relevant to the new OAT coolants or they need to work with OAT coolants. Finally, a test procedure needs to be developed that could substitute for the in-house tests of engine manufacturers.

The focal point of the new test guideline is the new construction of the hot test apparatus (HTA) in accordance with FVV R443/1986 in respect of the new hot test apparatus (NHTA). It is planned to substitute the costly pressure aging test with the extension of the NHTA. The vibratory test will be transferred to new cavitation test apparatus.

Characteristics of the NHTA

The new hot test apparatus is equal to the HTA, a dynamic recirculation test without time/temperature cycles (they are, however, envisaged), which simulates the heat transfer through the hot cylinder wall.

A new feature of this apparatus is its modular structure whereby all modules consist of high temperature resistant, inert synthetics, so that the corrosion is concentrated on the samples within the circuit, whose corrosion protection is the issue. The advantage of the modular construction is that if certain modules are removed, studies of influence parameters can be conducted. As a result, this apparatus is not only usable with the standardized structure for test and approval purposes, but also for research and development of coolant additives. Figure 9 shows the basic structure of the NHTA.

Each module has a specific task. It is connected to transparent, inert PFA (perfluoralcoxy-copolymer) tubes so that the cleansing process is considerably improved and simplified and the danger of influence of steel pipes, which are invariably used in such test equipment, is prevented. According to research carried out at the IfW, the use of synthetics contributes towards a considerable improvement of the statistical quality. Similar to the French double chamber test, two hot test chambers, positioned above each other, are each fitted with a round sample. However, both hot test modules are integrated independently from each other in the circuit. In each synthetic chamber made out of PEEK (polyetheretherceton) a surface power density of 70 W/cm is generated at the round sample. This is adjusted at the beginning of the test and remains unchanged throughout the test duration. Layers generated by the coolant result in a temperature increase that is recorded and incorporated in the evaluation. The coolant heated to a temperature of 115°C enters the first test chamber containing the cast iron sample via two jets, and exits via three jets. The heated coolant then reaches the second test chamber containing an aluminum sample. It leaves the chamber at a temperature of approximately 130°C. The

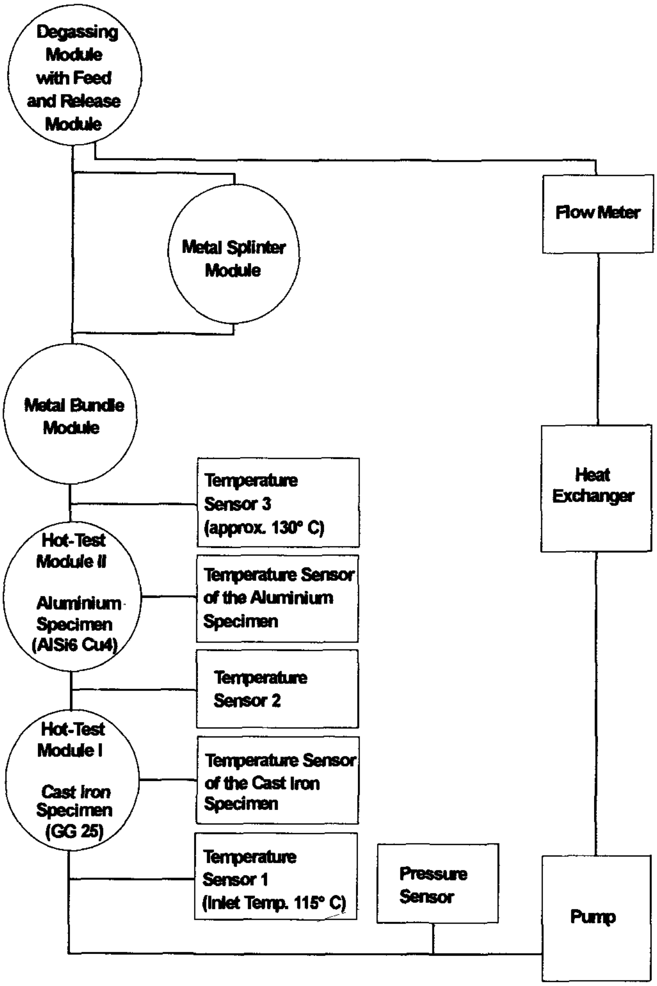


FIG. 9—*New hot test apparatus (NHTA).*

adjusted surface power density as well as the resulting temperature are adapted to the current engine technology. Subsequent to the second hot test module, the coolant reaches the synthetic test bundle module. There are two test bundles in this module, which are each fitted with the following materials: GK-AlSi6Cu4, AlCuMg2, AlMn, E-Cu57, L-PbSn15Sb, CuZn37, and GG25. Thus the test bundles that had so far been part of the pressure aging test (as per FVV R443/1986) are also tested in the NHTA.

In order to create real engine ratios between coolant and material surfaces, a metal splinter module developed by Mercedes-Benz was integrated [7]. There are 300 g of cast iron chips and 300 g of aluminum chips in a plastic housing. Both materials are separated from each other. One-third of the coolant flow runs through this module. Thus the corrosion inhibitors in the coolant are extremely stressed. The chips are used only once. Generated gases are collected in the degassing module. They can be analyzed subsequent to the test.

After passing through the flowmeter the coolant enters the heat exchanger. The heat exchanger consists of a pipe-in-pipe construction. The coolant enters a plastic pipe fitted with an aluminum pipe. The cooling agent in this aluminum pipe cools the coolant to 115°C. The aluminum pipe is changed after each test. By way of this construction it is possible to increase as well as cool the aluminum surface in the circuit; furthermore, a simulation of a pipe heat exchanger is created. One can also simulate a phenomenon which is here defined as fouling. This is the formation of a deposit on cool walls in contact with hot coolant, as can be observed with car radiators. During investigations at IfW, it was observed that deposits occur with the use of coolants whose corrosion stabilizers do not work efficiently or whose additives react with the coolant hoses. It was further observed at IfW that sulfur-cured hoses react with the coolant components and cause the formation of a slimy deposit on the cool surface, which impedes the heat flow. Such a phenomenon was not observed with the use of peroxide-cured hoses. The heat exchanger is therefore also used for the simulation of this process when original coolant hoses are installed in the circuit system. From the heat exchanger the coolant enters a magnetically linked plastic pump. Each plastic hose can be replaced by a motor vehicle coolant hose to facilitate the investigation of this influence as well. The coolant hoses are changed after each test. The equipment is controlled and regulated via a Programme Logic Control System (PLC) which records the entire test.

The test apparatus itself is not larger than 2 m by 1 m and is housed in a mobile case in an air-conditioned room. The PLC is separated from the case. Table 6 shows the HTA and NHTA test parameters.

Intensified test procedures can be seen from the surface power density increase and the coolant temperature. Extension of the test duration also leads to intensification of the tests and had become necessary due to the elimination of the pressure aging tests and tests of the long-

TABLE 6—*Comparison of test conditions between new hot test apparatus (NHTA) and hot test (HTA) according to FVV directive R443/1986.*

Test Conditions	HTA	NHTA
Free scanning zone material, cm^2	30 (G-AlSi10Mgwa)	2 × 30 (GG25; GK-AlSi6Cu4)
Electric power, W	1500	5000
Surface power density, W/cm^2	(50)	2 × 70
Filling volume, L	3	1
Chamber inlet temperature, °C	80 ± 0.5	115 ± 0.5 (outlet 130°C)
Flow rate, L/min	4.3 ± 0.05	4.3 ± 0.05
System pressure, kPa	150 ± 0.05	free
Test time, h	30	72

life coolants. Due to the continuously increasing use of OAT coolants, changes were made to the cleansing process of the metal samples. Results from IfW investigations and experiences gained in the motor industry provided evidence that the protective layer formed on the metal surface also consists of corrosion products. By using the chromium/phosphoric acid mixture this layer is removed. It is therefore anticipated that—as in the CEC standards—formic acid will be used for cleansing the samples.

A further change will be seen in the use of test cooling water. To date the FVV R443/1986 directive stipulates the use of water with hardness of 10°dHG and deionized water. As the NHTA is also used on an international level (CEC) and a comparison is to be facilitated, deionized water is replaced by corrosive water according to ASTM D 1384. Water with hardness of 10°dHG is also to be tested. IfW investigations showed that some coolant additives provided efficient protection when mixed with corrosive water according to D 1384. However, considerable erosion was noted when mixing water with water hardness of 10°dHG [*8*]. Other coolants showed the opposite effect. Testing with two cooling waters and two concentrations (40 and 20 volume %) is subject to considerable expenditure. However, water affects the protection efficiency greatly and the water composition throughout the world varies extensively, making this type of test essential if the idea of a global coolant is to be realized.

New Cavitation Test Apparatus (NCTA)

It was suggested during discussions of the working group to revise the vibratory test. The proposals ranged from a revision of the evaluation modalities to a totally new construction of the test.

The knocking chamber test developed by MTU is used as an example for the apparatus. It is the recognized cavitation test. The final construction is still in the planning stage. The cavitation module is to be integrated in a simple circuit system consisting of a heater, pump and heat exchanger. The basic MTU principle in the cavitation module remains [*4,5*]: the heated coolant is fed through a sample chamber (knocking chamber), one chamber wall being static while the opposite wall is vibrated via a striking pin. The static wall consists of cast aluminum, the vibrating wall consists of cast iron. The number of strikes is approximately 1200 per minute. The vibrating metal moves at a frequency of 3 kHz, measured at the cylinder bushing sleeves. This creates pressure variations leading to the formation of cavitation bubbles in the liquid, which can collapse asymmetrically on the sample surfaces resulting in the feared, but in this case desired, jet impact. As this apparatus will be subjected to a number of revisions and the MTU working group members will propose changes, no final test parameters can be provided at this stage.

Whether the test in this new format will be introduced into the new test guideline is the subject of a research project financed by the IfW working group members. This development will be conducted in cooperation with the IC40 of the CEC, as they are also searching for a cavitation test.

It is planned that the new test directive will be introduced at the end of 1998, when the NCTA has been newly developed, the statistical values are available, and the engine tests confirming the test results have been concluded.

Conclusion

The testing of coolants can be divided into two segments: those designed for coolant approval and those designed to improve or to develop coolant additives. An observation of the apparatus and methods used in the tests alone shows the complexity of the topic. Although most organizations worldwide base their test systems largely on ASTM, test apparatuses were developed especially in Europe that make more realistic demands on the coolant because of intensified test conditions. Consequently, committees such as the CEC have carried out a standardization of these tests within the framework of the European Union, in order to limit the number of unclear regulations for coolants in Europe. It is evident that a standardization of simple chemical/physical test methods presents a minor problem. A "simple" glassware corrosion test can be standardized only at considerable cost; however, the costly circulation tests are based on extensive development work. This fact was acknowledged by the FVV working group "Coolant Additives" and a recirculation test was developed using the NHTA, which simulates the high demands made on a coolant and will therefore provide a good statistical quality. The apparatus can be used for standardized tests as well as for research and development because of its modular structure. It is anticipated that the new FVV test directive will be published at the end of 1998.

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Development of an Extended-Service Coolant Filter

REFERENCE: Mitchell, W. A. and Hudgens, R. D., "**Development of an Extended-Service Coolant Filter,**" *Engine Coolant Testing: Fourth Volume, ASTM STP 1335,* R. E. Beal, Ed., American Society for Testing and Materials, 1999, pp. 409–425.

ABSTRACT: An extended-service engine coolant filter has been developed, using conventional supplemental coolant additive (SCA) technology. This has been achieved by the use of a proprietary polymer coating, which delays the release of active engine coolant chemistry. Initial field data show a gradual release pattern for introducing SCA chemistry into the coolant, with complete release typically occurring in the range of 70 000 to 140 000 miles (112 651–225 302 km).

KEYWORDS: supplemental coolant additive (SCA), extended service, extended-service interval, slow release, coolant filter, coolant, heavy duty

Extended-service interval (ESI) coolant maintenance systems for heavy-duty engines are attracting a lot of attention, for a number of reasons. The extension of service intervals clearly reduces downtime. But, perhaps the real value of ESI systems to heavy-duty users is that ESI systems can reduce the complexity of coolant maintenance, while improving performance [*1*] and reducing overall cost.

To achieve a true extended-service system, while not adversely affecting the integrity of the engine cooling system, the following must be accomplished:

1. Reduce the frequency of servicing the coolant.
2. Maintain liner cavitation protection (that is, maintain a minimum level of liner cavitation inhibitor, which is usually nitrite or a combination of nitrite plus molybdate).
3. Maintain corrosion protection of other system components (multimetal system).
4. Maintain scaling and deposit protection in the cooling system.

Background

Three approaches to extended-service intervals have been developed in recent years. The first, an organic acid-based heavy-duty engine coolant, has already been discussed at ASTM Subcommittee D15.11 meetings [2] and will be the subject of another paper. The present paper will briefly examine a second approach, the use of a corrosion inhibiting coolant inhibitor container, before exploring the main subject, the development of the polymer-coated supplemental coolant additive combined with a robust filter.

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Corrosion Inhibiting Coolant Inhibitor Container

One approach to extending service intervals is to extend the life of the coolant filter. This implies that the materials of construction used in the filter will withstand duration of service and that the level of supplemental coolant additive will remain in the recommended range for the length of the extended service.

Cheadle and Rusiniak teach about the use of a coolant filter that has a life of up to 80 000 miles (128 744 km) [*3,4*]. This is a sizable extension over a normal 15 000 to 20 000 mile (24 140 to 32 186 km) filter life. The invention permits "controlled release of corrosion inhibitor into a coolant when the coolant has a corrosiveness above a predetermined level" [*4*]. Release of the supplemental coolant additive occurs as the partition or membrane which separates the coolant from the SCA disintegrates (corrodes). The partitions are preferably formed from magnesium or magnesium alloys.

Three basic assumptions should be made regarding the use of this device: (1) corrosion products from the partition are not detrimental to the performance of the cooling system, (2) the partition will corrode when the coolant becomes corrosive to one or more system metals, and (3) the partition will not corrode until the coolant becomes corrosive to one or more system metals.

In practice, the corrosion of magnesium alloy partitions results in the formation of magnesium (hardness) ions in solution. This is not desirable, as the introduction of hardness in engine coolant can lead to the formation of hardness sludge and deposits (that is, magnesium carbonate, magnesium silicate, and magnesium phosphate deposits). Note that Appendix I of the ASTM Specification for Low Silicate Ethylene Glycol Base Engine Coolant for Heavy Duty Engines Requiring a Pre-Charge of Supplemental Coolant Additive (SCA) (D 4985-94) states that "water having a high mineral content or corrosive materials is unfit for cooling system use."

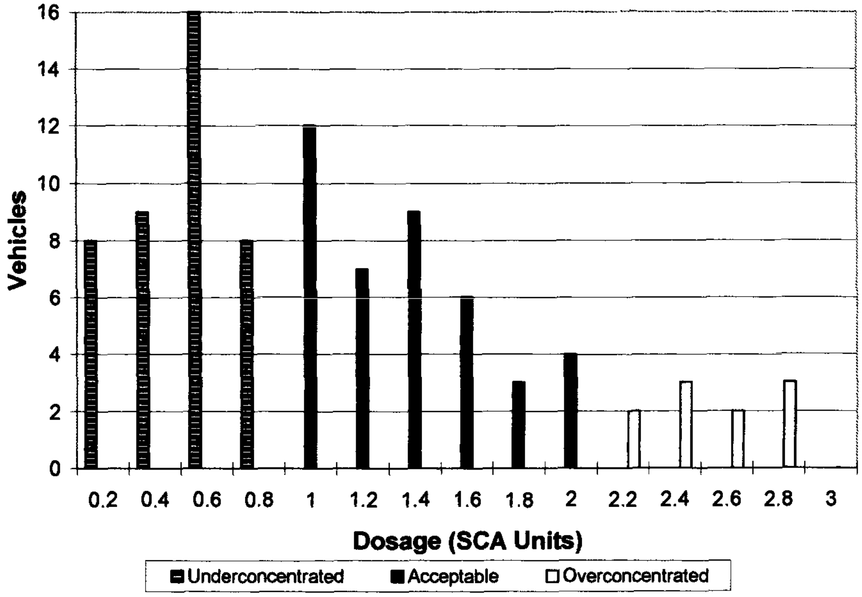

FIG. 1—*1989 fleet test using partition filters.*

The remaining assumptions rely on the premise that the corrosion of a magnesium alloy is somehow related to the corrosion of typical cooling system components. Perhaps the most critical component of a heavy-duty cooling system is the cylinder liner. Cavitation or perforation of the liner causes failure of the engine. The use of the corrosion inhibiting coolant inhibitor container, then, presupposes that the corrosion of the magnesium alloy in the partition filter (no heat transfer or cavitating conditions present) may be correlated to the cavitation corrosion of a cast iron cylinder liner. While the authors are unaware of any data showing this correlation, perhaps the issue is best examined by referring to data developed in two fleet tests. If release of SCA from the filter is related to liner corrosion, the level of SCA should never be less than the minimum required for liner cavitation protection.

The first set of fleet data for a combination Midwest/East Coast fleet was developed after a number of engine failures were attributed to insufficient SCA concentration to prevent liner cavitation [5]. For the coolant taken from 92 vehicles treated with partition filters, Fig. 1 shows SCA dosage levels determined. Note that the optimal SCA dosage is in the range of 1 to 2 units (or about 1000 to 2000 ppm nitrite as NO_2). For the case of the first field trial, 45% of the vehicles treated with the partition filter were undertreated; that is, the partition filter did not provide sufficient chemical to prevent liner cavitation.

The second set of fleet data, for a Midwestern fleet which installed the partition filter on each engine at 5000 to 8000 miles (8047 to 12 874 km) of service, is shown in Fig. 2 [5]. For the coolant taken from 44 vehicles, underconcentration of inhibitor was limited to about two vehicles. While 39% of the vehicles had the proper level of SCA present in their coolants, 57% of the vehicles had exceeded the proper level of SCA; that is, the partition filter added SCA when it was not required.

Summarizing experience with the corrosion inhibiting coolant inhibitor container, magnesium hardness is added to the coolant, and this method of treatment can either severely under-

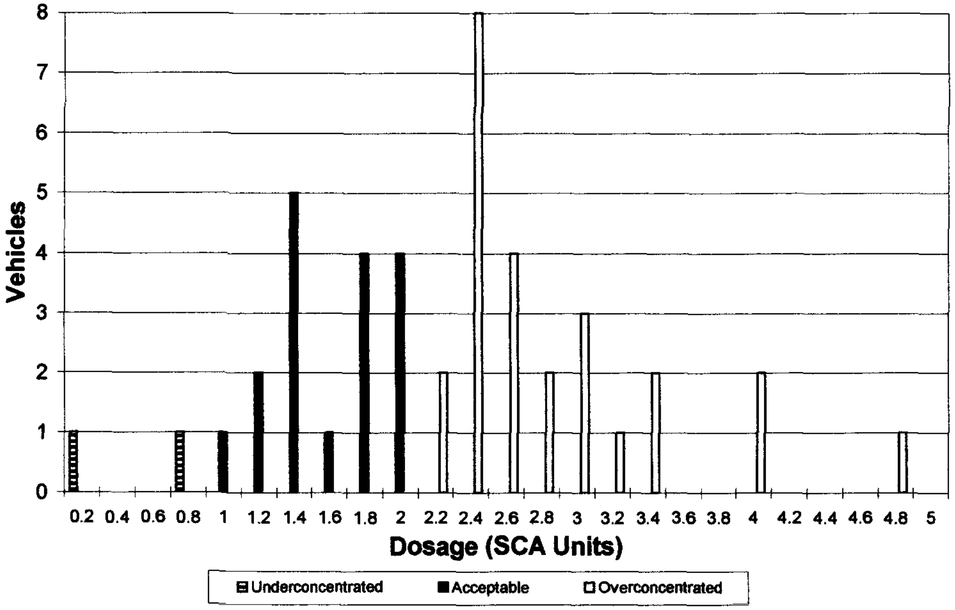

FIG. 2—*1993 fleet test using partition filters.*

treat or overtreat a coolant. Undertreatment or overtreatment would not occur if SCA addition were directly related to cavitation corrosion of cylinder liners.

Development of a True Extended-Service Interval Filter

Work to develop a true extended-service maintenance system began with a goal of achieving annual, 150 000 mile (241 395 km), or 4000 h filter changes. To accomplish this, the following was necessary:

- True heavy-duty coolant meeting TMC-329/330 that is compatible with other heavy-duty coolants.
- ESI-type SCA designed to offset inhibitor depletion.
- Robust filter design (U.S. Patent No. 5,662,799).
- Slow-release additive (patent pending) chemistry.

Description of Heavy-Duty Coolant

The heavy-duty coolant uses conventional phosphate chemistry combined with nitrite and molybdate for liner protection. The coolant, which contains dispersants and polymers for the prevention of both inorganic (hardness) and organic (oil) deposits and/or sludges, meets TMC-329/330 specifications.

Component Depletion and Resulting Supplemental Coolant Additive (SCA) Development

1. *Reduced Solids/Component Depletion*—Reduced-solid SCAs have been available since the mid-1980s. GraceDearborn (now BetzDearborn, a division of Hercules, Incorporated) introduced this concept to heavy-duty SCAs using the term ''component depletion'' [*6*]. The component depletion concept utilizes the fact that components of a heavy-duty coolant inhibitor deplete at different rates. Greater proportions of rapidly depleting components and lesser proportions of slowly depleting components are formulated into the SCA.

To determine the true depletion rate of the various inhibitors used in antifreeze and SCAs, Fleetguard (now Fleetguard/Nelson Incorporated) ran a field test on their phosphate/molybdate products. Twenty over-the-road trucks powered by Cummins 14-liter engines belonging to a Wisconsin-based fleet were chosen as test units. This particular fleet was chosen for the following reasons:

- Low coolant loss (<2 gal (7.6 L) per year, which was less than 20% of the cooling system volume). This is far less than the 50 to 100% yearly loss experienced by many fleets and limits the effect of ''sweetening'' with fresh coolant.
- Very disciplined maintenance which included proper cooling system top-up when required.

In most cases, the units returned home on a daily basis, which limited the amount of top-up with improper coolant on the road. No SCA was added to the cooling system over the duration of the approximately one year, or 100 000 to 120 000 mile (160 930 to 193 116 km) test.

Figure 3 shows the results of this field test. In general, additives were affected as follows:

- Nitrite loss was about 50% (330 to 470 ppm as NO_2).
- Tolyltriazole loss was about 50% (300 to 400 ppm as tolyltriazole).
- Molybdate loss was about 25% (70 to 90 ppm as Mo).
- Silicate loss was about 25% (75 to 100 ppm as SiO_2).

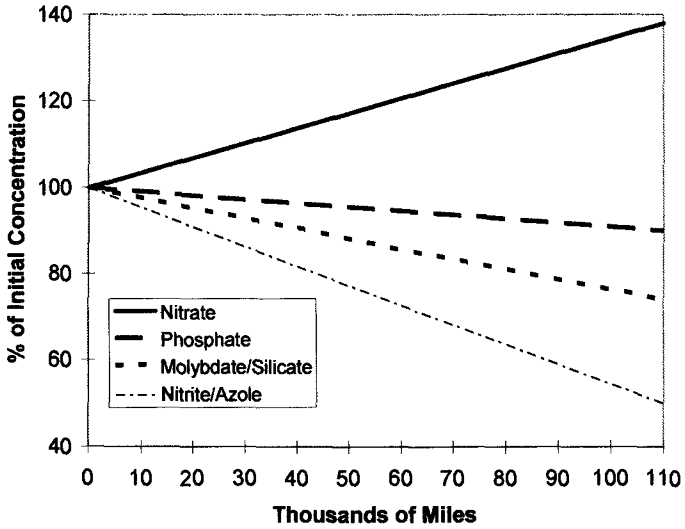

FIG. 3—*Inhibitor depletion versus mileage.*

- Phosphate loss was about 10% (330 to 670 ppm).
- Nitrate actually increased (a reaction product of depleted nitrite).

It is noted that the depletion rates presented are not absolute values for all vehicle and engine configurations as well as service conditions. Engine problems, such as head gasket leakage, aggravated additive depletion in this particular test. Absolute depletion rates will vary somewhat from fleet to fleet. As an example, nitrite depletion rates are quite different for similar phosphate/molybdate coolants examined in three Fleetguard field tests. Figure 4 compares nitrite depletion for the these trials. Results indicate:

- Nitrite loss was 50% (330 to 470 ppm as NO_2) for the above trial in 120 000 miles (193 116 km) on Cummins 14 liter engines.
- Nitrite loss was 15% (130 to 200 ppm as NO_2) for a 200 000 mile (321 860 km) trial using Caterpillar 3406 engines [7].
- Nitrite loss was 20% (130 to 200 ppm as NO_2) for a 6000 h trial using Cummins KT-38 engines.

While absolute depletion rates may vary from fleet to fleet, what is important is the relative depletion rates of the various inhibitors in the SCA and coolant. For the particular SCA evaluated, relatively high amounts of nitrite and copper inhibitor (tolyltriazole) are used, while phosphate and nitrate levels are minimized.

2. *Product Form*—Once the SCA composition was determined, product form was chosen to be small tablets. For the tablets to be suitable to coat, the following criteria had to be met:

- The tablets must easily release from the dies and punches used.
- Tablets must have sufficient hardness (a minimum of about 9 kiloponds) to avoid disintegration.
- Tablets must have sufficient integrity (that is, friability is less than 0.5%) to withstand the tumbling action of a pan or fluidized bed coater.

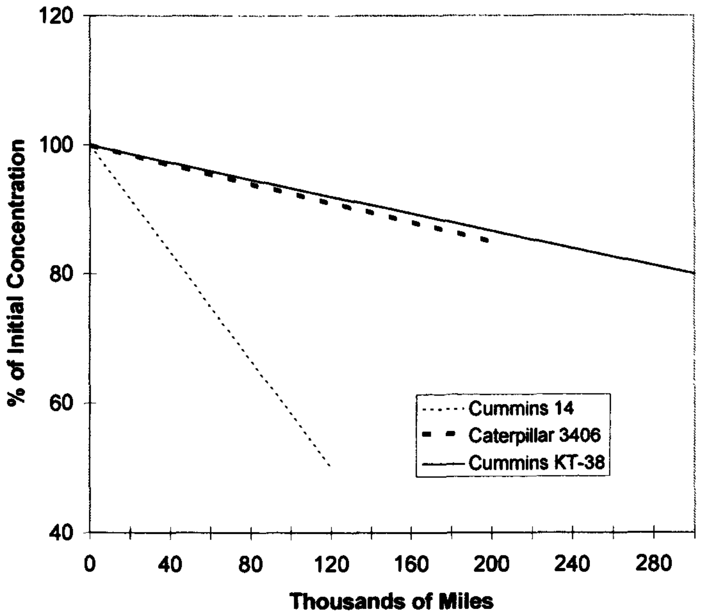

FIG. 4—*Nitrite depletion versus mileage (assumes 6000 h = 300 000 miles (482 790 km)).*

- No release agents, binders or other additives can be added that are not fully understood in the context of a heavy-duty cooling system. (That is, unless an engine manufacturer is willing to test the effect of the new material on system components.)

Robust Filter Design

The filter is constructed so as to withstand the rigors of extended exposure to hot coolant beyond the typical two month or 20 000 mile (32 186 km) service interval. In order to improve durability to at least one year or 150 000 miles (241 395 km) of service (Fig. 5), the filter utilizes:

- A more chemically resistant gasket and epoxy adhesive.
- A thicker nut plate for increased vibration resistance.
- A more corrosion-resistant shell and spring.
- Synthetic, layered polypropylene media with high efficiency and greater durability than conventional cellulose media, which degrade when exposed to coolant for more than 75 000 miles (120 698 km) [7, pp. 8, 9].

Slow-Release Additive

Coating—The shortest route to a slow-release product was determined to be a polymer barrier coating applied to the exterior of tablets. This would provide a mechanism to delay the release of the inhibitor package. The coated tablets could be easily added to the filter, while

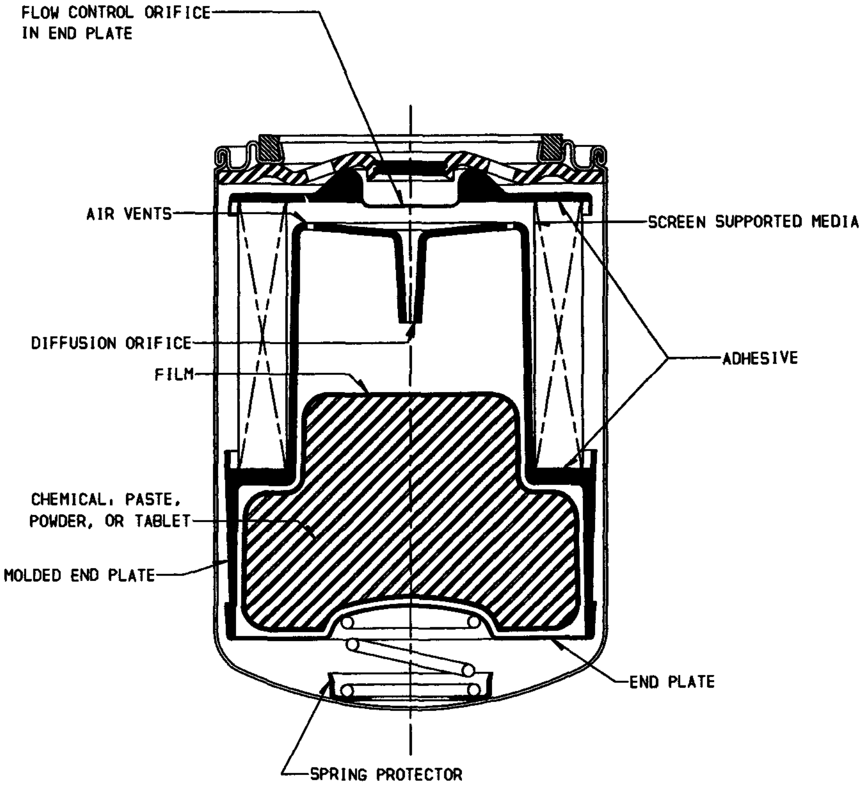

FIG. 5—*Coolant filter, chemical version (drawing for patent disclosure).*

the filter could be modified, if necessary, to contain the coated tablets before and during release and to contain the remaining polymer capsules after release is complete.

Criteria for Success of the Coating—In order for the polymer barrier coating to be successful, the following requirements are critical:

- Polymer barrier must be either made of a soluble material well understood as acceptable in a heavy-duty coolant environment or the polymer barrier must be insoluble in heavy-duty coolant.
- Polymer used for the barrier must be a film former; that is, it must be capable of forming a film on the substrate to which it is applied.
- Polymer barrier must not introduce unacceptable amounts of undesirable materials into the coolant.
- Polymer barrier must delay the release of the SCA for a minimum of 1000 h or 50 000 miles (80 465 km).
- The polymer should release the SCA gradually. Ideally, the polymer barrier releases active chemistry at about the same rate as the SCA depletes.

Development of the Coating—Initial work to develop the polymer barrier coating was borrowed from time-release fertilizer technology developed by W.R. Grace's Washington Research Center. The concept was to spray coat the tablets in a pilot scale pan coater, using a water-based emulsion polymer. The resulting coated tablets are shown in Fig. 6. Polymers which proved successful at delaying the release of fertilizer over the course of an entire growing season were chosen as the first candidates to examine for the heavy-duty coolant water filter application. As an added criterion, polymers were to be essentially water/glycol insoluble.

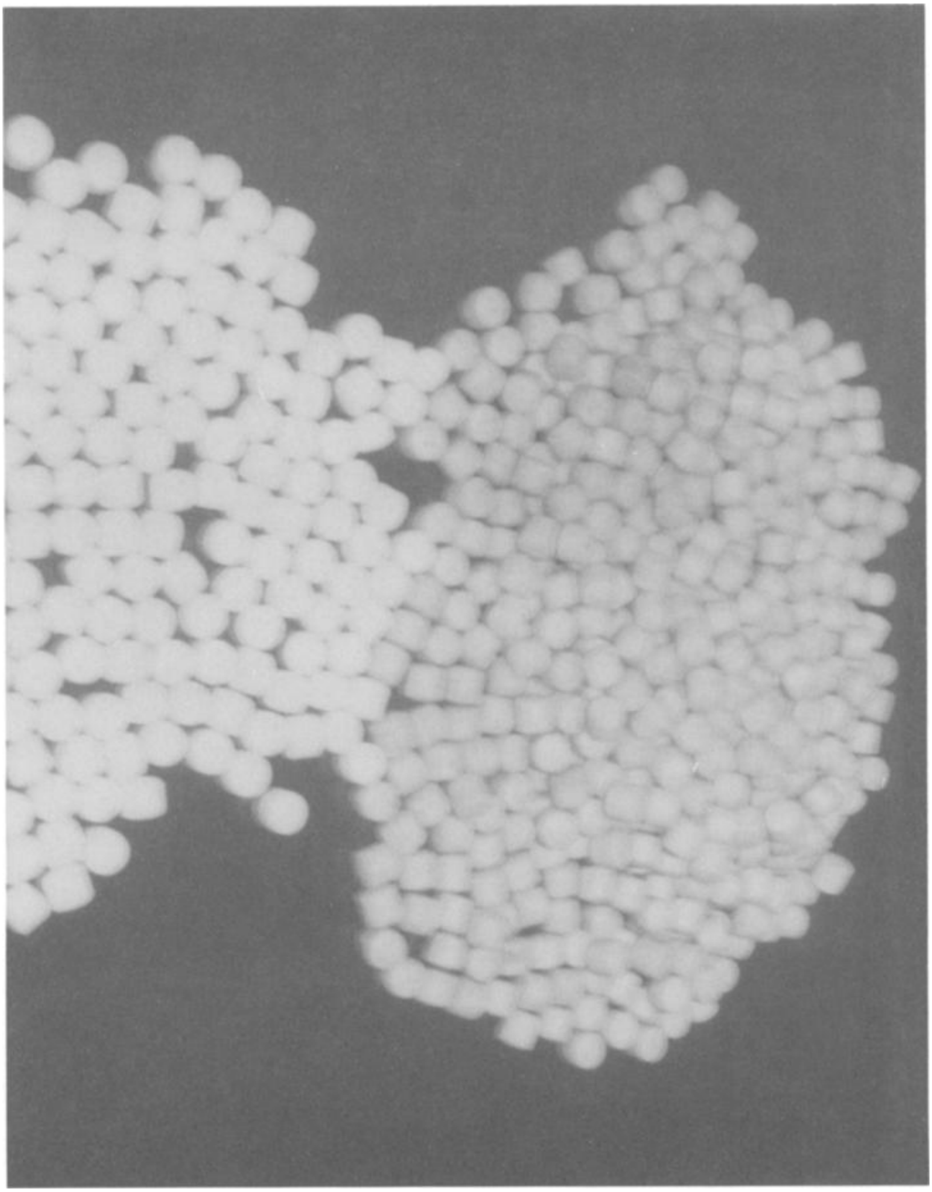

FIG. 6—*Coated tablets.*

Initial Evaluation with Beaker Tests and Simulated Service Tests

Beaker Evaluations

Initial coatings were evaluated using simple beaker tests. Ten coated tablets (about 10 to 11 g total weight) were added to 700 mL of 50/50 coolant concentrate/water. The solution was heated to 230°F (110°C) and tablets were observed thereafter. Coolant samples were also taken in order to track release rates.

Figure 7 shows nitrite release data for SCA coated with three different polymers and for the noncoated SCA. Nitrite release is rapid for the noncoated SCA and for polymer-coated WRC No. 6, with essentially all of the nitrite in solution for the first sample taken. The fact that WRC No. 1 and WRC No. 7 show delayed release of nitrite confirms that it is possible to slow down the release of active chemistries into the engine coolant by a polymer barrier. With the proper polymer barrier, release has been extended, in this case to at least two weeks.

Simulated Service Rig Evaluations

To get a better picture of release for a polymer barrier coating, the barrier coating must be evaluated in a dynamic environment. The simulated service rig (per ASTM Test Method for Simulated Service Corrosion Testing of Engine Coolants (D 2570-96)) provides an opportunity for this. Two rigs were used for these evaluations. One rig is essentially unmodified. The other had previously been modified to use a Mack Truck radiator; this increases rig volume to about 10 gal (38 L). Both rigs were then modified to run a ¼-in. (0.635 cm) line of tubing to a filter

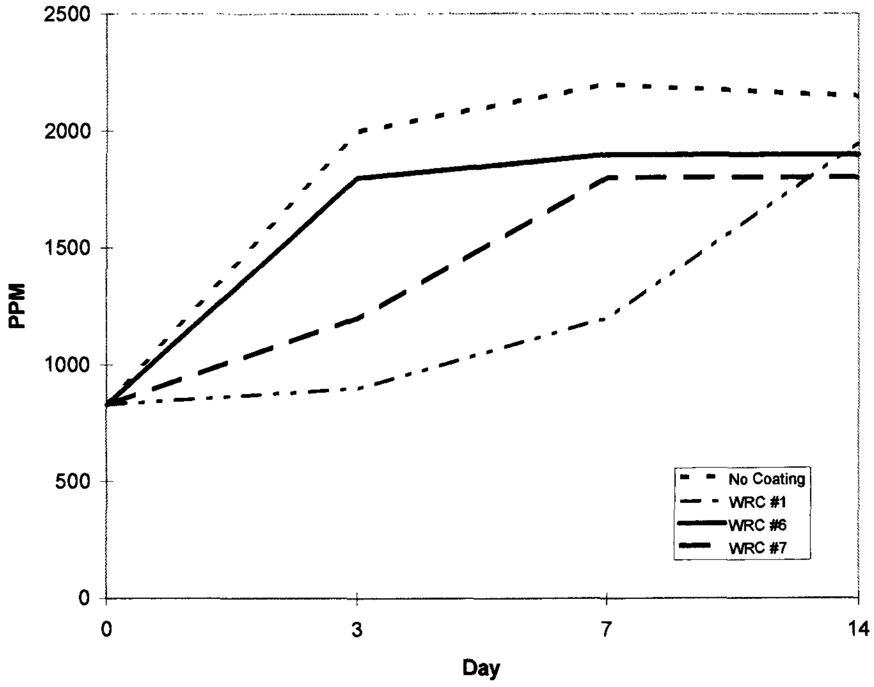

FIG. 7—*Beaker evaluations: nitrite release versus time.*

TABLE 1—*Method for simulated service rig evaluation of slow-release SCA.*

1. Modify rig to accommodate a filter adapter.
2. Place a premeasured amount of slow-release SCA tablets into an empty filter canister and install on rig, or alternately use a production filter with slow-release SCA.
3. Fill rig with the appropriate volumes of antifreeze concentrate and deionized water to achieve 30, 50, or 70% glycol concentrations.
4. Turn on rig. Allow to circulate 10 min and pull initial coolant sample.
5. Set temperature control (190, 150, or 204°F) (88, 65, or 95°C).
6. Adjust flow through the filter to a rate of about 1 gpm (3.7 L/min).
7. Set automatic timers to shut rig off for two, 8 h intervals per week.
8. Pull 4 to 8 oz (113 to 226 g) coolant samples at appropriate intervals (usually weekly).

adapter and then to the top of the radiator. Flow was adjusted to a rate of about 1.5 gpm (5.6 L/min) through the filter adapter (and filter). The method for running this test is described in Table 1.

Table 2 and Fig. 8 show simulated service results for WRC No. 7 (tablets coated with a polyvinyl chloride polymer). Results show gradual release of SCA for the 20-day duration of the test. This translates to about 24 000 miles (38 623 km) of service (50 mph (80 km/h) × 20 days × 24 h or about 24 000 miles (38 623 km) of service).

Analysis of coolant samples showed chloride levels increased during the 20-day simulated service test. It is speculated that the high-temperature conditions of the coolant caused the vinylidene chloride polymer to unzip, releasing small amounts of hydrogen chloride. This increase in chloride levels and acidity made the polymer used for WRC No. 7 unacceptable.

Because of the failure of vinylidene chloride polymers to remain stable, WRC No. 6, a terpolymer based on vinylacetate, was evaluated. Even though WRC No. 6 showed no delayed release in beaker tests, simulated service rig results showed a different story. Table 3 and Fig. 9 show the gradual release of SCA over the 43-day duration of the run (equivalent to about 52 000 miles (83 684 km)). This appeared to be a significant step toward a new slow release product.

Regarding the performance of the WRC No. 6 polymer, tablet shells were examined during the stimulated service run. The tablets soften, forming a honeycomb-like mass of material (Fig. 10). The SCA must pass through as many as 30 to 40 layers of coating in order to enter the coolant.

Applications Profile

In order to more fully understand performance of the WRC No. 6 polymer coating, simulated service tests were run to evaluate the effects of glycol concentration, temperature and propylene glycol versus ethylene glycol on delayed release performance. In order to compare product

TABLE 2—*Simulated service rig: slow-release profile for WRC No. 7 polymer-coated SCA.*

Day	Boron as B*	Nitrite as NO_2	Nitrate as NO_3	Molybdenum as Mo	Chloride as Cl
0	1.8	760	430	232	10
6	4.3	810	450	243	15
13	24	1100	680	334	50
20	33	1100	690	363	60

*All amounts in parts per million.

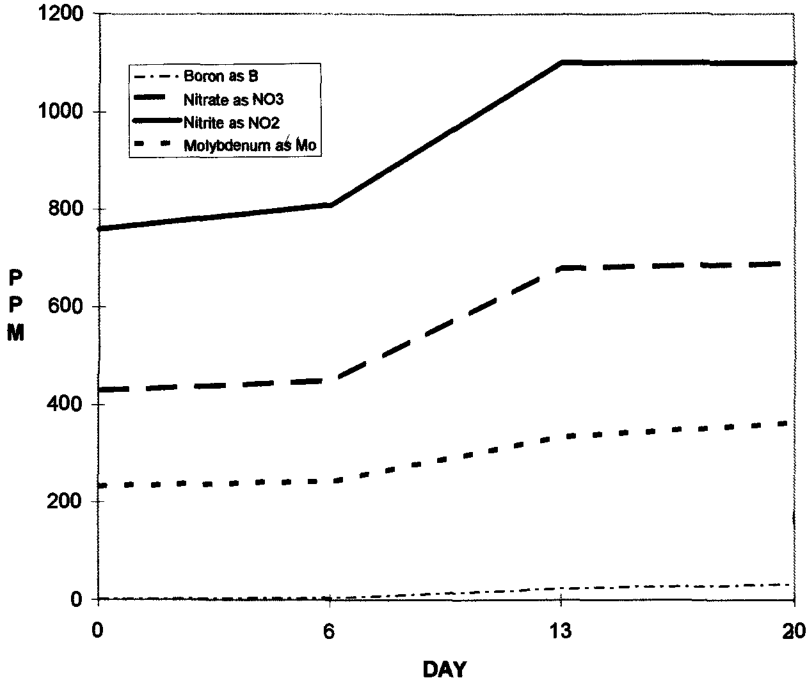

FIG. 8—*Simulated service rig: WRC No. 7 inhibitor release versus time.*

release, an average release rate was calculated for each simulated service run, using data for nitrite, nitrate, molybdate and boron. Average release rates are compared.

Ethylene Glycol Concentration

Figure 11 examines release of the WRC No. 6 polymer versus ethylene glycol concentration, varying glycol from 30 to 70%. Results for the three-week tests indicate the slowest release occurs for 50% ethylene glycol. In the short-term tests, the release rate in 30% glycol is nearly double the rate in 50% glycol.

TABLE 3—*Simulated service rig: slow-release profile for WRC No. 6 polymer-coated SCA.*

Day	Boron as B*	Nitrite as NO_2	Nitrate as NO_3	Molybdenum as Mo	Chloride as Cl
0	1.8	730	440	245	<10
2	6	740	470	245	<10
5	7.6	800	490	266	<10
8	N/A	870	500	N/A	N/A
14	16	920	530	323	N/A
20	18	940	590	282	N/A
22	19	1000	650	279	N/A
29	24	1100	690	333	N/A
43	32	1260	818	262	<10

*All amounts in parts per million.
N/A = not available.

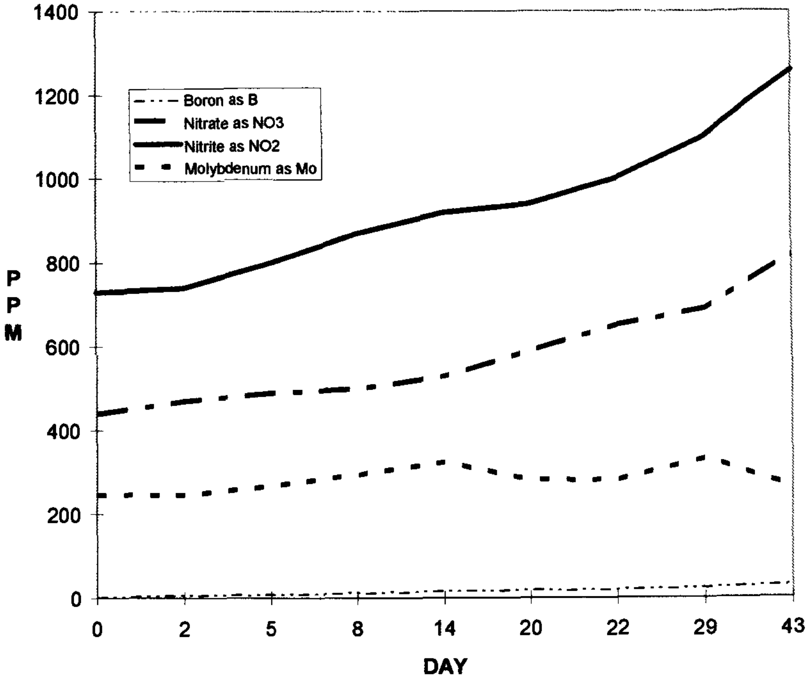

FIG. 9—*Simulated service rig: WRC No. 6 inhibitor release versus time.*

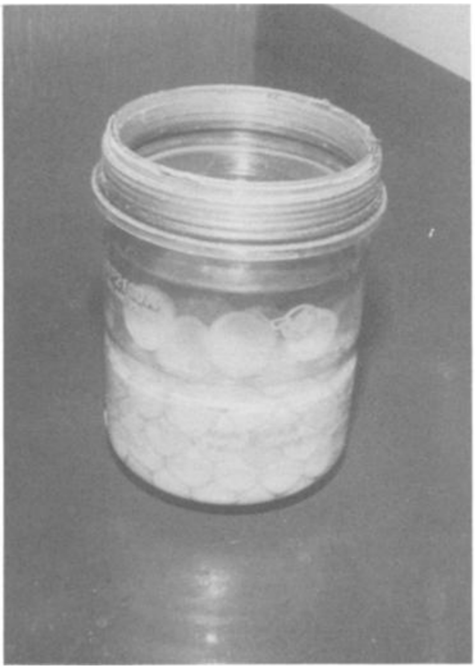

FIG. 10—*Coated tablets exposed to hot coolant.*

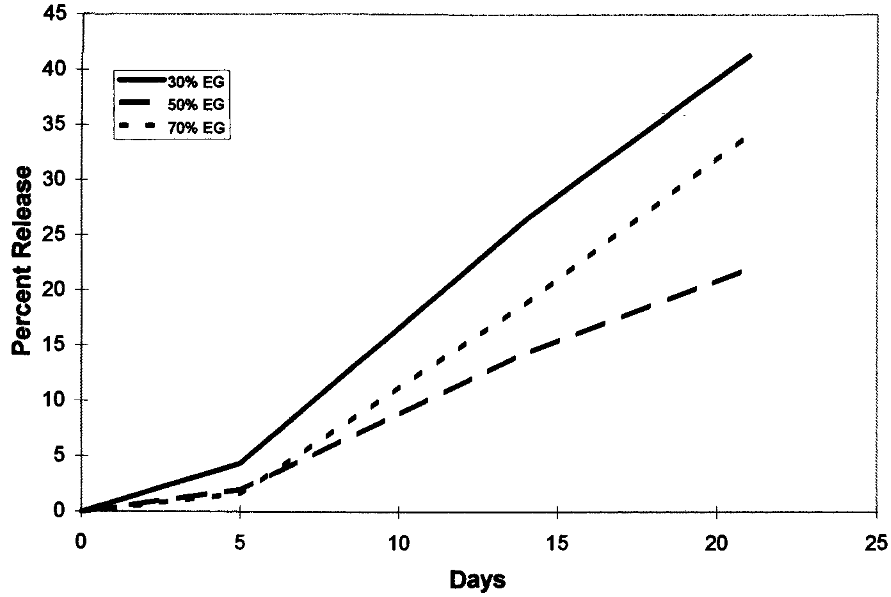

FIG. 11—*Simulated service rig: effect of glycol concentration—average inhibitor release versus time for WRC No. 6.*

Temperature

Figure 12 examines release for temperatures of 150, 190, and 204°F (65, 88, and 95°C). Release increases with increasing temperature. Extremely slow release rates are observed at 150°F (65°C), while release rates nearly double at 204°F (95°C) compared with 190°F (88°C).

Propylene Glycol (PG) versus Ethylene Glycol (EG)

Figure 13 compares four-week release rates for PG versus EG. The release rate in PG runs about three times that of release in EG.

Field Trial

Field tests sites were chosen in southern Indiana and in Wyoming, east of Salt Lake City. In both cases, 20 units powered by Cummins 14 L engines were put on test. These small fleets were chosen in part because of their disciplined maintenance practices. Of more importance, however, was the fact that both fleets accumulate about 200 000 miles (321 860 km) per year. This allowed the rapid generation of data on chemical release rate for the long life filter.

About 50 filters were removed from the field test units with a range of 20 000 to 200 000 miles (32 186 to 321 860 km) of service. All filters were cut open and visually evaluated for the amount of additive release (see Fig. 14). In addition, the exposed tablets from 20 filters were dried (see Fig. 15 for examples) and subjected to chemical analysis to determine the amount/type of additive remaining and the extent to which the polymer coating had dissolved. Data on chemical release versus mileage are graphed to present an envelope of performance

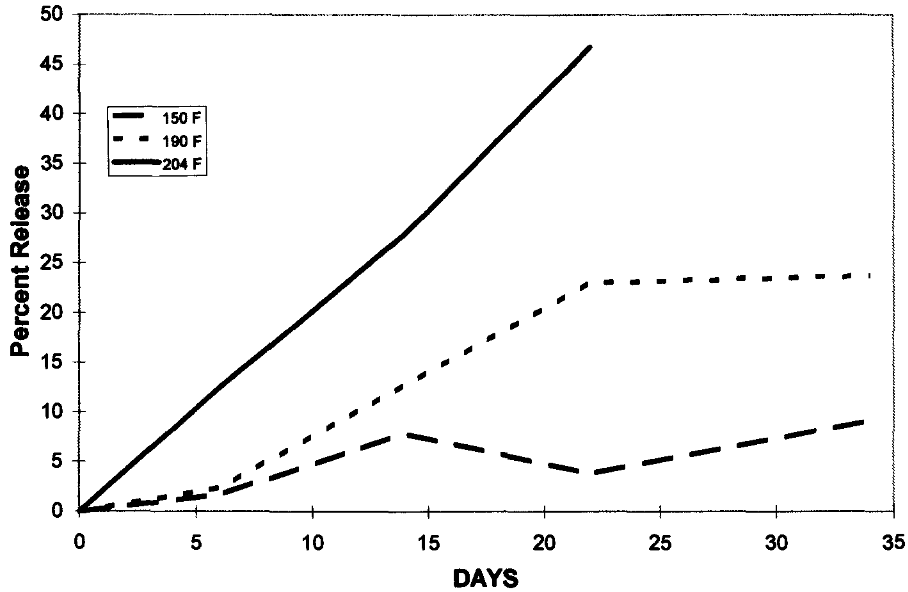

FIG. 12—*Simulated service rig: effect of temperature—average inhibitor release versus time for WRC No. 6.*

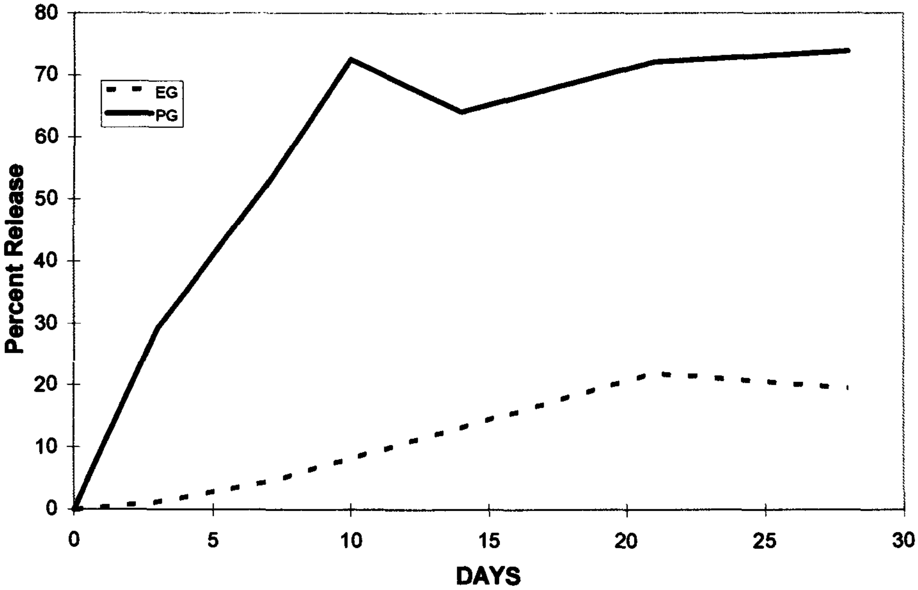

FIG. 13—*Simulated service rig: effect of ethylene glycol versus propylene glycol—average inhibitor release versus time for WRC No. 6.*

FIG. 14—*Coated tablets: after 156 000 and 48 000 miles (251 050.8 and 77 246.4 km) of exposure compared with new coated tablets.*

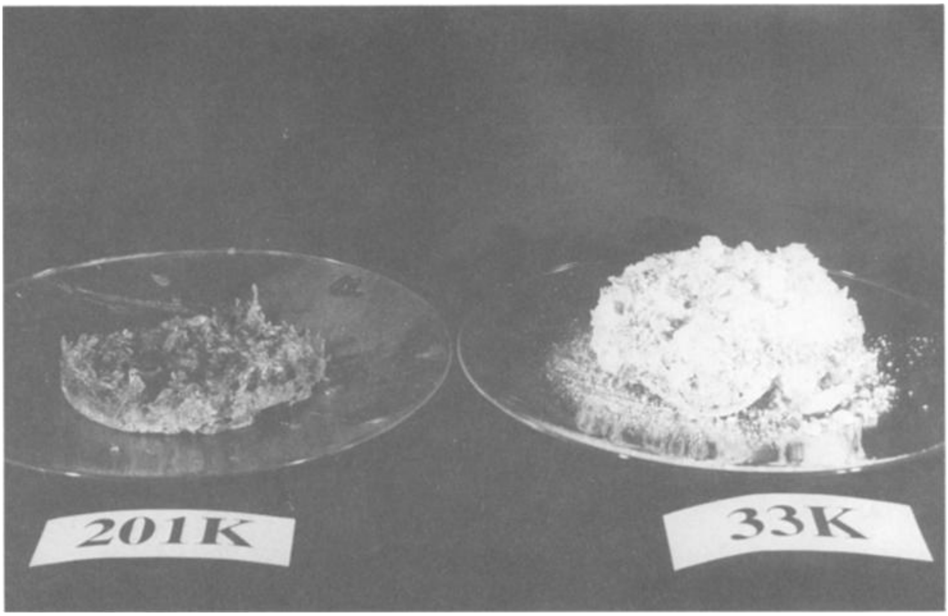

FIG. 15—*Coated tablets: remainder after exposure to 201 000 and 33 000 miles (323 469.3 and 53 106.9 km) of exposure.*

in Fig. 16. Additional findings on the chemical release from the long-life filter/coated tablets are given as follows:

- 90% of the SCA was dissolved in 50 000 to 100 000 miles (80 465 to 160 930 km).
- Release was essentially total at 150 000 miles (241 395 km).

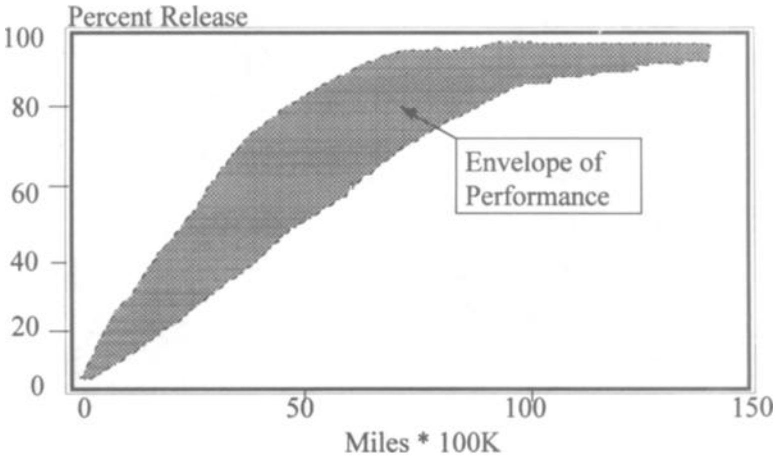

FIG. 16—*Fleet test: slow-release envelope of performance for 41 vehicles.*

- Silicate was the slowest releasing component of the additive package. Typically, it was all or most of what remained beyond 100 000 miles (160 930 km) of service.
- Little (<5%), if any, of the polymer coating dissolved into the coolant at 150 000 to 200 000 miles (241 395 to 321 860 km).

The preceding findings verify that the extended-service filter gradually releases SCA under field conditions.

Conclusions

Laboratory beaker and simulated service rig data, and field data, document performance of the new extended-service coolant filter. Conclusions include:

- Slow or delayed release of a conventional SCA can be achieved by the use of an insoluble polymer barrier coating.
- The proper polymer coating introduces no harmful contaminants to the coolant.
- Release of the SCA is gradual.
- Release is dependent upon temperature.
- Slow release occurs for over 1000 h (>50 000 miles (80 465 km)) in simulated service tests.
- Field results show gradual release lasting between 50 000 and 150 000 miles (80 465 and 241 395 km).

This robust SCA with polymer barrier in a quality filter offers the opportunity for fleets to take advantage of extended maintenance service intervals for heavy-duty cooling systems, while still using well known conventional SCA technology.

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