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Engine Coolant Testing: Third Volume

Roy E. Beal, editor

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Overview

Engine coolant usage continues to increase on a worldwide basis as the overall vehicle population becomes larger. Many off-highway vehicles and stationary equipment facilities also use engine coolant. Water preservation and environmental concerns are reflected in a gradually expanded use of coolant for industrial cooling applications. Vehicle cooling predominates and is the major concern for the symposium. Average vehicle size and coolant capacity has recently reduced in the United States. More efficient engine designs tend to use less coolant volume for equivalent heat rejection purposes. Modern automobiles are made with newer and lighter weight materials. The importance of aluminum alloy protection by engine coolant has become evident, together with an increased use of composite plastics. Meanwhile, the average age of vehicles on the highway has increased, and these older vehicles require engine coolant replacement at regular intervals. The engine coolant specialist has therefore many technical challenges and the technology is developing sufficiently that a meeting to present advances and discuss current problems was needed.

The first symposium was held in Atlanta, GA, in 1979. It was well supported and resulted in ASTM *Engine Coolant Testing: State of the Art,* (STP 705), which still provides a good reference. Success led to a second conference in 1984, held in Philadelphia, PA, at which the rapid changes in material usage and testing requirements were expounded upon by many of the authors. This symposium resulted in ASTM *Engine Coolant Testing: Second Symposium,* (STP 887), and probably the most important development was the basis of a new standard for evaluating hot surface protection for aluminum engine alloys that has now become an international standard for the coolant industry. Propylene glycol was introduced as an alternate base fluid for coolants. Electrochemical test methods were evaluated and discussions of specific needs for heavy duty engines highlighted.

The third symposium was held in Scottsdale, AZ, *Engine Coolant Testing: Third Symposium,* 6–8 Nov. 1991, and was well attended with presentations from European, Japanese, and United States authors.

Papers presented at the conference covered advances in the development, testing, and application of engine cooling fluids for automobiles and heavy duty engines that have occurred since the last meeting.

A keynote opening address by Hannigan set a good tone to the conference by presenting a brief history of ethylene glycol engine coolant. Ethylene glycol was first suggested for use as an engine coolant in military aircraft in England in 1916. Other aircraft applications followed, with the Curtiss Hawk PIA in 1926 being of particular note. Use of ethylene glycol in automobiles began in 1927. Wide adoption occurred in the period 1949 through 1955 as a factory fill in place of methanol. Developments have continued, and Hannigan presents the highlights bringing us up to the present time.

Four authors presented papers on new families of engine coolant that operate in a medium pH range. Maes and Van Den Ven's work in Europe on the use of low depletion monoacid diacid inhibitor technology reveals good high-temperature corrosion protection of aluminum when acids are properly balanced. An evaluation program included ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions (D

4340) hot surface tests, a dynamic heat transfer test, and a coolant aging test. These were used with top quality commercial engine coolants and the monoacid dibasic acid technology, for direct comparisons. Static heat transfer testing gave good results with all technologies. Dynamic heat transfer testing was more discriminating and favored the new monoacid and diacid combinations for aluminum corrosion protection under hot surface conditions with apparently better heat transfer at the metal/coolant interface.

Burns carried out an extensive fleet test with a carboxylic acid long life coolant formulation with very good results. Two hundred and three Ford Crown Victoria Taxi cabs were used. The chief objective of the program was to evaluate coolant pump failure with respect to the new carboxylic long life coolant, when compared to more traditional formulations. Coolant installation was color coded and pump failures from each group identified. Four conditions and a factory fill were involved. The new carboxylic formulation resulted in the lowest pump failure rate, although reasons why could only be speculated upon. A new coolant pump bench test is recommended for comparative study of coolant formulations.

Mercer examined experimental carboxylic acid inhibitor formulations, to test their efficiency in both laboratory and fleet tests. Problems were encountered with lead based solder and aluminum alloy corrosion, although other metals were adequately protected. Aluminum protection required high levels of acids present. Compatibility of the carboxylic acid formulations and phosphate buffered coolant was poor, and mixtures resulted in reduced protection. No inhibitor depletion was observed, but this did not prevent corrosion of the aluminum and high lead solder alloys in fleet testing.

Extended life coolant with sebacic acid was compared to current high silicate alkaline phosphate coolant prevalent in the United States in a three-year municipal fleet test by Adamowicz and Falla. Results demonstrated no particular advantage with the sebacic acid formulation over current North American coolant. They also concluded that factory fill coolant life can be extended far beyond previous expectations. Metal coupon corrosion losses were minimal for either coolant throughout the test. The relatively high cost of the sebacic acid coolant precludes its use on an economic basis.

Durability of aluminum alloy automotive radiators in service depends on the alloy selected and the expected engine coolant environment. Beal and El-Bourini investigated accelerated testing procedures for alloy development with appropriate coolant conditions. New alloys are continually under development to improve radiator service life. The challenge is to find testing methods that correlate with service experience without resorting to long-term vehicle exposure trials. A combination of electrochemical studies and simulated service has demonstrated a viable approach. Unless related to a particular engine coolant environment, serious mistakes can be made in aluminum alloy radiator materials chosen.

Heavy duty diesel engines use significant quantities of coolant and emphasis on long operation periods continues as engine design changes, resulting in higher efficiencies. Hercamp presented an historical overview of cavitation corrosion in diesel cylinder liners, relating various factors that are involved with liner pitting. A major problem in the 1950s, much work has been done since to identify causes and develop solutions. The paper covers scientific background and theories, and not all workers agree on the damage mechanism. Coolant effects and the use of supplement coolant additives (SCAs) are covered with some reference to engine related factors. Education of maintenance personnel is important to follow prescribed procedures in coolant and SCA practice. Testing can assist in avoiding trouble and is cost effective in checking coolant condition.

Hudgens briefly covered the history of supplemental coolant additives used in heavy duty diesel engines, and then went on to describe a new family of phosphate molybdate packages that are designed to perform better with aluminum components and cause less problems if overtreatment occurs. A test scheme involved most ASTM standards and the German FVV Test, in addition to bench cavitation work. The phosphate molybdate formula provides better protection in hard water, and the ability to reduce nitrite levels is beneficial to solder protection. Liner pitting is prevented at lower overall inhibitor addition.

Toxicity and disposal of engine coolants is a topical subject that was reviewed and discussed by Hudgens and Bustamante. Properties of ethylene and propylene glycols and major additives used in engine coolants are included. Propylene glycol is not toxic and provides an environmentally acceptable coolant base. However, inhibitors used have varying degrees of toxicity, and after use, when heavy metals are dissolved into the coolant, the resultant fluid is definitely toxic, whether propylene glycol or ethylene glycol are used as the base fluid. Present laws and regulations are referenced, and a discussion on the hazardous concept is included. Used coolant may or may not be hazardous depending on its condition when tested against EPA threshold values. Both ethylene and propylene glycols are biodegradable. 400 million gal (1514 million L) of coolant are sold every year. 10% of coolant may be lost by leakage, 25% or more by improper disposal, and the remainder generally handled according to regulations. Recycling is becoming a commercial feasibility and is being done in the western United States in particular on a large scale. Total volume of recycled coolant is still low compared to coolant sold per year. The paper gives a good overview of facts and concerns regarding handling and disposal of engine coolants.

Test strips have been developed for rapid on-site analysis of engine coolants for some specific attributes. Hemmes et al. described their efforts. Strips for nitrite and molybdate measure protection for cavitation erosion. One has been developed for MBT in conjunction with chloride level identification. Test strips for pH and RA also are available. Measurement of freeze point has been carried out for over ten years. The wider range of test strips assist in maintenance programs and for identifying when SCAs should be used in heavy duty vehicles.

Engine coolant analysis techniques use standard equipment with particular procedures for accurate results. Advances coincide with new analytical instrumentation. Problems in coolant systems can be solved by application of inductively coupled plasma (ICP) emission spectroscopy and laser ablation ICP according to Zamechek and McKenzie. Coolant analysis by ICP is enhanced by specially developed software for interferences and data reduction. Aqueous standards are used with 50-fold dilution of the analytical samples. Preparation methods are described. The laser ablation system was used for spacial mapping of elements on the surfaces of water pump seals. A uniquely adapted sample cell and target area was devised with optical focusing and alignment.

Oxalic acid cleaning of engines removes inhibitors, rusts, and other deposits. Some concern has been expressed on the post cleaning effect of the process when vehicles are used for coolant testing. Woyciesjes reviewed the chemistry involved. Oxalates form a variety of complexes with typical metals in the engine circuit. Ferrous oxalate can be 10 μm or more in thickness. Borate conditioning removes some of the oxalate. Oxalates can affect subsequent coolant properties by having a detrimental influence on pH, RA, and inhibitor levels. A high pH, borate conditioning fluid minimizes the consequences, and in new vehicles the effect is small. Vehicles exhibiting heavy corrosion should not be used for coolant testing, because cleaning will not be totally effective.

Pump seal failures are a contemporary problem with disagreements on causes and solutions. This topic was received with much interest by the attendants. Deposits on water pump seal faces were examined by Stafford from heavy duty diesel on-highway engines. Coolant leakages were traced to deposit films built up on the siliconized graphite seals. Surface analyses of the buildup revealed elements from the coolant, coolant additives, corrosion metals from the engines and calcium from hard water. Mileage at pump removal ranged from 28 000 to

199 000 miles (45 060 to 320 251 km). A calcium-iron-phosphate complex precipitated during nucleate boiling episodes was determined as the cause of seal leakage because of seal face separation caused by the deposit.

Kiryu et al. examined the effect of coolant on water pump mechanical seals in a very thorough investigation. There is an urgent problem attributed to coolant formulation contamination and an increase in engine operation condition severity. Leakage occurs by deposit formation and growth of the film, which creates a gap at the seal face. Oxygen-rich conditions at 150°C can cause inhibitor solidification that deposits on the seal. Test work confirmed that high-temperature seal operation causes deposits related to silicates, when they are present. In triethanolamine coolant, copper and iron salts were the culprit, usually from breakdown acids promoting corrosion of copper parts. A third coolant formulation resulted in precipitation of dibenzothiazyl disulfide on seal ring surfaces leading to leakage. All the deposition problems were solved by designing seals with lower interface operating temperature, controlling materials used, and reducing surface roughness at the seal face.

Depletion of engine coolant inhibitors, contamination, and breakdown of the glycols occurs during the use of engine coolant in service. Vehicle makers provide recommendations on changing coolant on a regular basis. These changes provide the waste stream that can be used for recycling. Statistical analysis of used coolants gathered from New England through Georgia was performed by Woodward and Gershun. A total of 2500 vehicles was reviewed in the results. Standard laboratory techniques were used for the analyses with appropriate conditions for accuracy of data collected. A wide range with nonnormal distribution was found for residual inhibitors. Corrosive contaminants, such as chloride and sulfate, varied widely with chloride levels similar to ASTM corrosive water and sulfates significantly higher. Degradation of the glycol to acetates, glycolates, and formates depletes the reserve alkalinity. A prediction is made that 20% of used engine coolant will have lead in excess of 5 ppm, and thus be regarded as hazardous waste. Suspended solids are found regularly with over 25% of those coolants tested having 500 ppm or more. Recycling needs careful consideration because of variations in fluid conditions and the need for a balanced product.

Extension of coolant life in automobiles is feasible when a three-step examination is made that determines coolant has not been used for 65 000 km, is not oily, murky, or rusty, or is less than 25% concentrated with a reserve alkalinity of less than 3. Under these conditions Hercamp and Remiasz show that a supplemental coolant additive package can provide at least a further year of life to the coolant. Standard ASTM tests were used for verification, and field experience has been satisfactory. The additive is used in conjunction with a closed-loop coolant flushing system attached to the vehicle.

Richardson described a recycling process for used coolant that involves a multistage process with dual bed deionization. The process purifies the coolant removing contaminants and particulates. The resulting fluid has very low concentrations of all species providing a clean fluid for reinhibition. The process used and data obtained are described. The author considers that efficient removal of contaminates to a low total dissolved solids level is necessary for a consistent finished product.

Recycling processes were discussed by Bradley. The paper reviewed several different approaches to providing the service. Awareness of environmental issues in the disposition of spent engine coolant prompted a study to examine the efficiency of various systems. A reference coolant was utilized that was collected from many vehicles, resulting in a mixture of several types of inhibitor packages and degradation products. All recycling processes used the same coolant for test purposes. Processes evaluated were filtration, filtration-flocculation-coagulation, deionization, reverse osmosis and vacuum distillation. Some systems were combinations of these processes. These systems are described. Off site coolant recycling is performed on a large scale typically by fractional distillation, and these companies are included in the G.M. approval program. Recycled coolants must meet or exceed GM 1825 M coolant specification. A progressive test program was undertaken. Coolants failing any test in the sequence were rejected. Physical tests, followed by ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384) and ASTM D 4340 hot surface evaluation were performed. Only those passing proceeded to pump cavitation and simulated service. Results were not available at the conference and will be published later.

Two keynote papers were invited covering automotive and heavy duty vehicles technologies. The objective was to educate the newcomers and remind the veterans of coolant technology development over the years to the present time. Both papers were timely and a success at the symposium. Hannigan covered automotive cooling technology in which he has been personally involved over many years making a good presentation of history and finishing with highlights of present challenges. A summary of current heavy duty technology in coolants was ably addressed by Kelley with discussion on liner pitting, silicate drop-out, water pump seal leakage, and other problems. He discussed the value of ASTM standards and new requirements for the future with a good overview.

The symposium was a success and reflected advances in coolant technology and present areas of concern. A special thanks to all the authors, the symposium subcommittee, chairmen of the individual sessions, and the ASTM staff is warmly given. Jenny Beal, Denise Steiger, and Gloria Collins deserve specific mention for the organization of the conference and social events. This volume will make a valuable contribution to publicly available information on coolant technology.

Roy E. Beal

Amalgamated Technologies Inc., Suite 208,
13901 N. 73rd St., Scottsdale, AZ 85260;
symposium chairman and editor.

H. J. Hannigan[1]

A Review of Automotive Engine Coolant Technology

REFERENCE: Hannigan, H. J., "**A Review of Automotive Engine Coolant Technology,**" *Engine Coolant Testing: Third Volume, ASTM STP 1192,* Roy E. Beal, Ed., American Society for Testing and Materials, Philadelphia, PA, 1993, pp. 6–10.

ABSTRACT: A brief history of ethylene glycol application as an engine coolant is presented. Concurrent engine cooling system corrosion problems and coolant corrosion inhibition requirements are reported. Comments on current engine system corrosion problems are provided. Resistance to corrosion failure is shown to depend upon the correct combination of cooling system design, materials, coolant inhibition, and coolant retention.

KEYWORDS: ethylene glycol, engine coolants, engine cooling systems, corrosion, corrosion inhibition

Automotive engine coolant technology probably began in 1885 when Karl Benz invented and patented the first automotive radiator to provide recirculation cooling for the water-cooled engine that he built for his first horseless carriage. The radiator was developed to eliminate the problem with evaporative cooling, which boiled away one gallon of water each hour of operation of the single cylinder engine.

It is interesting to note that ethylene glycol, propylene glycol, and their derivatives were first synthesized in 1859 by Charles Wurtz, a French chemist. It was not until World War I that a commercial process for making ethylene glycol from alcohol was developed in Germany for use in explosives.

The first engine coolant application of ethylene glycol was suggested in England in 1916 for high performance military aircraft engines. In the United States, the initial experimental glycol coolant applications took place in 1923. Shortly thereafter, a liquid cooled Curtiss Navy Racer captured the world seaplane speed record. The monoplane was powered with a Curtiss inverted V12 aluminum engine cooled with an ethylene glycol-water solution. The cooling system used heat exchanger panels in the wings to combine cooling with aerodynamic efficiency. By 1926, this engine, equipped with an underslung radiator and cooled with an ethylene glycol-water solution, was the power plant for the Curtiss Hawk P1A, which became the standard U.S. Army Air Corps pursuit plane. Parallel development of glycol cooling was underway in Great Britain and Europe. The recognized advantage of glycol-water coolants was the high boiling point, which permitted high temperature cooling with reduced frontal area. Also, the lower vapor pressures raised the threshold of coolant pump cavitation, enabling operation at higher altitude. In the following years, coolant inhibitors were developed to control corrosion and coolant degradation at coolant temperatures as high as 275°F (135°C) in normal pressurized operation. Triethanolamine phosphate MBT inhibitor compositions were eventually specified for military aircraft coolants both in England and the United States.

Although a U.S. patent was issued in 1918 for the use of ethylene-glycol to lower the freezing

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[1] Consultant, International Copper Assoc., Ltd., Dallas, PA.

point of water in automobile cooling systems, large scale production of ethylene glycol did not begin until 1925. At that time, Union Carbide and Carbon Corporation was the sole volume producer of ethylene glycol until the beginning of World War II. Initially, small quantities of uninhibited ethylene glycol were sold for automotive antifreeze use. Very soon it became apparent that uninhibited glycol solutions could become corrosive to cooling system metals. Engine cooling systems were commonly afflicted with large amounts of residual water jacket rust, even when new. Substantial coolant pump air induction was to be expected and cylinder heat joint exhaust gas leakage was a fact of life.

Prestone brand ethylene glycol antifreeze was first marketed by the National Carbon Co. in 1927. It was the only commercial glycol based antifreeze brand. Its competition was glycerol and the older existing brands of methanol and alcohol volatile antifreezes.

By 1930, the National Carbon Co. and the Linde Research Laboratories jointly developed a two-phase chemical and insoluble oil inhibitor system to prevent corrosion, rust loosening, and rust transport to the radiator. Mr. Daniel H. Green of the National Carbon Co. was appointed as manager of the automotive engineering department to direct coolant research, applications engineering, and field technical support. This position presented a real challenge of major proportions. Here was a new brand, a new product, with no track record in the automotive after-market, or the automotive industry. It was priced at $5.00 per gallon, against alcohol brands selling for about $1.00 per gallon in a depression economy. Like the good news and bad news stories, the good news might have been that things couldn't be any worse. Then again, maybe they could.

In many instances, automobile factory engineering personnel, service representatives, and after-market service dealers firmly believed that ethylene glycol solutions "leaked more than water" and "ate through" cylinder head gaskets and coolant pump seals, and "would find a leak where water wouldn't." The high visibility of leakage residue with glycol solutions contributed to leakage misconceptions. Water and alcohol solutions would quickly evaporate at the point of leakage. In one situation where internal coolant leakage and engine seizures were at issue, a laboratory supervisor at a leading car manufacturer declared, "The only way to keep ethylene glycol out of the crankcase is to keep it out of the cooling system." The fact was that cylinder head gaskets were leaking frequently due to lack of recommended retorquing of the cylinder head bolts after the engine was operated for a short time. Cylinder head gaskets were relatively thick and conformable with very little torque retention.

The internal coolant leakage problem disappeared in the middle 1950s with the advent of numerous higher performance overhead valve V8 engines. These were designed with much improved cylinder head joints to withstand increased compression ratios and higher combustion pressures. Between 1949 and 1955, the U.S. car manufacturers recognized the need for increased coolant temperatures to reduce engine sludging and wear. Consequently, ethylene glycol base coolant was widely adopted for factory fill in place of methanol. Thermostat opening temperatures were increased to 180°F (82°C). Water with corrosion inhibitors was still installed at the factory during the warm-weather months.

Methanol and ethanol were steadily losing market share. Little or no inhibitor research and development were dedicated to alcohol antifreezes. The usual inhibitors were borate or nitrite, offering marginal, if any, corrosion protection to aluminum.

Despite the limited concern about aluminum corrosion, some of the older L head engines were equipped with aluminum cylinder heads. Examples were the 1934 and 1935 Ford V8s and the 1937 and later Lincoln Zephyr V12s. Other car manufacturers offered optional higher compression ratio cylinder heads of aluminum. Crevice corrosion at the cylinder head joint was a frequent problem. Consequently, the car manufacturers reverted to cast iron cylinder heads.

From the post war period to about 1960, commercial North American glycol coolant inhibitors were usually borate buffered with small amounts of various supplementary inhibitors, such as sodium salts of MBT, arsenite, nitrite, molybdate, or phosphate. Second phase insoluble polar oils were also used as supplementary inhibitors.

In Europe and England, the British Standards Institute composition specifications dominated the markets. BS 3150 Type A was a triethanolamine orthophosphate, sodium MBT inhibitor system. BS 3151 Type B consisted of sodium benzoate and sodium nitrite. BS 3150 Type A was used with aluminum component engines and BS 3151 Type B with cast iron engines. Glycol concentrations were held to the minimum in Europe and England. Ethylene glycol was widely regarded as an inferior heat transfer agent, to be removed as soon as possible at the arrival of warm weather.

Up to the 1950s, there was little or no uniform performance testing among the car factories and the antifreeze industry. Each company, if indeed it did coolant testing or research, or both, devised its own in-house tests. These usually consisted of a glassware test method, a bench circulating test on occasion, and short-term vehicle tests using subjective evaluation of engine cooling system components, such as coolant hoses, coolant pumps, thermostats, and coolant outlets.

The Linde Laboratory of Union Carbide pioneered the full-scale engine dynamometer test method with an interesting approach. The L head Ford V8, in production from 1932 through 1953, was designed with a coolant pump for each cylinder bank along with separate outlet and inlet radiator hoses on each side. By modifying the upper and lower radiator tanks with a center sealing baffle the engine could be operated having identical twin cooling systems with exactly same coolant temperatures, temperature differentials, heat load, and heat flux concentrations. This unusual feature enabled performance evaluation of two different coolant formulations simultaneously under precisely same conditions.

Beginning in 1958, radiator core solder alloys for original equipment radiators were changed from 70% lead, 30% tin to about 97% lead, 3% tin composition. Radiator solder corrosion increased dramatically. Voluminous corrosion consisting of lead hydroxide and occluded inhibitors would obstruct the radiator tube openings causing restricted coolant flow and overheating. Coolant suppliers were caught unaware of this situation. Manufacturing methods were also involved. If the radiator tube-to-header joints were soldered externally, little or no tube opening obstruction occurred. Where the tube-to-header joints were soldered internally, excess solder would enter the tube opening by capillary action and cause corrosion clogging. Residual flux containing chlorides also increased the rate and volume of corrosion. To prevent the problem, insoluble oils and emulsifiable oils were installed with the factory fill coolant on the assembly line by some car manufacturers. High lead solder corrosion proved difficult to control with single phase soluble salts inhibitor systems. Short term laboratory tests could identify more aggressive inhibitor systems, but could not predict long term protection. Extended vehicle tests lasting 12 months or more became necessary to reliably indicate satisfactory in situ high lead solder inhibition. Recent field surveys of radiator corrosion modes show solder bloom in 5-year-old and older cars to still be prevalent. In contrast, Japanese radiators soldered with 60% to 40% or 70% to 30% lead–tin solder do not encounter solder bloom even after long-term use and marginal coolant maintenance.

In 1962 and 1963, the U.S. car factories adopted year-round installation of inhibited ethylene glycol coolants. This was done to eliminate freeze damage to left over new car inventories and to provide increased corrosion protection. To assure adequate freeze protection, minimum glycol concentration was set at 44% (−20°F) (−29°C) in the United States and 53% (−40°F) (−40°C) in Canada. The antifreeze industry changed its recommendation from 33% minimum glycol concentration to 50% to ensure year-round adequate corrosion protection.

This period marked the introduction of die cast aluminum coolant pumps and mating die cast aluminum timing chain covers on most of the then current production V8 cylinder engines. Before long, the pumps and covers were encountering perforation from cavitation-erosion-corrosion in police fleets and other high engine speed duty such as ambulance operation. Existing circulating tests, engine dynamometer tests, and company fleet tests did not produce the attack. Special aluminum pump cavitation-erosion-corrosion tests were developed by the car factories and were adopted by the coolant suppliers to develop improved inhibitor systems. Increased phosphate inhibitor concentration, along with adequate coolant concentrations provided control of the problem.

Cooling system design factors showed a significant effect on pump cavitation corrosion incidence and severity. Pump impeller clearances and configuration in relation to housing scroll configuration and internal pressure differentials could improve or worsen cavitation corrosion attack. Today, North American factory fill inhibitor systems provide very satisfactory inhibition of aluminum pump cavitation even with marginal designs.

In the mid 1960s, there were early clues to the potential problem of aluminum cylinder head heat rejecting cavitation corrosion and transport deposition at the radiator and heater core. U.S. rebuilt P51 fighter plane cooling systems were filled with high phosphate inhibited automotive coolant. The fighters were flown to South American countries for military duty. By the time they arrived, the engines were overheating due to aluminum corrosion deposition in the radiator. This did not happen when the Air Force specification triethanolamine phosphate inhibited coolant was used.

Occasionally an imported car aluminum cylinder head would leak coolant into an exhaust port due to perforation of the exhaust port wall from the coolant side. Usually, the failure was accompanied by a partially clogged radiator core. Certain model U.S. cars equipped with aluminum cylinder heads and factory fill high RA borate phosphate formulas would develop overheating from radiator deposition when the cars were driven from Michigan to Arizona for proving ground track testing. Other lower RA differently balanced inhibited coolants did not cause the problem. At the time, none of these situations appeared significant enough to generate a demand for new inhibitor technology.

In 1973, one of the U.S. car manufacturers elected to use an aluminum cylinder head engine in a new line of cars to be introduced in 1974. Durability track testing revealed radiator deposition caused engine overheating about halfway through the test schedule. The coolant inhibitor system in use was the factory specified high RA, high phosphate formula. Further comparative testing established that an existing stabilized silicate supplemented coolant composition widely available in the after-market effectively controlled the problem. This coolant brand was approved for the new car factory fill in 1974. Subsequent coolant research and development testing revealed the mechanism of cavitation erosion corrosion in relation to nucleate boiling at aluminum heat rejecting surfaces.

It became apparent that cylinder head design could be a critical factor in relation to cavitation corrosion. Coolant jackets having very high surface to volume ratios, siamesed exhaust ports, drilled passages in attempt to relieve "hot spots," and other marginal coolant flow distribution conditions were much more prone to cavitation corrosion and transport deposition.

Coolant composition has played an interesting role in designing the engine cooling system to eliminate or minimize heat transfer deficiencies. In the early 1960s, International Harvester Engine Div. developed an engine dynamometer test to identify high heat flux areas and inadequate coolant flow. A magnesium borate inhibited coolant solution provided a reliable graphic in situ pattern of heat transfer in the engine cylinder head and cylinder block. The magnesium borate inhibitor deposited progressively on increasingly higher temperature heat rejecting surfaces. This technique is currently used by some U.S. car manufacturers to confirm satisfactory cooling in a new engine design.

It is worth noting that the discovery of this invention was serendipitous. In 1950, magnesium borate was used in a Canadian after-market antifreeze. The product was used in a roadgrader engine that suffered cylinder head cracking in the combustion chamber area. Excessive inhibitor deposition was concentrated at the high heat flux areas. The engine manufacturer and the antifreeze supplier were at issue whether the coolant caused the cracking or the cylinder head design was deficient. Subsequently, the engine manufacturer increased the by-pass flow rate through the engine and the coolant supplier discontinued the magnesium borate inhibitor system.

At present, contemporary brazed aluminum radiators and heater cores have shown down-tube random pitting to be a significant problem for the coolant inhibitor system, in the southern tier and west coast of the United States. Inhibitor depletion due to loss of glycol concentration continues to be a common condition in this southern region with three year old and older passenger cars. Also, the lack of freezing weather provides a market for bogus "engine coolant" labeled products which are little or no more than colored water. The use of these products in a brazed aluminum radiator will program the radiator for tube pitting perforation failure. Perforation can occur as early as 6 weeks and certainly within 12 months, depending on the chloride ion concentration in the coolant water source. In the middle U.S. and northern frontier areas premature pitting perforation failures have been relatively rare. None-the-less, the presence of high chloride concentration may initiate pitting despite adequate glycol concentration and normal inhibitor condition.

In retrospect, these experiences confirm that coolant technology is driven by material and design changes in the engine cooling system. In terms of engine durability, coolant side corrosion is a critical factor. Long term resistance to failure from corrosion is inescapably dependent upon the combined effects of coolant inhibition and the materials and design of the total engine cooling system.

Jean-Pierre Maes[1] *and Paul Van de Ven*[1]

Corrosion Protection of Aluminum Heat-Transfer Surfaces in Engine Coolants Using Monoacid/Diacid Inhibitor Technology

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REFERENCE: Maes, J.-P. and Van de Ven, P., **"Corrosion Protection of Aluminum Heat-Transfer Surfaces in Engine Coolants Using Monoacid/Diacid Inhibitor Technology,"** *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 11–24.

ABSTRACT: A low depletion monoacid/diacid corrosion inhibitor technology that provides superior high-temperature aluminum corrosion protection combined with excellent heat-transfer characteristics has been identified. The efficiency of the inhibitor technology was evaluated gravimetrically on aluminum specimens under static and dynamic heat-transfer conditions. Testing techniques and results are discussed. The thermal properties of the protective film and the coolant were evaluated under dynamic heat-exchange conditions. Information on composition and structure of the protective film formed under conditions of heat-transfer was obtained through the use of microscopy and Fourier transform infrared spectrometry (FTIR).

KEYWORDS: engine coolants, corrosion, inhibitors, aliphatic acid, heat-transfer, monoacids, diacids, aluminum, heat-exchange surface

The physical and, more particularly, the heat-transfer properties of a coolant are largely determined by the choice of the freezing point depressant. Specific heat, thermal conductivity, fluidity, freezing point, and boiling point relate directly to the nature and the concentration of the diol used. The chemical and corrosion properties can however be controlled by the use of additives. Reserve alkalinity and hard-water stability can be improved by the use of a pH buffer and stabilizer, respectively. Additionally coolants may include an antifoaming compound, a dispersant to avoid deposit formation, and a dye for identification.

Corrosion in an engine cooling system will have two main effects: (1) deterioration of the metal component either by uniform wastage or localized attack (pitting, crevice corrosion) and (2) the production of insoluble corrosion products that can block radiators, thermostat valves, and so forth, and impede heat-transfer by deposition on the heat exchange surfaces. The major additive constituents of engine coolants are therefore corrosion inhibitors.

Because of the increased use of aluminum and other light metals for engine and cooling part components, the inhibition of localized forms of corrosion, such as pitting and crevice corrosion, has become crucial. Several engine manufacturers have introduced test requirements that relate directly to protection against localized corrosion of aluminum. More specifically, the galvanic pitting corrosion test [*1*] was introduced as a measure of the long-term effectiveness of coolants in preventing pitting corrosion attack in aluminum heat exchangers. Together

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[1] Research group leader and development chemist, respectively, Texaco Research and Development—Ghent, Technologiepark—Zwignaarde 2, Ghent, Belgium.

with some conventional tests, cyclic polarization techniques can be used to determine susceptibility to pitting and crevice corrosion [*2,3*].

Early inhibited coolant formulations in Europe contained a combination of triethanol amine, phosphoric acid, and sodium mercaptobenzothiazole (MBT). Triethanol amine phosphate (TEP) coolants are still used, but most European coolants are now based on a borate-benzoate package containing varying amounts of nitrite, nitrate, silicate, and triazole. In recent formulations salts of organic aliphatic acids have been substituted for nitrite.

In the United States, coolants currently on the market may contain a relatively large amount of phosphate and varying amounts of nitrate, silicate, and triazole. Other formulations with less phosphate, contain borate in addition to nitrate, silicate, and triazole.

As experience was growing [*4*], some adverse properties of the used inhibitors and inhibitor combinations have come to light. Sodium mercaptobenzothiazole, for example, relatively insoluble at low temperatures, which can form insoluble calcium salts in hard waters, has been largely replaced by benzotriazole or tolyltriazole. In the absence of nitrite, benzoate is relatively ineffective for the protection of steel and cast iron. If not correctly stabilized, silicate can form gels on standing. Borate can cause corrosion of aluminum alloys at high temperatures [*5*] as well as phosphate that can also be precipitated by hard waters.

Silicate is still considered to be an effective inhibitor of aluminum corrosion, and silicate stabilizers have alleviated some of the problems associated with gel formation and precipitation of this chemical.

While these disadvantages were being discovered, encouraging progress was being made in inhibitor development. Based on work by Butler and Mercer [*6*], disodium sebacate, the sodium salt of decandioic acid, was found to be an effective corrosion inhibitor for both ferrous and aluminum alloys. Various other monobasic and dibasic carboxylic acids have also been identified as effective corrosion inhibitors by Hersch et al. [*7*].

Where conventional inhibitors, such as nitrite and silicate, are subject to rather rapid depletion in service, this is not the case for organic monoacids or diacid salts [*8*]. The introduction of formulations that use organic acid salts as the major inhibitor constituent has opened new prospectives for the development of long-life coolants.

Work by Darden et al. [*9*] showed that inhibitor combinations of monoacid and diacid salts provide improved protection of aluminum, particularly against pitting and crevice corrosion. The cyclic polarization scans for different combinations of monoacids and diacids are shown in Fig. 1.

The higher pitting potentials found for aluminum in synergistic combinations of the acid salts indicate improved protection against pitting [*2,9*]. The difference between the pitting and protection potentials, as determined by cyclic polarization, can be correlated directly with susceptibility to crevice corrosion [*3*]. Reduced hysteresis indicates improved ability to repassivate active corrosion cells.

Most current coolant formulations include silicate for high-temperature corrosion protection of aluminum heat-transfer surfaces. However, because of the limited solubility of silicate in propylene glycol, monoacid-diacid inhibitor technology also appears to be a preferred choice for incorporation in less-toxic propylene glycol based coolants.

These silicate-free inhibitor formulations offer not only improved corrosion protection and a stability that is easier to maintain but also contribute to the durability of water pump seals [*10*].

The efficiencies and heat-transfer properties of monoacid- diacid inhibitors have been evaluated on aluminum coupons under static and dynamic heat-transfer conditions. Test results have been compared to the results obtained with more traditional coolant solutions.

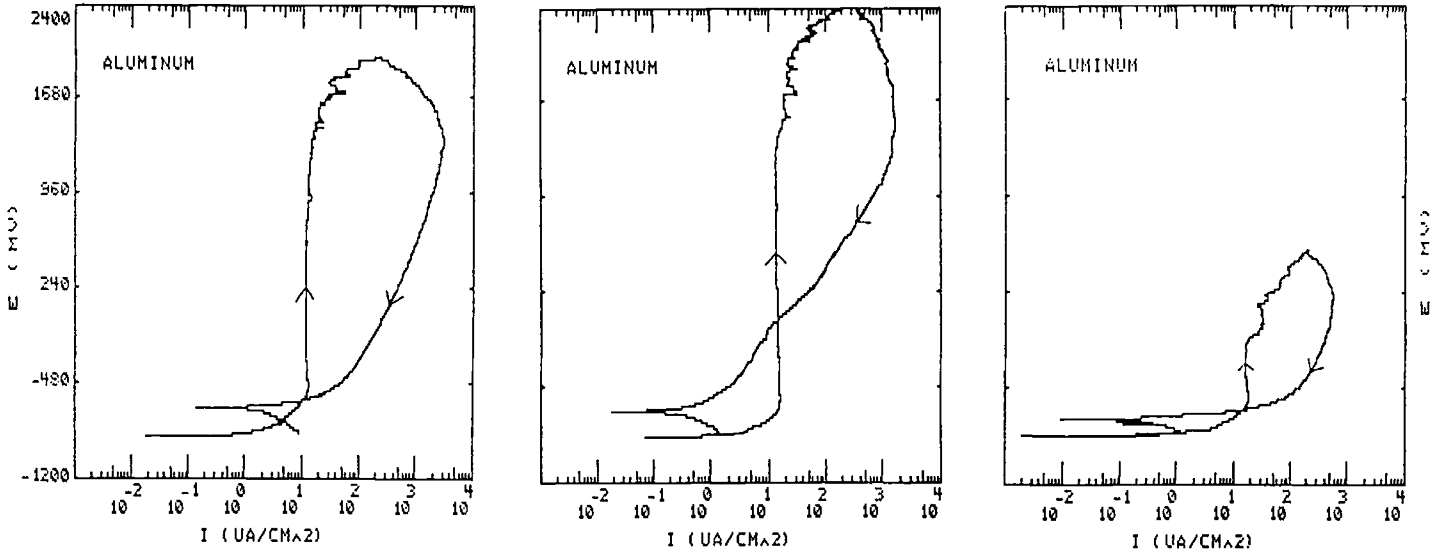


FIG. 1—*Electrochemical corrosion test results on aluminum from left to right: increasing amount of dibasic acid and decreasing amount of monoacid.*

Experimental Procedures

Performance Tests

Evaluating the heat transfer and high-temperature corrosion properties of an engine coolant requires specific testing. Test conditions have to be controlled and recorded for analysis, and repeatability has to be ensured. Two computer controlled test rigs were constructed for this purpose. The performance of the coolant at high temperature was evaluated by weight loss examination of the test specimens, inspection of the test rig components, and analysis of the cooling fluid.

ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants under Heat-Rejecting Conditions (D 4340) covers a laboratory screening procedure for evaluating the effectiveness of engine coolants in preventing corrosion of aluminum castings under static heat-transfer conditions.

The dynamic heat transfer test evaluates corrosion protection at heat-transfer surfaces on metal specimens under dynamic conditions. Similar test rigs have been described in the literature [*11,12*]. The test apparatus (Fig. 2) consists of a circulating rig comprising a pressurized container with a cooling element, a pump, and two corrosion specimens mounted in a high-temperature corrosion chamber with a heating block, inducing a constant heat input into one of the specimens. The test fluid was a 20% volume mixture of the engine coolant in de-ionized water.

The aging test simulates the aging process of a coolant in use by alternately heating and cooling the coolant while circulating it through the pressurized test rig (Fig. 3). Again a 20% volume solution of the engine coolant in de-ionized water is used. Corrosion during the aging cycle was monitored by weight loss of metal specimens, similar to those used in the ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384). The aged coolant was re-used in the dynamic heat transfer test to assess performance of the aged coolant.

Results

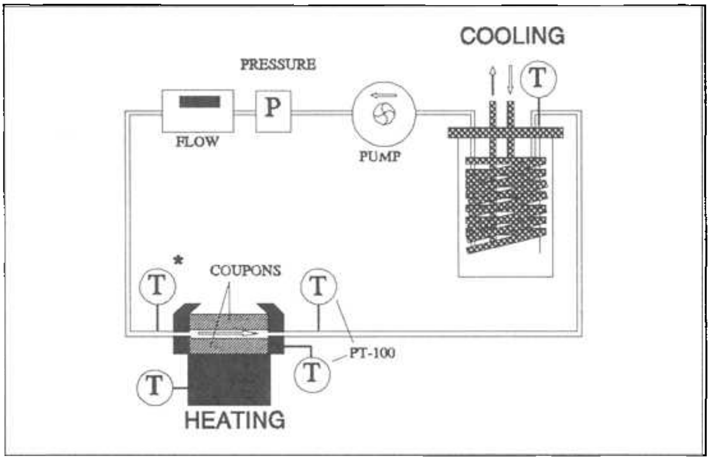
High Temperature Corrosion Tests

Some of the advantages of monoacid-diacid inhibitor combinations versus conventional inhibitor technologies were put forward earlier. The performance testing at high temperature of the different inhibitor technologies included:

- Monoacid-dibasic acid technology (Sample A)
- Nitrite-free formulations (Sample B)
- Conventional benzoate-nitrite-silicate technology: high and low silicate (Samples C and D, respectively)
- Inorganic phosphate technology (Sample E)
- Triethanol amine phosphate technology (Sample F)

All tested formulations are top quality commercial engine coolants available on the European or U.S. market. Table 1 provides a listing of the inhibitors used in these coolants. The test data were developed mainly for ethylene glycol based coolants. Test results for propylene glycol (1,2 propanediol) based coolants are included for the monoacid-diacid formulation only (Sample A_p). The additive packages in Sample A and A_p are identical (Tables 2 and 3).

Two different aluminum alloys were used: SAE 329 (UNS A03190) and alloy 6082 (DIN AlMgSi1). SAE 329 is the cast aluminum alloy used in ASTM D 1384 and D 4340. The microstructure of this material usually shows segregation (dendrites) of silicon-rich phases and some



TEST PARAMETERS

	Aluminum
Controlled	
Nominal heat input	2000 W
Input temperature*	85 °C
Coupon Surface	$25.7\ cm^2$
Pressure	1.5 atm.
Flow	3.5 l/min
Fluid content	1 l
Monitored	
Block temperature	240 °C
Output temperature	92 °C
Temperature of the upper coupon	92 °C
Temperature of the lower coupon	160 °C
Temperature in the cooling vessel	86 °C

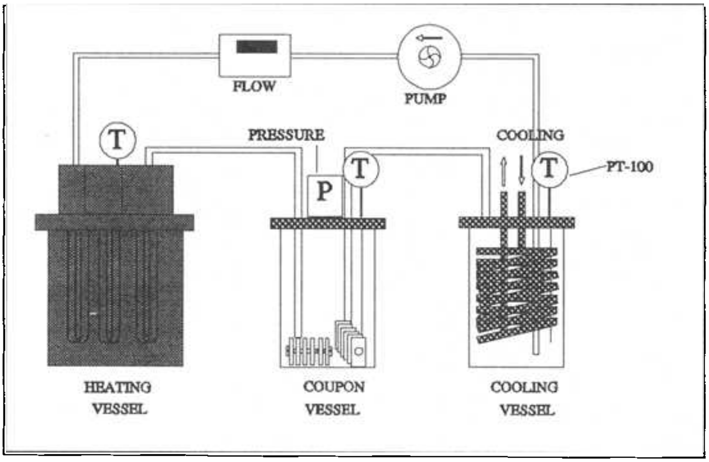
PT-100 is a Resistance Temperature Device

FIG. 2—*Dynamic heat transfer test.*

TABLE 1—*Engine coolant inhibitors.*

Inhibitor	A	B	C	D	E	F
Borax		X	X	X	X	X
Sodium Benzoate		X	X	X		
$NaNO_2$			X	X		
$NaNO_3$		X	X	X	X	
Triazole	X	X	X	X	X	X
$NaSiO_3 \cdot 5aq.$		X	X	X	X	
Phosphoric acid					X	X
Triethanol amine						X
Monoacid	X	X				
Dibasic acid	X					

NOTE: X is presence of inhibitor shown by analysis.



TEST PARAMETERS

Controlled

Temperature in the heating vessel	115 °C
Temperature in the cooling vessel	95 °C
Pressure	2.5 atm.
Flow	3.5 l/min
Fluid content	6 l
Test duration	504 h

Monitored

Nominal heat input	5000 W
Temperature in the coupon vessel	115 °C

FIG. 3—*Aging test.*

cast porosities. The wrought alloy 6082 material has a more uniform microstructure and contains about 1% magnesium.

Results of the ASTM D 4340 tests are reported in Table 2. The tests were run under standard ASTM conditions for a 25% solution of the different engine coolants. Passing results (ASTM Specification for Ethlyene Glycol Base Engine Coolant, for Automobile and Light Duty Ser-

TABLE 2—*The ASTM D 4340 corrosion test.*

	Corrosion Results, mg/cm^2/week						
Test	A	A_p	B	C	D	E	F
SAE 329	0.30	0.32	0.39	0.21	0.07	0.00	0.29
Alloy 6082	0.09	−0.01	6.73	−0.05	−0.06	−0.05	0.76

NOTE: Negative values indicate a weight gain. ASTM D 3306: maximum 1 mg/cm^2/week.

vice [D 3306] for ASTM D 4340: maximum 1 mg/cm^2/week) were obtained for all the tested coolants. This confirmed that the selected coolants are of high quality and representative for their technology group. Good results were also obtained with alloy 6082, in monoacid-diacid and in the conventional silicate and phosphate coolants.

Different corrosion rates for the tested coolants were found in the dynamic heat transfer test for SAE 329 test specimens (Table 3). Low silicate conventional coolants and the phosphate coolants showed high corrosion rates, even after a test duration of only 48 h. The high silicate conventional coolant performed well, but high corrosion rates were found when the test duration was extended to 69 h. The monoacid-diacid coolant (Sample A) showed consistently low corrosion, even when the test duration was extended to 116 h and aged test solutions were used. Corrosion during "aging" for 504 h (not shown in Table 3) ranged from 69 mg/coupon for Coolant A to 384 mg/coupon for Coolant C (SAE 329 corrosion coupons).

Heat-Transfer Properties

Coupon temperatures were monitored during the dynamic heat transfer tests. A constant heat input was maintained (2000 W). Figure 4*a* shows the mid-section temperature rise of the heated aluminum coupon (SAE 329) as recorded for the best performing conventional coolant, Sample C (high silicate), and the monoacid-dibasic acid coolant, Sample A. This temperature pattern can be related to the heat transfer through the protection/corrosion layer at the metal/liquid interface.

The coupon/protective layer system can be considered as serial steady-state heat conductors. The heat flux through each layer is the same and equal to the power received by the flowing coolant solution (the heat flux actually induced will be slightly higher as there is some loss of power by radiation). The power received by the fluid can be calculated as:

$$P = d_m c \Delta T$$

where

P = received power,
d_m = mass flow,
c = heat capacity of the fluid, and
ΔT = temperature difference of the fluid before and after heating.

TABLE 3—*Dynamic heat transfer test.*

	Corrosion Results, mg/coupon						
Test Duration, h	A	A_p	B	C	D	E	F
			SAE 329				
48	10.7	4.2	512	−18.0	...	607	...
69	26.0	10.3	...	261	1260	1243	1510
116	21.6	46.5	...	...	...	...	...
aged 48	...	...	...	255	...	...	...
aged 116	48.4	...	...	...	...	...	...
			ALLOY 6082				
48	...	...	...	2130	...	1600	...
116	23.0	8.7	...	...	...	...	...
aged 116	34.1	...	...	...	...	...	...

NOTE: Negative values indicate a weight gain.

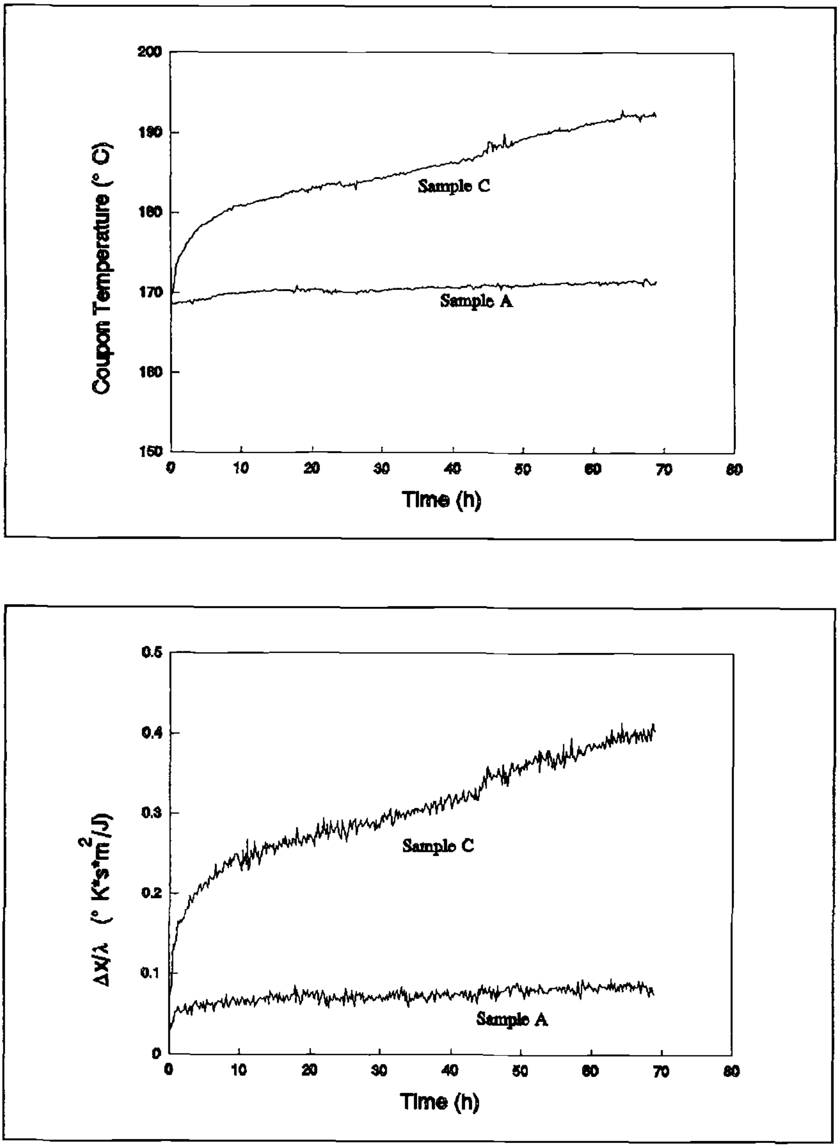


FIG. 4—(a) *Coupon temperature versus test duration and* (b) *heat transfer characteristics* ($\Delta x/\lambda$) *versus test duration.*

Actual values for the power received by the fluid based on the monitored temperature differentials are approximately 1850 W for a controlled total input power of 2000 W.

The heat flux Φ is given by

$$\Phi = Sq$$

where S is the surface through which heat is transferred and q is the heat-current density. The heat-current density can be calculated using Fourier's law [*13*]

$$q = -\lambda \frac{\Delta T}{\Delta x}$$

where

λ = heat transfer coefficient,
ΔT = temperature drop through the metal, and
Δx = metal thickness.

Knowing the heat transfer coefficient for SAE 329 [*14*]

$$\lambda = 1.09\ 10^{-2} Jm^{-1}K^{-1}s^{-1}$$

and the temperature at a point x_T, we can calculate the temperature profile through the aluminum coupon and deduce the temperature of the protective layer at the interface with the aluminum surface.

When we assume the temperature of the layer surface at the interface with the fluid to be at the boiling temperature of the coolant solution (123°C for a 20% mixture of ethylene glycol in water), we can calculate the temperature drop over the protective layer. This temperature difference is a direct measure for the ratio of thickness of the layer over the heat transfer coefficient (Fig. 4*b*).

Microscopic Examination

Figure 5 shows micrographs (dark field illumination) of surface layers formed on the heat-transfer surfaces of the heated SAE 329 coupons after dynamic heat transfer tests in the high silicate conventional coolant (Sample C, Fig. 5a) and the monoacid-diacid coolant (Sample A, Fig. 5b), respectively. The conventional coolant (Sample C) produces a uniform surface or reaction layer on the coupon surface while the aliphatic acids form a structured film covering only certain areas that might be associated with segregation phases (silicon-rich dendrites) or material defects (cast porosity, inclusions) on the metal surface while the remaining surfaces are apparently uncovered.

Analyses of Protective Film

The University of Antwerp (Universitaire Instellingen Antwerpen) was contacted to analyze the film formed on the heat-transfer surfaces in coolant *A*. FTIR studies of the coupon surfaces indicated the presence of organic matter, while X-ray fluorescence analyses of scrapings indicated the presence of silicon and aluminum. Although this work is not decisive in identifying the film composition, it indicates that an interaction between the organic acids and the metal surface occurs, as suggested by Darden et al. [*9*]. Further work, which includes scanning electron microscopy (SEM) and FTIR mapping of the coupon surface, is ongoing.

Discussion

High-Temperature Corrosion Protection

Different inhibitor technologies have been evaluated. Phosphate and conventional silicate coolants provide good protection of aluminum heat-transfer surfaces under the conditions of the ASTM D 4340 static heat-transfer test. No significantly different weight losses are observed. The corrosion rates are well within the specification limits.

The dynamic heat transfer test clearly distinguishes between the different inhibitor tech-

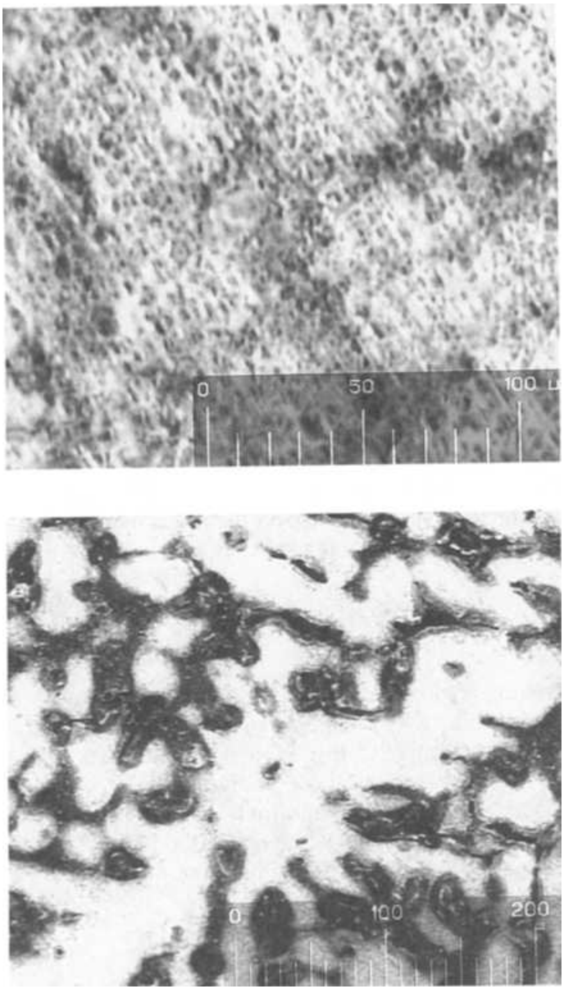


FIG. 5—*Protective layer on the aluminum surface from Sample C (top) and Sample A (bottom).*

nologies. High corrosion rates are found for the phosphate containing coolants under tests conditions of high fluid flow and heat flux. The low silicate conventional and nitrite-free coolants provide better protection, but corrosion rates are still high. High silicate coolants will provide protection in the short duration heat transfer test (48 h). Silicate coolants and particularly high silicate coolants generally perform well in short duration tests [*11,12*]. Silicate adsorbed on the metal surfaces and retained in cast porosities will protect the metal surface and contribute to some weight gain. However, silicate depletion eventually results in high corrosion rates when test duration is extended, or when aged coolant is used. High corrosion rates are also found with the low silicate containing alloy 6082.

The synergistic [*9,15*] combination of aliphatic monoacid and diacid salts provides lasting protection even when test duration is extended. Under heat-transfer conditions a thin organic containing film or reaction layer is apparently formed on selective areas of cast microstructure. Chemical cleaning after the test, according to the FVV cleaning procedures [*12*], generally does not remove this protective layer. After the 48-h tests, a weight loss is observed for the different aluminum coupons. Extending the test period does not significantly increase the measured weight losses. This becomes even more manifest when alloy 6082 is used.

Tentative protection mechanisms for aluminum provided by the aliphatic acids have been given by Darden et al. [9]. In case of film formation, the inhibitor anion would complex with the metal while it is still bound to its solid lattice. No bulk layer is formed, rather a layer of microscopic thickness is formed at the anodic sites of the metal surface. This is confirmed by our current microscopic and analytical work.

Heat-Transfer

The heat transfer characteristics of the silicate film and aliphatic acid film differ widely. The difference in temperature drop over the protective layers can be explained on the basis of the postulated protection mechanisms. If we assume that the film heat-transfer coefficient λ is a constant factor over the temperature interval, the shape of the film thickness over heat transfer coefficient ($\Delta x/\lambda$) curve (Fig. 4*b*) provides an indication of protective film buildup and decay.

The silicate film (Sample C) grows fast initially. After 10 to 15 h, the growth rate stabilizes. The effect of inhibitor depletion, marked by increasing corrosion rates between 48 and 69 h of test duration, is not evident from Fig. 4*b*. This is not unusual, as corrosion products will gradually substitute the decaying silicate film. As such, the heat-transfer properties of the "protective" film are those of the combined silicate/corrosion layer gradually shifting to those of a corroded metal surface.

For the monoacid-dibasic acid coolant (Sample A), Fig. 4*b* shows only a small initial growth of a protective layer, after which the heat-transfer properties related to $\Delta x/\lambda$ remain practically constant. The excellent heat-transfer characteristics can also be explained by the selective way the film is formed on anodic areas in the microstructure (Fig. 5*b*), leaving sufficient blank areas for good heat transfer. On wrought materials, such as alloy 6082, a more uniform but lighter film was formed as the microstructure of the metal is more homogeneous.

Further work, which should provide more insight in the actual protection mechanisms, is planned.

Conclusion

Synergistic inhibitor combinations of monoacid and diacid salts have been shown to provide good corrosion protection at high-temperature heat-transfer surfaces. Improved heat-transfer properties are found compared to conventional coolants. These inhibitor formulations also provide good corrosion protection against localized forms of corrosion, such as pitting and crevice corrosion.

The inhibitors are virtually depletion-free and can be used in less-toxic propylene glycol coolants. As development work is continuing, further advantages of this technology come to light making it an ideal candidate for use in future world-wide, long-life engine coolants.

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DISCUSSION

William P. Weeks[1] *(written discussion)*—In a 1990 SAE paper, Fleetguard, Inc. showed lower aluminum weight loss for propylene glycol compared to ethylene glycol using an identical, conventional, inhibition package. Scanning your data on this new inhibition technology, I see the same trend. Can you comment or speculate on why?

J.-P. Maes and P. Van de Ven (authors' response)—Based on these results, the results you quote, and similar findings it appears that it is the corrosiveness of propylene glycol, or better the glycol/water mixture, compared to monoethylene glycol that plays a role. Differences in physico-chemical characteristics are the most likely cause of the observed phenomena.

So far, no thorough investigation to determine the cause of these differences has been performed. So any answer from the author is mere speculation. The cause could be the difference in dissolved oxygen; propylene glycol has a lower oxygen solubility than monoethylene glycol. The oxygen reduction reaction is the common cathodic reaction for corrosion processes. Reducing the oxygen amount in the solvent with a similar diffusion rate would probably reduce the corrosion rate.

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[1] Arco Chemical Co., 3801 West Chester Pike, Newton Square, PA 19093.

John Arnold[2] *(written discussion)*—The cyclic polarization test used to optimize monoacid/diacid ratios were run at room temperature. Since passivation potentials change with temperature and since corrosion is minimal at room temperature, are your coolants optimized for room-temperature operation, instead of the corrosive thermal region where engines operate?

J.-P. Maes and P. Van de Ven (authors' response)—We have run tests both at room temperature and high temperature (88 °C). Although the actual values of the different parameters did change with temperature, the overall conclusions on the corrosion protection for the different metals did not. Therefore running the test at higher temperature does not significantly influence the optimizing process.

Performance-test results, obtained at conditions that exist in actual engines, further prove the efficiency of these optimized formulations. The dynamic heat transfer test discussed in the paper is just one example of a high-temperature performance test.

John Arnold[2] *(written discussion)*—You stated that carboxylic acids protect aluminum by bonding to the silicon rich dendrites. The support for this conclusion was observation of carbon on the dendrites by SEM/EDAX and the observation of some organic on the surface by FTIR. Please explain how the carbon at the dendrites was determined to be due to carboxylic acids and not due to the carbon normally present at dendrites in heat tempered aluminum alloys? Also, explain how the organic observed by FTIR was determined to be carboxylic acid and not residual glycol.

J.-P. Maes and P. Van de Ven (authors' response)—The proposed mechanism is only tentative, as is stated in the paper. However when looking at the combination of all the results, the proposed mechanism becomes more than just speculation:

- Microscopic examination: dendrite structure coinciding with discolored areas.
- SEM microprobe analysis: dendrite structure coinciding with silicon rich phases. Carbon was not determined.
- FTIR analysis: Organic material in conjunction with the discolored areas.

In a blank test the coupon showed no FTIR signal nor did microscopic examination indicate any discolored areas. Although none of this is conclusive, it would be rather shortsighted to just discard them. The authors do agree however that further investigation is necessary to give a definite answer.

Peter Woyciesjes[2] *(written discussion)*—It was suggested in your presentation that current North American coolants can have a larger effect on heat transfer properties of aluminum in the dynamic heat transfer test as compared to Coolant A. Can the results of this test be related to vehicle performance since there are no heat transfer problems observed in the field with these coolants? Has it been demonstrated that this small change in heat transfer properties has any effect on vehicle performance?

J.-P. Maes and P. Van de Ven (authors' response)—No field test data are yet available, however, the dynamic heat transfer test simulates the heat transfer conditions of the hottest areas in an engine. We must also stress the fact that an effective heat transfer fluid is one of the most important requirements of an engine coolant. The trend toward smaller, more efficient engines that operate at higher temperatures cannot be denied. Our research aims at the development of coolants for this next generation of engines that will definitely operate under more stringent heat exchange conditions.

William Mercer[2] *(written discussion)*—You have stated that deionized water and not corrosive water is used in many of your tests. Is deionized water also used in your electrochemical

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[2] First Brands Corporation, Danbury, CT 06810.

tests? If so, please explain why pitting would be expected to occur in the absence of chloride ions.

J.-P. Maes and P. Van de Ven (authors' response)—The electrochemical test used for this work involved the dilution of the engine coolant with corrosive hard water of the following composition (per litre deionized water):

148 mg Na_2SO_4
165 mg $NaCl$
138 mg $NaHCO_3$
275 mg $CaCl_2$

William Mercer[2] *(written discussion)*—Can you comment on the use of Rapid Cyclic Polarization scans to measure corrosion since they are more properly used to measure capacitative changes of surface layers?

J.-P. Maes and P. Van de Ven (authors' response)—The cyclic potentiokinetic polarization technique has previously been described to determine the susceptibility of various metals and materials to localized corrosion in various environments. The pitting potentials and repassivation potentials, thus determined, can be directly related to the pitting tendency of the material in the particular environment. Correlation between measurements and the occurrence of crevice corrosion has been established. References 1 to 7 elaborate on the experimental technique and the interpretation of the experimental data.

William Mercer[2] *(written discussion)*—Can you explain in more detail how synergism between the monoacid and the diacid is shown by electrochemical techniques?

J.-P. Maes and P. Van de Ven (authors' response)—The synergism between the monoacid and diacid was not the subject of this paper. It has been established before and has been extensively discussed in Refs *9* and *15*. This synergism involves an improved protection against localized corrosion phenomena as indicated by changes in pitting potentials and repassivation potentials.

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Jeffrey M. Burns[1]

Fleet Test Correlations of Original Equipment Coolant Pump Failures and Engine Coolant Formulations

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REFERENCE: Burns, J. M., **"Fleet Test Correlations of Original Equipment Coolant Pump Failures and Engine Coolant Formulations,"** *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 25–43.

ABSTRACT: Automobile coolant pump failures can be minimized by choosing an engine coolant formulation that has a relatively insignificant effect on the seal as well as the other materials used in the construction of the pumps. A fleet test involving 203 1990 Ford Crown Victoria taxi cabs provided data demonstrating that the number of pump failures experienced by the group of taxis employing a unique experimental coolant free of most traditional corrosion inhibitors was much lower than the number experienced by any of the other four test groups employing different, more traditional, formulation variations.

Sixty to eighty-five percent of the original equipment coolant pumps on the four groups of vehicles employing the more traditional coolant formulations had to be replaced during the test period, which nominally covered the vehicles' first 160 000 km. Only 15% of the original coolant pumps installed on the experimental coolant test group required replacement.

KEYWORDS: coolant pump, engine coolant formulation, fleet test, corrosion inhibitor, silicate, carboxylic acid, long-life coolant, heavy-duty coolant, universal coolant, notched box and whisker plot

Global competition and increasing environmental awareness are creating markets for products that reduce consumer maintenance and impact the environment more favorably. One method of achieving both goals is to produce products with a longer service life. This can not be done unless there is no adverse effect on the durability of the system components with which the product interacts.

Recent fleet testing has yielded data comparing the compatibility of several different coolant formulations with coolant pump component materials. A short-term, high-mileage taxi test, employing four different engine coolant formulations, revealed differences between traditional, current, and potential future inhibitor technologies with respect to coolant pump life expectancy and replacement rate.

New technology for corrosion inhibitors has yielded engine coolant formulations that are potentially life-time fill due to the slow depletion rate of the inhibitors in service [*1*]. The data derived from this fleet testing indicate that there is also improved compatibility with the coolant pump. This technology is a step toward the goal of a maintenance-free system for automotive service, which will also reduce the environmental impact by generating less waste.

[1] Senior engineer, Texaco Chemical Company, Austin Research Laboratories, 7114 N. Lamar Blvd., Austin, TX 78752

Background

A fleet test, involving four groups of 20 1990 Ford Crown Victoria taxis, was established in the fall of 1989 to develop inhibitor depletion data, corrosion rates from coupon bundle results, and general applicability information for four different coolant formulations. These cars were equipped with the Ford 5.0 liter V8, which has a cast iron block and combustion chamber heads. The cooling systems employed brass heavy-duty radiators with the exception of a group of 24 cars, which had experimental aluminum radiators installed as part of a component evaluation program. The vehicle identification numbers in the test groups were not sequential and were randomly distributed throughout the fleet.

The taxi company also operates 123 new vehicles and 12 older model standby vehicles that were not included in the coolant test or sample evaluation program. These vehicles retained the factory-fill coolant and were monitored as a representative population. The data from these cars are presented for comparison as being representative of the situation experienced in the field. After several months, a high number of coolant pump replacements were required throughout the entire fleet.

This fleet is an ideal test to track part failure data because the city of New York requires that every taxi must be inspected once a quarter, and the fleet maintenance supervisor maintains excellent maintenance records. The initial signs of component failure are noted early.

The fleet has long-time experience with lubricant evaluation, and recently added engine coolant to their evaluation program. The maintenance personnel have demonstrated exceptional ability to follow proper procedures and to generate extremely reliable data.

The cabs were filled with five different coolant formulations which included the factory-fill coolant and a commercial, traditional, high silicate, American formulation, commercial European and American universal formulations, and an experimental long-life coolant based on patented inhibitor technology [*2*]. The commercial formulations were all obtained through commercial outlets while the experimental coolant was blended at the Texaco Chemical Company's Austin, TX, research laboratories.

Because of the logistics of fleet testing, each coolant used was a different color except for the factory-fill coolant, which was also green. This was the commercial circumstance at the time the fleet test was initiated. The colors will be used to identify the individual products while the factory-fill coolant will be identified as FF.

Yellow and Factory-Fill (FF)

The high-silicate formulation tested is the single most popular formulation sold in the United States. It will be identified as the yellow test coolant. It includes both phosphate and borax as the buffer system and contains nitrate. The factory-fill coolant was very similar. It will be identified as the factory-fill (FF) test coolant. These coolants are representative of the traditional technology intended for automotive service where aluminum protection is required and are the types of coolants employed as factory-fill for light-duty engines by all three major American manufacturers.

These coolants meet the ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light Duty Service (D 3306) and most of the automobile original equipment manufacturers' (OEMs) specifications [*3*]. The factory-fill systems were topped-off with a common aftermarket formulation corresponding to the General Motors GM6038-M formulation [*4*].

Purple and Green

The universal formulations meet the corrosion inhibition performance specifications for both light- and heavy-duty cooling systems and provide adequate aluminum protection while meeting the low silicate definition, having 0.1 wt% sodium metasilicate (250 ppm as silicon) or less as specified in the ASTM D 4985. The low-silicate level is the common factor that characterizes all of the common so-called universal formulations. The European universal coolant is a borax buffered formulation incorporating some carboxylic acid technology. This coolant will be identified as the purple fluid. The American universal product is a phosphate buffered formulation. It will be identified as the green test coolant.

Blue

The long-life coolant tested incorporates a combination of monobasic and dibasic carboxylic acids to produce a product with a longer service life due to slow inhibitor depletion rate [*1*]. This product will be identified as the blue test coolant. It contains no silicate, borax, phosphate, amines, nitrite, or nitrate. Like all of the coolant formulations, it contained tolyltriazole. The constituents in each of these six formulations are detailed in Table 1.

Test Procedure

The test coolants were installed in the taxi cooling systems as soon as practical for the fleet after the new automobiles arrived at the fleet garage. The cooling system was drained, flushed with tap water, and filled with the test coolant prediluted to 50% with deionized water. Startup mileage in the test vehicle groups ranged from 0 km on all of the factory-fill vehicles to an average of over 9750 km for the purple coolant test group.

Stop-leak additive, typically carboxymethyl cellulose, is added to the automotive cooling system at the factory to plug minor gasket leaks. It is possible, but not likely, that most of this additive was flushed out when the cooling systems were drained during the conversion of the four test groups to the test coolants. However, it was retained in the factory-fill coolant cooling systems that remained intact throughout the test period. No stop-leak additive was added to the coolant test group vehicle systems when they were charged with the test coolants.

TABLE 1—*Engine coolant inhibitor comparison for the test coolant formulations, the factory-fill coolant, and the top-off coolant for the factory-fill systems.*

Inhibitor	FF	Yellow	Green	Purple	Blue	GM6038-M
Borax	yes	yes	no	yes	no	yes
Phosphate	yes	yes	yes	no	no	yes
Nitrate	yes	yes	yes	yes	no	yes
Nitrite	no	no	no	no	no	no
Silicate Level (Low = <250 ppm High = >250 ppm)	high	high	low	low	none	low
Tolytriazole	yes	yes	yes	yes	yes	yes
Carboxylic acids	no	no	no	yes	yes	no
Amines	no	no	no	no	no	no
Silicate stabilizer	yes	yes	yes	yes	no	yes
Antifoamant	yes	yes	yes	yes	yes	yes
Initial pH	>10	>10	>10	<9	<9	>10

The vehicles were maintained according to standard operating procedure by the taxi company. The overflow bottles were topped-off, with the appropriate coolant prediluted 50% with deionized water, by the maintenance personnel. The concentration was monitored by measuring the freezing point with a hand held refractometer and adjusted, if necessary, to −37°C by adding either deionized water or coolant concentrate, which was the standard procedure in this fleet.

The factory-fill cars were topped-off with a coolant corresponding to the GM6038-M [*4*] formulation specification as was their practice before initiating this fleet test. Although the GM6038-M is not approved for the service fill for these systems, it is inexpensive, and is commonly used by this type of fleet. It was the coolant purchased for topping-off by this fleet before the inception of this test. GM6038-M is a low-silicate, phosphate, borax, heavy-duty coolant that meets ASTM D 4985, but does not meet ASTM D 3306 because of poor performance in ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions (D 4340) [*3*].

Coolant samples were taken at every oil change, which were at approximately 3000- to 5000-mile (4828- to 8047-km) intervals. One hundred millilitres of sample was captured each time. Full chemical analysis of the majority of the samples, with respect to inhibitor and contaminant concentration, was undertaken to generate inhibitor depletion rate data and monitor the quality of the cooling system in each vehicle.

The results of the analysis also served as an indication of the care being taken in maintaining the cabs.

The taxis are subject to a quarterly inspection by the city of New York Limousine and Taxi Commission. Among other things, each car is inspected for fluid leaks. Any fluid dripping from the bottom of the engine compartment constitutes a failure. The cab company conducts a thorough preinspection to reduce potential of the cabs not passing the city inspection. Components that would jeopardize the audit are repaired or replaced. If the coolant pump is leaking from the weep hole, it is subjected to pressure and dynamic testing. It is replaced if the leak is steady and noticeable.

Results

Coolant pump replacements throughout the test fleet provided the results that are the basis for this paper. Three of the test coolants, the yellow, purple, and green coolants, produced roughly the same results. Seventy-five to eighty-five percent of the original equipment coolant pumps on the 60 cabs filled with these three test coolants were replaced during the test period due to leakage. The factory-fill control group experienced a 60% failure rate. The blue coolant test group, however, required only 15% of the pumps to be replaced.

The pumps that did not fail either survived until the end of the test or were removed with the engine during an overhaul procedure that was part of lubricant testing that this fleet is also used for. The number of pumps that survived to the end of the test or were removed with the engines that were overhauled reveals as much about the effect of the coolants on the pump as the failures do.

Nine of the original equipment pumps (45%) installed on the blue coolant test cars were retired on the cabs at the end of test. Twenty-two of the original pumps (18%) on the factory-fill cabs reached the end of test. Three of the purple coolant cabs' original pumps (15%) survived. There were two surviving pumps (10%) among the green coolant test group. None of the original pumps (0%) survived the testing with the yellow coolant.

The pumps that were removed at overhaul were on engines involved in a lubricant evaluation program. The engines were removed for wear and deposit measurement. The coolant pumps were replaced with new, original equipment, pumps during the rebuilding process. The engines that were chosen for removal were picked because of the oil formulation tested, for reasons completely unrelated to the coolant test. It was not possible to predict which engines would be chosen for inspection because the lubricant formulations being tested were randomly distributed throughout the fleet.

An average of 9 (45%) engines were removed from each test of the four coolant test groups while 50 (41%) of the 123 engines in the factory-fill test group were removed. The only engine overhauls that matter to the data presented here are those on which original equipment pumps were still operational. Test groups with a large number of early failures had few pumps that survived to the point at which the engine was removed from service whereas test groups that provided longer service life for the pump lost more of the original equipment pumps at this point.

The number of original pumps removed with these engines was dependent on the number of early life pump failures. The blue coolant that had few failures had 8 of the original pumps removed at overhaul (40%). The other 4, more traditional coolant formulation test groups had a smaller percentage that did not complete the test for this reason. The yellow coolant had 3 pumps (15%) removed in this manner. The purple coolant lost 2 pumps (10%) to this process. Only 1 of the original pumps (5%) was removed from the green coolant test group because of the lubricant testing. Because the number of factory-fill coolant vehicles was greater, 27 of the original pumps were removed for the engine inspection process, but the overall percentage (22%) was not significantly different than that of the other three traditional formulations. Table 2 details number and percentage of the original pumps that failed, were removed with engines intended for overhaul, or survived the test period.

Removal of engines for this overhaul and inspection process reduced the failure data that was available by removing pumps from the test before they had a chance to fail. Most of the engines were removed between 96 500 and 112 500 km. This event could not be avoided because lubricant testing is this fleet's primary function.

Tables 3 through 7 list the original pump failures in each of the test groups, the pumps that survived, and the pumps that were removed at the engine overhaul. The final disposition of each original pump can be obtained here.

The number of repeat failures in each group was also quite different. With the blue and green coolant groups none of the new pumps that replaced the failed original equipment failed again. The purple coolant group had 3 repeat failures. The factory-fill cars had 11 repeat failures out of the 74 cars that had their original pumps replaced, while the yellow coolant cars had 8 repeat

TABLE 2—*Original equipment water pump disposition for the 5 coolant test groups.*

Coolant Formulation, Total Number of Pumps	Original Pumps that Failed During Test, % of Total	Original Pumps Removed at Overhaul,[a] % of Total, Total Number of Engines Removed for Overhaul from Group	Original Pumps that Survived Cab Life, % of Total
FF, 123	74, 60%	27, 22%, 50	22, 18%
Yellow, 20	17, 85%	3, 15%, 9	0, 0%
Green, 20	17, 80%	1, 5%, 8	2, 10%
Purple, 20	15, 75%	2, 10%, 10	3, 15%
Blue, 20	3, 15%	8, 40%, 9	9, 45%

[a] The number of original equipment pumps removed at overhaul depended entirely on the number of original equipment pumps still operating at that mileage. The test groups with earlier failures lost fewer pumps for this reason. Each test group had approximately the same number of engines remover for overhaul at approximately the same mileages.

TABLE 3—*Factory-fill coolant test group original equipment coolant pump final disposition information.*

Car Number	Actual Mileage, km	Test Mileage, km	Coolant Used	Mileage at Fill, km	Date at Failure
FACTORY-FILL CABS THAT HAD FAILURES OF THE ORIGINAL COOLANT PUMP DURING TEST PERIOD					
766	20 246	20 246	FF	0	10 March 90
744	36 638	36 638	FF	0	25 April 90
761	40 607	40 607	FF	0	25 April 90
757	43 589	43 589	FF	0	29 April 90
743	47 431	47 431	FF	0	16 May 90
706	50 366	50 366	FF	0	22 May 90
889	52 833	52 833	FF	0	28 April 90
756	54 648	54 648	FF	0	16 June 90
800	56 303	56 303	FF	0	08 July 90
714	56 910	56 910	FF	0	21 May 90
801	57 870	57 870	FF	0	15 July 90
707	58 484	58 484	FF	0	27 May 90
948	60 025	60 025	FF	0	25 May 90
910	60 288	60 288	FF	0	26 May 90
758	61 168	61 168	FF	0	11 July 90
764	62 179	62 179	FF	0	18 July 90
767	62 433	62 433	FF	0	05 July 90
797	62 486	62 486	FF	0	03 Aug. 90
900	63 093	63 093	FF	0	08 July 90
763	64 010	64 010	FF	0	07 July 90
941	64 290	64 290	FF	0	04 May 90
932	64 617	64 617	FF	0	04 May 90
723	65 272	65 272	FF	0	02 July 90
746	65 748	65 748	FF	0	03 July 90
795	66 427	66 427	FF	0	19 July 90
936	68 415	68 415	FF	0	22 July 90
894	68 674	68 674	FF	0	03 July 90
739	70 330	70 330	FF	0	14 July 90
796	70 517	70 517	FF	0	21 Aug. 90
919	70 608	70 608	FF	0	22 July 90
909	70 758	70 758	FF	0	14 July 90
768	71 065	71 065	FF	0	06 Aug. 90
754	71 186	71 186	FF	0	31 July 90
742	72 150	72 150	FF	0	09 July 90
741	72 429	72 429	FF	0	15 July 90
748	74 255	74 255	FF	0	27 July 90
762	74 513	74 513	FF	0	30 Aug. 90
805	75 061	75 062	FF	0	07 Sept. 90
898	75 171	75 171	FF	0	06 Nov. 90
802	76 416	76 416	FF	0	03 Sept. 90
794	77 091	77 091	FF	0	30 Aug. 90
916	77 165	77 165	FF	0	06 Aug. 90
755	77 857	77 857	FF	0	25 Aug. 90
905	77 870	77 870	FF	0	27 Aug. 90
899	78 489	78 489	FF	0	16 Oct. 90
753	78 557	78 557	FF	0	18 Aug. 90
938	78 909	78 909	FF	0	22 June 90
912	79 717	79 717	FF	0	16 Nov. 90
738	80 498	80 498	FF	0	16 Aug. 90
897	81 727	81 727	FF	0	02 Sept. 90
765	86 953	86 953	FF	0	03 Oct. 90
720	87 616	20 418	FF/green	67 198	08 Sept. 90
737	90 249	90 249	FF	0	14 Nov. 90

TABLE 3—*Continued.*

Car Number	Actual Mileage, km	Test Mileage, km	Coolant Used	Mileage at Fill, km	Date at Failure
FACTORY-FILL CABS THAT HAD FAILURES OF THE ORIGINAL COOLANT PUMP DURING TEST PERIOD					
915	90 778	90 778	FF	0	20 Sept. 90
745	91 781	91 781	FF	0	29 Sept. 90
914	93 511	93 511	FF	0	05 Aug. 90
747	96 108	96 108	FF	0	30 Sept. 90
901	96 232	96 232	FF	0	08 Nov. 90
906	98 550	98 550	FF	0	05 Sept. 90
749	98 585	98 585	FF	0	02 Sept. 90
917	101 175	101 175	FF	0	18 Oct. 90
946	102 327	102 327	FF	0	25 Sept. 90
799	102 382	102 382	FF	0	07 Nov. 90
911	103 177	103 177	FF	0	18 Nov. 90
769	103 817	103 817	FF	0	29 Oct. 90
939	103 894	103 894	FF	0	24 Sept. 90
760	109 207	109 207	FF	0	20 Nov. 90
903	113 859	113 859	FF	0	26 Aug. 90
933	119 500	119 500	FF	0	24 Sept. 90
895	125 695	125 695	FF	0	18 Sept. 90
943	133 793	133 793	FF	0	09 Jan. 91
803	139 945	139 945	FF	0	14 Feb. 91
719	152 831	80 813	FF/green	72 018	17 Feb. 91
710	170 608	95 083	FF/green	75 525	06 March 91
Average	77 174	76 241		933	...
FACTORY-FILL CABS THAT HAD ORIGINAL PUMPS THAT SURVIVED TEST DURATION					
940	79 226	79 226	FF	0	27 Feb. 91
907	106 131	106 131	FF	0	01 April 91
751	111 650	111 650	FF	0	24 March 91
949	117 799	117 799	FF	0	26 March 91
703	128 421	128 421	FF/blue	0/54 492	25 Feb. 91
750	131 944	131 944	FF	0	24 March 91
893	132 269	132 269	FF	0	27 Feb. 91
704	135 100	135 100	FF/blue	0/54 713	25 Feb. 91
942	138 965	138 965	FF	0	06 Feb. 91
711	141 251	141 251	FF/green	0/71 939	05 March 91
944	141 854	141 854	FF	0	06 Feb. 91
937	143 597	143 597	FF	0	05 Feb. 91
721	146 413	146 413	FF/green	0/70 443	12 March 91
717	146 611	146 611	FF/green	0/66 300	11 March 91
701	149 601	149 601	FF/blue	0/68 784	25 Feb. 91
798	149 748	149 748	FF	0	15 April 91
715	154 231	154 231	FF/green	0/65 874	11 March 91
712	155 569	155 569	FF/green	0/71 646	06 March 91
913	155 801	155 801	FF	0	14 Feb. 91
708	168 436	168 436	FF/blue	0/75 810	27 Feb. 91
888	176 411	176 411	FF	0	08 Feb. 91
934	194 814	194 814	FF	0	21 Feb. 91
Average	141 175	...	...	...	...
FACTORY-FILL CABS THAT HAD THE ORIGINAL PUMP REMOVED WITH THE ENGINE AT OVERHAUL					
702	105 404	105 404	FF/blue	0/64 090	24 Oct. 90
705	108 687	108 687	FF/blue	0/54 480	04 Dec. 90
709	97 214	97 214	FF/green	0/67 100	01 Oct. 90
713	96 625	96 625	FF/green	0/76 468	31 Aug. 90
716	105 443	105 443	FF/green	0/69 023	03 Nov. 90
718	96 553	96 553	FF/green	0/72 960	12 Sept. 90
722	102 480	102 480	FF/green	0/67 240	17 Oct. 90

TABLE 3—*Continued.*

Car Number	Actual Mileage, km	Test Mileage, km	Coolant Used	Mileage at Fill, km	Date at Failure
FACTORY-FILL CABS THAT HAD THE ORIGINAL PUMP REMOVED WITH THE ENGINE AT OVERHAUL					
724	108 092	108 092	FF/green	0/64828	07 Nov. 90
725	97 510	97 510	FF	0	27 Sept. 90
726	101 178	101 178	FF	0	26 Sept. 90
740	98 690	98 690	FF	0	28 Sept. 90
752	108 088	108 088	FF	0	05 Nov. 90
759	112 240	112 240	FF	0	09 Nov. 90
804	123 491	123 491	FF	0	04 Feb. 91
806	107 767	107 767	FF	0	03 Dec. 90
807	103 622	103 622	FF	0	26 Dec. 90
890	96 577	96 577	FF	0	14 Sept. 90
891	99 268	99 268	FF	0	03 Aug. 90
892	96 960	96 960	FF	0	13 Aug. 90
896	96 487	96 487	FF	0	20 Aug. 90
902	101 704	101 704	FF	0	15 Nov. 90
904	99 868	99 868	FF	0	05 Oct. 90
908	96 789	96 789	FF	0	04 Sept. 90
918	97 074	97 074	FF	0	17 Sept. 90
935	101 983	101 983	FF	0	01 Aug. 90
945	98 434	98 434	FF	0	30 July 90
947	98 823	98 823	FF	0	31 July 90
Average	102 113	...	...	...	...

TABLE 4—*Yellow coolant test group original equipment coolant pump final disposition information.*

Car Number	Actual Mileage, km	Test Mileage, km	Coolant Used	Mileage at Fill, km	Date at Failure
YELLOW COOLANT CABS THAT HAD ORIGINAL COOLANT PUMP FAILURES DURING THE TEST PERIOD					
885	25 365	25 365	yellow	0	19 May 90
879	43 530	43 530	yellow	0	27 June 90
886	49 378	49 378	yellow	0	25 July 90
874	52 159	52 159	yellow	0	05 Aug. 90
869	55 350	55 350	yellow	0	02 Aug. 90
882	58 068	56 327	yellow	1741	20 Aug. 90
870	59 261	59 261	yellow	0	19 Aug. 90
871	60 442	60 442	yellow	0	06 Sept. 90
875	66 168	66 168	yellow	0	12 Sept. 90
876	67 279	67 279	yellow	0	11 Sept. 90
877	76 940	76 940	yellow	0	12 Oct. 90
880	79 804	79 804	yellow	0	30 Oct. 90
872	90 622	90 622	yellow	0	10 Feb. 91
868	91 593	91 593	yellow	0	08 Nov. 90
873	120 026	120 026	yellow	0	26 March 91
883	130 582	130 582	yellow	0	24 April 91
887	138 516	138 516	Y to G	0	31 May 91
Average	74 417	74 314	...	102	
YELLOW COOLANT CABS THAT HAD ORIGINAL PUMPS THAT SURVIVED TEST DURATION					
NO PUMPS IN CABS WITH YELLOW COOLANT SURVIVED THE TEST					
YELLOW COOLANT CABS THAT HAD THE ORIGINAL PUMP REMOVED WITH THE ENGINE AT OVERHAUL					
878	118 652	118 652	yellow	0	18 Feb. 91
881	124 132	122 011	yellow	2121	28 Feb. 91
884	122 371	122 371	yellow	0	12 March 91
Average	121 718				

TABLE 5—*Green coolant test group original equipment coolant pump final disposition information.*

Car Number	Actual Mileage, km	Test Mileage, km	Coolant Used	Mileage at Fill, km	Date at Failure
GREEN COOLANT CABS THAT HAD ORIGINAL COOLANT PUMP FAILURES DURING THE TEST PERIOD					
831	45 580	25 717	green	4 192	05 July 90
844	54 805	29 560	green	7 232	20 Aug. 90
829	55 508	29 438	green	8 132	22 July 90
838	56 414	29 827	green	8 412	31 July 90
840	73 153	39 283	green	9 933	10 Sept. 90
846	73 158	41 404	green	6 524	09 Oct. 90
841	76 091	42 767	green	7 265	07 Oct. 90
837	88 593	48 408	green	10 688	05 Nov. 90
833	91 380	49 713	green	11 375	02 Nov. 90
843	93 913	53 889	green	7 187	24 Nov. 90
835	101 134	57 629	green	8 390	20 Dec. 90
834	102 254	57 153	green	10 276	23 Nov. 90
830	102 924	59 304	green	7 483	23 Nov. 90
826	103 838	58 339	green	9 951	22 Jan. 91
832	121 723	69 406	green	10 025	03 Feb. 91
847	122 424	70 569	green	8 855	23 Jan. 91
845	142 112	83 527	green	7 688	14 April 91
Average	93 641	52 710	...	8 812	...
GREEN COOLANT CABS THAT HAD ORIGINAL PUMPS THAT SURVIVED TEST DURATION					
839	153 387	143 510	green	9 877	08 May 91
Average	95 310	...	...	...	...
GREEN COOLANT CABS WHICH HAD THE ORIGINAL PUMP REMOVED WITH THE ENGINE AT OVERHAUL					
828	107 842	97 612	green	10 231	07 Dec. 90
842	116 999	107 995	green	9 004	28 Jan. 91
Average	112 421	...	...	...	...

failures among the 17 cabs that had the original pump replaced once. Both of these two groups, the factory-fill and the yellow, had replacement pumps that also subsequently failed.

Figure 1 is a multiple notched box-and-whisker plot [5] of all five groups of vehicles discussed in this report. It is a graphical comparison of the data generated by each group of vehicles. The mileage of the original equipment coolant pumps that failed during the test and that survived the entire test period were included in this figure. The mileage of the pumps removed because of the overhaul and inspection process were not.

This plot is a modification of the standard box-and-whisker plot. A notch is added to each box corresponding to the width of a confidence interval for the median, while the width of the box is proportional to the square root of the number of observations in the data set. The confidence level on the notches is set to allow pair-wise comparisons to be performed at the 95% level by examining whether two notches overlap [5].

The whiskers are drawn to include data points that fall outside of the box but fall within a distance one and one half times its total length. Points not included in the whiskers are drawn as dots on the figure and can be considered outliers that are not representative of the population. The pumps that survived the test in the purple and green cars can be considered flyers while the early failures in the blue coolant test group fall into this category.

This plot clearly demonstrates as shown in Table 8 that the blue coolant provides a much longer service life for the coolant pump than any of the other four formulations.

Table 9 compares the numerical average mileage at startup and at failure for each of the groups. The average listed in this table is the numerical average of mileage at which the original

TABLE 6—*Purple coolant test group original equipment coolant pump final disposition information.*

Car Number	Actual Mileage, km	Test Mileage, km	Coolant Used	Mileage at Fill, km	Date at Failure
Purple Coolant Cabs That Had Original Coolant Pump Failures During the Test Period					
816	65 813	55 336	purple	10 477	21 July 90
808	71 350	59 005	purple	12 345	01 Aug. 90
813	72 412	61 089	purple	11 323	10 Aug. 90
827	78 575	69 168	purple	9 407	29 Sept. 90
810	79 595	62 848	purple	16 747	03 Sept. 90
812	84 495	73 368	purple	11 127	02 Oct. 90
819	88 054	77 282	purple	10 771	20 Nov. 90
818	91 361	80 926	purple	10 435	16 Oct. 90
809	97 116	85 529	purple	11 587	01 Nov. 90
823	97 592	89 703	purple	7 889	22 Nov. 90
825	98 091	91 002	purple	7 089	20 Nov. 90
814	98 239	86 588	purple	11 652	14 Sept. 90
817	102 750	93 313	purple	9 437	21 Nov. 90
811	104 086	92 652	purple	11 434	29 Nov. 90
826	113 365	103 067	purple	10 298	21 Dec. 90
Average	89 526	78 725	...	10 801	...
Purple Coolant Cabs Which Had Original Pumps that Survived Test Duration					
815	159 066	148 000	purple	11 066	02 May 91
821	156 522	146 394	purple	10 128	03 May 91
824	154 946	147 640	purple	7 306	03 May 91
Average	156 845	...	...	...	...
Purple Coolant Cabs Which Had the Original Pump Removed with the Engine at Overhaul					
820	74 218	59 702	purple	14 516	04 Jan. 91
822	66 500	60 287	purple	6 213	13 Dec. 90
Average	70 359	...	...	...	...

pumps failed. It does not take into account pumps that are still in service. Again, the fact that there were only 3 occurrences out of a possible 20 make calculated numerical averages for the blue coolant test group statistically meaningless. This is why utilizing statistical techniques, such as the notched box and whisker plot is crucial to understanding the data.

The data on which this report is based can be obtained by writing to the author.

Discussion

This data represent the distribution of original equipment coolant pump failures that would be expected over the service life of vehicle populations employing the coolants tested. This discussion does not attempt to address the failures that occur in the first 12 months/24 000 km of service that have been the topics of other papers [*6,7*]. The failures experienced by this fleet appear to be directly related to coolant formulation by incidence and by distribution of occurrence.

There is currently no theoretical mechanism offered to interpret these failures. The pumps that failed were the coolant pumps present in the cars as delivered from the factory. No determination of their general quality or consistency could be made. It is assumed that this population represented a normal distribution of the total population of similar pumps. Information concerning the common causes of pump failure in vehicle populations is available through the

TABLE 7—*Blue coolant test group original equipment coolant pump final disposition information.*

Car Number	Actual Mileage, km	Test Mileage, km	Coolant Used	Mileage at Fill, km	Date at Failure
BLUE COOLANT CABS THAT HAD ORIGINAL COOLANT PUMP FAILURES DURING THE TEST PERIOD					
867	29 548	22 957	blue	6 590	16 May 90
865	86 193	79 603	blue	6 590	20 Oct. 90
857	132 869	131 443	blue	1 426	11 May 91
Average	82 870	78 001	...	4 869	...
BLUE COOLANT CABS THAT HAD ORIGINAL PUMPS SURVIVED TEST DURATION					
849	156 243	152 641	blue	3 602	14 May 91
852	147 372	140 092	blue	7 281	14 May 91
853	146 211	139 026	blue	7 184	14 May 91
854	138 780	135 581	blue	3 199	15 May 91
856	149 786	143 166	blue	6 621	16 May 91
860	157 207	150 870	blue	6 338	17 May 91
861	154 980	150 863	blue	4 117	21 May 91
862	155 302	150 469	blue	4 833	21 May 91
866	140 029	133 516	blue	6 513	21 May 91
Average	149 546	...	...	...	...
BLUE COOLANT CABS WHICH HAD THE ORIGINAL PUMP REMOVED WITH THE ENGINE AT OVERHAUL					
848	115 120	107 440	blue	7 680	13 Dec. 90
850	118 116	111 083	blue	7 033	21 Jan. 91
851	111 125	104 192	blue	6 933	21 Dec. 90
855	121 699	115 478	blue	6 220	29 Jan. 91
858	118 882	112 514	blue	6 368	06 March 91
859	114 469	106 683	blue	7 786	25 Jan. 91
863	113 385	106 421	blue	6 964	27 Dec. 90
864	120 324	113 515	blue	6 809	14 Feb. 91
Average	116 640	...	...	...	...

TABLE 8—*Average pump life expectancy and standard deviation by notched box and whisker plot.*

Coolant	Service Life Mean, km	Size of 95% Confidence Interval Notch, km	Failures Per Total[a]
Factory-fill	77 250	17 700	74/96
Yellow	67 600	24 000	17/17
Green	91 750	20 900	17/18
Purple	98 200	29 000	15/18
Blue	148 000	22 500	3/12

[a] The total number of pumps is the sum of the original equipment pumps that failed during the test period and the original equipment pumps that survived to the end of the test. The original equipment pumps that were removed as part of the lubricant evaluation program are not included or considered in the service life evaluations.

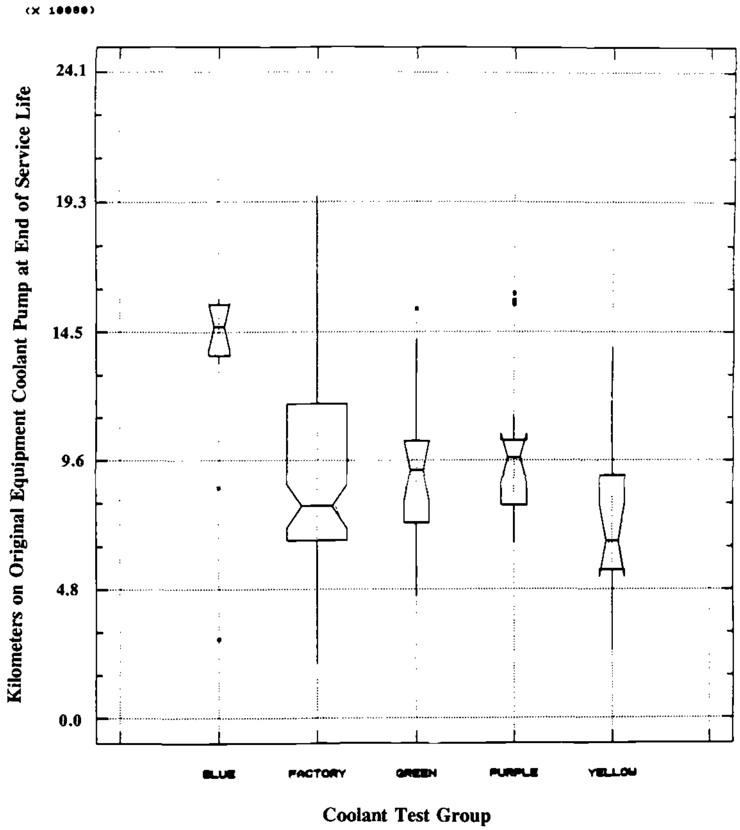

FIG. 1—*Notched box and whisker plot comparing coolant pump service life distribution of the 5 coolant test groups.*

seal manufacturer [*8*]. The coolant pumps used to replace the original pumps were obtained from an original equipment parts dealer and were not remanufactured.

The chemical differences between the coolant formulations are cited as one possible explanation of the failure distribution. All of the test coolants were ethylene glycol based and blended roughly 50% with deionized water. The factory-fill formulation was mixed according

TABLE 9—*Average kilometres at failure of the original equipment pumps in each test group.*

Coolant	Average Kilometres at Failure	Average Kilometres at Start-up of Failures/ Whole Group	Failure Occurrences Per Total Pump Population
Factory-fill	77 174	933/0	74/123
Yellow	74 416	102/193	17/20
Green	88 530	8 447/8 636	17/20
Purple	89 526	10 802/10 547	15/20
Blue	82 870	4 868/6 030	3/20

to assembly plant practices by the manufacturer with water of unknown quality. The average water concentration was found to be approximately 47% by weight.

The factory-fill coolant in these vehicles was quite similar to the yellow coolant, and it may have been made by the same manufacturer. The difference in failure distribution between these two groups may be attributable to the stop-leak additives used by the auto manufacturer at initial fill, or it could be attributable to the fact that these cars were topped-off with a different formulation, GM6038-M.

The stop-leak additives are used by the automobile manufacturer to reduce warranty problems caused by variable head bolt and gasket sealing quality throughout the engine. They are added to the cooling systems of most domestically produced cars. The coolant pump seal manufacturer believes that the stop-leak additives help rather than hinder the service life of the seal [9]. The additives appear to aid in the reduction of filming and wear, but it is not understood how. It is possible, but not likely that most of these stop-leak additives originally in the 80 test vehicles employing the 4 test coolants were flushed out when the cars were converted to the test coolants.

Another phenomenon may be responsible for the few longer life pumps that do not fit the distribution predicted in the notched box and whisker plot of the failure occurrences of the majority of the units in the factory-fill, yellow, green, and purple coolant test groups. One of the cars filled with the yellow coolant that had the original pump, cab 887, was flushed out and filled with fresh green coolant at 130 672 km. The pump was found to be leaking at the next inspection, 7844 km later.

In the field, it is common for coolant pump seals to leak soon after the coolant is changed, especially if the change interval was longer than recommended because of neglect. The cause of this behavior is not known, but one explanation is that the higher pH of the fresh coolant redissolves precipitates that have formed in the system as the alkalinity decreased.

Solids can also be formed by inhibitor drop-out, most notably silicate, products of corrosion, and hard water ion salts. The coolant change may simply remove solids by the mechanical action of the flush. The precipitates or solids may have acted as a stop-leak for the coolant pump seal preventing excessive amounts of coolant from escaping through leak paths on an already damaged seal surface.

The universal coolant formulations, with lower additive levels, may not be as prone to this phenomenon. Additionally, the purple and blue coolants have a much lower initial pH than traditional American coolant formulations. Addition of a sequestering agent to the formulations employing the more traditional inhibitor technology may reduce this effect, but it would predict a reduced average durability of the pump according to this mechanism.

A group of 24 cabs, numbered 701 to 724, which originally were part of the factory-fill test group, were switched over to two of the test coolants for a component test (Table 3). The average mileage at this conversion was approximately 66 000 km for all 24 cabs. Eight of the cars, cabs 701 to 708, were switched over to the blue test coolant. The other 16 cabs were filled with the green test coolant. The top-off coolant was not used because it does not meet the original equipment manufacturer's service fill requirements.

Handling these cars posed some difficulties since they do not fit the profile of the fleet at large. The majority of the failures experienced by this group of cars occurred before the conversion from factory-fill to the test coolants used for the radiator test.

The cabs that were switched to the blue coolant experienced two failures among the eight units before the switch occurred. It should be noted that none of the coolant pumps in the group of cabs numbered 701 to 708 (Table 10) failed after they were flushed and refilled with the blue coolant.

The 16 cabs that were flushed and replaced with the green test coolant saw 2 failures before the switch and 3 additional failures after the switch. The failure rate among the 24 cars

TABLE 10—*Radiator test group failures.*

Cab Numbers/ Coolants/Number of Cabs	Average Kilometres at Flush and Fill	Failures Before Change[a]/Average Kilometres	Failures After Change[b]/Average Kilometres
701 to 708/factory-fill to blue/8 cabs	63 355	2/54 425	0/does not apply
709 to 724/factory-fill to green/16 cabs	69 907	2/61 091	3/137 018

[a] The failures before the change over are included in the factory-fill group (see Table 3).
[b] Only the failures of original equipment pumps were considered.

involved in this radiator test was lower than in the general taxi population. The percentage of failures was considerably lower than any of the other test groups except for those cabs filled with the blue coolant initially.

The data from these two test groups are included with the rest of the factory-fill cabs for purposes of calculating durability of the factory-fill test group. The average results for the factory-fill vehicles are, consequently, probably somewhat better than would normally be expected because a lower percentage from this group failed at a higher average mileage. The two highest mileage failures reported as factory-fill cabs were from this group of vehicles. If these vehicles were omitted from the data presented for the factory-fill test group, the average life expectancy of the coolant pump would decrease slightly.

These data may indicate that proper maintenance of the cooling system can extend the life of the cooling system or that replacing the factory-fill coolants, which are typically of the high silicate type, with low-silicate universal coolants improves the chances of pump survival. The three failures that occurred in the group of cabs that were switched to the green coolant, numbers 709 to 724, occurred at mileage nearly twice the average for the rest of the factory-fill group.

Experimental Procedure

From Table 1, the only common differences that could explain the distribution of pump failures are that the blue coolant lacks nitrate, silicate, and silicate stabilizer, whereas all of the other coolants tested contained these three additives.

A test of silicate, nitrate, and a silicate stabilizer with exposed seal halves was performed to evaluate inhibitor effect on the seal material. The seals used for this evaluation were not the same seals that are used in the Crown Victoria coolant pump. They are composed of the same phenolic material, but incorporate a bronze ring into the sealing surface and are of the design used in many General Motors coolant pumps. These seals were used because they were easily accessible and because no supply of the correct seals could be obtained.

The individual halves of the coolant pump seal were immersed in a 50% solution of coolant mixed with deionized water and placed in an oven at 100°C. The phenolic portion of the coolant pump seal, the stationary side, caused colorless coolant, formulated without dye, to turn yellow-brown in a hot soak test.

This phenomenon only occurred when the seal halves were soaked in the formulations based on traditional inhibitor technology, not the experimental, long-life coolant formulations. When the individual inhibitors were tested, only the silicate, and, to a lesser degree, the silicate stabilizer, reproduced the results with respect to color hue and intensity.

The solution containing the nitrate changed color slightly, but it did not resemble the results produced by soaking the seal in the colorless coolant solution. The alkalinity of the solution may also come into play [*7*], but the results produced by the purple coolant, which has the lowest initial pH, were the same as that produced by the higher pH coolant formulations in about the same amount of time in the oven.

The nature of this change is not known. It is possible that there is an interaction between the silicate inhibitor, silicate stabilizer, or silicon in solution and the phenolic surface. It is also not known if this potential interaction is related to the failures experienced by this fleet, but it is one possible explanation. Reactions involving silicon that can take place in engine cooling systems are discussed by Kiryu et al. [*7*]. If silicate is involved in the failure mechanism, a linear relationship between the number of failures in the coolant test group and the relative silicate level of the traditional inhibitor formulations can not be shown from these data.

Conclusions

The goal of the original equipment manufacturers is to produce products with reduced maintenance, improved performance, and lower cost. Consumers' quality perception is based on the durability of and the amount of inconvenience encountered with products.

Because of the number of factors that affect the coolant pump, failures can not be eliminated, but their frequency can be reduced by employing alternative coolant formulations. Engine coolant formulations should provide corrosion inhibition for the metals used in engine construction, but must also be inert to the other materials.

Although the mechanism of failure is unknown at this time, the data presented clearly indicate that the blue coolant can provide a much longer useful life for the coolant pump. It is not believed that the blue coolant is beneficial for the pump, but rather that the adverse effect on the pump component materials is minimized.

A bench test to quantify the effect that coolant formulations have on the coolant pump would be a valuable tool for developing formulations with less adverse impact on the coolant pump. The ASTM Committee D-15 on Engine Coolants should undertake the development of such a test and should include favorable performance in the test in the standards covering engine coolants.

Acknowledgments

The author would like to thank Mr. Leonard M. Richmond and the Midtown Operating Corporation for the excellent control of this fleet and the level of organization that the data that they provided exhibited. The author would also like to thank Mr. Bradford S. Brown for his guidance on the statistical evaluations of the data, and Dr. James L. Jackson for the use of his statistical graphics software, his personal computer, and his time. Additionally, the technical and analytical assistance of Dr. Tristan A. Laurian, Mr. Charles F. Taylor, Mr. Stanley E. Whitfield, and Ms. Renee T. Bade was much appreciated.

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DISCUSSION

Norman Adamowicz[1] *(written discussion)*—How often were oil changes done?

J. M. Burns (author's response)—Approximately every 3000 to 5000 miles (4828 to 8047 km).

Norman Adamowicz[1] *(written discussion)*—How large were the size of the coolant samples?

J. M. Burns (author's response)—Approximately 100 mL.

Norman Adamowicz[1] *(written discussion)*—You flushed the cooling systems of all test cars before filling with test coolant but did not flush the factory-fill systems. Why did you not flush their coolant and refill with factory-fill coolant?

J. M. Burns (author's response)—The assumption was made that factory-filling the vehicles is a preferred way to introduce the test coolant into these systems. We believed that the system as delivered from the manufacturer was as good as it could be and any treatment that we tried would be poor by comparison. The directionally poorer performance of the yellow coolant relative to the factory-fill coolant seems to support this assumption. If it were possible to factory-fill all of the systems with the test coolants, it would have been done.

Norman Adamowicz[1] *(written discussion)*—Why did you mix a nonapproved AIF W OEM D/F? Actually then, what you tested was not coolant formulations in water pump seals but coolant formulations of the cooling systems. Therefore your data/info are not supportive of the title of the paper.

J. M. Burns (author's response)—The practice of the fleet was adhered to and no changes were made initially. Based on the data presented in the notched box-and-whisker plot, this variable did not introduce considerable bias. The factory-fill coolant group data are presented as anecdotal information that represents the situation in the field today. The similarity between the data yielded by this portion of the fleet and the data produced by three of the four test coolant groups that were established under comparable parameters indicates that the difference in top-off coolant from the factory-fill formulation did not introduce a great deal of bias. The performance of the four conventional coolant formulations was essentially the same.

Peter Woyciesjes[2] *(written discussion)*—You have stated that there was "tremendous top off" required in the test fleet. What was the amount of coolant added to the vehicles over the course of the test. What was the silicate level observed in the vehicles with silicate coolants? Given the known effects on components like water pumps by overdosing inhibitors, can you comment on the effects of "tremendous top off?"

J. M. Burns (author's response)—The silicate level (measured as silicon in solution) in the yellow coolant portion of the fleet ranged from a low of 3 parts per million (ppm) to a high of

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[1] Ford Motor Company.
[2] First Brands Corporation, Danbury, CT 06804.

364 ppm (although only two samples had more than 180 ppm) with an average of 90 ppm. The silicate level in the green coolant portion of the fleet ranged from 15 to 176 ppm with an average of 59 ppm, and the silicate level in the purple coolant portion of the fleet ranged from less than 1 ppm to 150 ppm with an average of 56 ppm. This certainly does not appear to be over concentration of silicate.

The comment about there having been tremendous top off was based on the fact that a large volume of coolant was used, not on the inhibitor levels found in the systems. There are other reasons for coolant usage.

I do not believe that overconcentration of silicate was the major cause of the incidence of pump replacements, but that silicate is involved in the failure mode. The blue coolant had a higher percentage of inhibitor additive, which is sometimes interpreted as total dissolved solids, but produced much better results. The differences in the silicate level accounts for only 0.036 wt% of the total solution. Even if overconcentration is involved, it would merely lend support to the conclusion that a silicate-free coolant have improved compatibility with the coolant pump.

Peter Woyciesjes[2] *(written discussion)*—It has been shown that silicate protects metals by quickly forming a protective layer. The remainder of the silicate remains in solution to reinhibit any corrosion sites that may develop. The protective film cannot be removed by water washing the cooling system.

Would not the drain and refill process with fresh silicate coolant lead to overconcentration effects described in earlier presentations? Would not a nonsilicate coolant benefit from this precharge of silicate coolant?

J. M. Burns (author's response)—Overconcentration of silicate is one possible explanation for the data that were generated. The measured silicon levels in the coolant samples averaged 56 to 59 parts per million for the low silicate, universal formulations and 90 ppm for the high silicate formulation.

These levels do not seem sufficient to explain the results through a mechanism related to overconcentration of silicate, although the conclusions of this study would remain unchanged even if they did. A silicate-free coolant would still have improved compatibility with the coolant pump.

The original equipment manufacturers recommend replacing the factory-fill coolant after a certain number of years to miles, and the consumer is likely to use the products that are available on the market which are high silicate and universal formulations. Your argument would suggest that a high silicate coolant should never be used in cooling systems other than for factory-fill. Although I would certainly agree with this, the data presented here does not suggest that simply lowering the silicate level provides much of an improvement.

The universal formulations, the green and the purple, which have half the initial silicate level of the typical high silicate formulations, and the factory-fill systems that were topped off with a low silicate formulation performed directionally better than the high silicate formulations, but the results were of the same population statistically.

For the purposes of this study, there is no way that the silicate precharge could be a benefit to the silicate-free coolant if the data are to be believed. The silicate would have a detrimental effect on the coolant pump from the point of initial fill. No corrosion data were presented, and it was not the author's intent to discuss that performance aspect in this publication. That has been covered in other publications and may be the topic for a future publication.

William Mercer[3] *(written discussion)*—High lead solder losses for coolants with monoacids are known to be very high and have been shown to be due to the formation of lead carboxylates. Lead carboxylates were also shown to be transported throughout the cooling system and

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[3] First Brands Corporation, Danbury, CT 06804.

are known to be excellent lubricants. You have stated that these vehicles were equipped with specimen bundles that contained high lead solder. What were the high lead solder losses with the blue coolant?

What evidence do you have that the extended pump life observed with the blue coolant is not serendipitous and due to the formation of an excellent pump seal lubricant by corrosion of high lead solder?

J. M. Burns (author's response)—High lead solder weight losses for the coolants with monoacids are not known to be very high; they are merely alleged to be high in formulations that may not be representative of this technology. The high lead solder weight losses for the different coolant formulations were 155 mg for the blue coolant, 106 mg for the purple coolant, 62 mg for the yellow coolant, and 46 mg for the green coolant. Although these are not excellent results for the blue coolant, neither are they excellent results for any of the other coolants tested, and it certainly does not support the theory that monoacids are generally aggressive to the high lead solder alloy.

One hundred twenty two of one hundred sixty five coolant samples had no measurable levels of lead in solution. The highest level of lead measured was 23 ppm while the average was less than 5 ppm. The levels of lead found in the 5 of the 20 cars that had corrosion coupons were not statistically different than the levels found in the other 15. Samples from the other coolant test groups were not tested for lead.

Based on this fleet test, there is no support for the monoacid/lead corrosion theory presented at this Symposium.

The data suggest that these formulations provide a lower degree of protection to the specific lead alloy in question. To determine if formulations containing monoacids are aggressive to lead solders, a performance comparison should be made with an uninhibited water/ethylene glycol mixture.

The allegation that carboxylic acids are generally corrosive to lead solder alloys are not supported by the data available. Two recent patents, U.S. 5,085,791 and U.S. 5,085,793 suggest that certain monoacids can even improve protection of the high lead solder alloy employed in these tests.

The formation of lead carboxylate is one explanation, but that has not been proven. The low depletion of the carboxylic acid suggests that this is not occurring. There is no evidence to suggest that lead carboxylates are actually formed in these systems. Only 5 of the 20 vehicles contained coupon bundles, and hence a source of the lead for formation of the lead carboxylate. This mechanism does not explain the difference in results between the various formulations.

The suggestion that lead carboxylates provide lubrication for the pump seal, thus explaining the differences in pump compatibility noted in this study is an unlikely explanation at best. Lead carboxylates have not been found on any of the coolant pump seal surfaces. The blue and the purple coolants both contain the same monoacid, yet produced radically different results. The purple coolant produced results that were statistically similar to the three formulations that contained no monoacids.

If this mechanism is involved with the modes of failure, then it is to a much lesser degree than the silicate is involved.

William Mercer[3] *(written discussion)*—The coolants were not randomized over initial starting mileage. Were they randomized over the fuel and lubricant tests run concurrently on these vehicles? What was the effect of the fuel and lube test products on vehicle performance? What is the effect of lack of randomization on the statistical analysis of the results?

J. M. Burns (author's response)—The effect of the different starting mileages of the cars is believed to be minimal. Figure 1 does not indicate that there is a considerable distinction between three of the test coolants, the yellow, the green, and the purple, and the factory-filled vehicles. The blue coolant test vehicles were filled at a average mileage between that of the factory-fill and the yellow, both of which represent low initial mileages, and that of the green and purple, both of which represent somewhat higher initial mileages, but produced statistically significantly better results than any of the other formulations involved.

Based on the data in Tables 3 to 7, no discernable bias was introduced by this variable. The coolant test was transparent to and independent of the lubricant tests conducted in this fleet. The coolant test groups were not related to the lubricant test groups. Different lubricants were distributed randomly throughout the coolant test groups. Evaluation of the data for the coolant testing has indicated no bias resulting from the lubricant testing which was concurrently conducted in these vehicles.

William C. Mercer[1]

An Investigation of Carboxylic Acids as Corrosion Inhibitors in Engine Coolant

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REFERENCE: Mercer, W. C., "**An Investigation of Carboxylic Acids as Corrosion Inhibitors in Engine Coolant,**" *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 44–62.

ABSTRACT: The ability of carboxylic acids to inhibit corrosion in automotive cooling systems was first reported more than 40 years ago. Aromatic carboxylic acids, such as benzoic acid and its derivatives, have been extensively studied and are used in Europe as corrosion inhibitors in commercial coolants. There are few studies of corrosion inhibition by aliphatic carboxylic acids in the open literature. Aliphatic dibasic acids, such as 1,10-decanedioic, and aliphatic monobasic acids, such as octanoic, have recently been proposed as inhibitors in automotive coolant formulations. To date, ASTM performance test data have not been available.

This paper presents a comparison of the performance of selected carboxylic acid coolants with each other and with a traditional North American coolant in laboratory and fleet tests. Protection of cooling system metals, inhibitor depletion, and mixed coolant effects were investigated.

KEYWORDS: corrosion, engine coolants, automotive coolants, organic acids, octanoic acid, 2-ethylhexanoic acid, 1,10-decanedioic acid, tolyltriazole, silicate

Alternative coolant formulations for improved corrosion inhibition have been an objective of research in coolant laboratories for many years. While many formulations are proposed, few are acceptable commercial engine coolants. The performance of proposed coolants is judged in laboratory and fleet tests against a standard. A minimum is ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light Duty Service (D 3306). Another standard is the performance of commercially available coolants. Proposed formulations that perform better than the standards are considered superior formulations and are likely to be commercialized.

Engine coolants must inhibit corrosion of cooling system metals. These include steel, cast iron, copper, brass, lead solders, cast aluminum, and wrought aluminum. Cooling system metallurgy is in a state of flux. In the last 15 years engine metallurgy has changed from primarily cast iron to a mix of cast aluminum and cast iron. Heat exchangers in newer cars are primarily wrought aluminum, but there are still many cars with soldered copper/brass radiators. Because of the variation in cooling system metallurgy, coolants must contain inhibitors for all metal combinations found in vehicles.

A consumer survey has shown that as many as 41% of cooling systems are neglected to some degree [*1*]. Automobiles are operated with little or no coolant in the overflow bucket, with low coolant concentrations, and coolant beyond its useful life. Cooling systems that have been neglected are difficult to reinhibit because of increased surface area and the presence of acidic corrosion products. Coolants must provide good performance in both new systems and corroded systems.

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[1] Group Leader, Coolant Group, First Brands Automotive R&D Laboratory, 55 Federal Road, Danbury, CT 06810.

The introduction of a new coolant should not cause compatibility problems with existing coolants. Coolant mixing can occur when systems are topped off or when coolant is changed. If coolant mixing causes degraded corrosion inhibition, the coolants are incompatible.

Aliphatic carboxylic acids have been under study in our laboratories for several years. Corrosion inhibition in automotive cooling systems by aliphatic carboxylic acids was first patented in the United States in 1945 [*2*]. There was little interest in the efficacy of aliphatic carboxylic acids until Butler and Mercer [*3*] published on the subject in 1977. This interest was followed by technical activity [*3*] and some recent marketing activity. For example, the Saturn factory fill contains an aliphatic carboxylic acid as a minor inhibitor.

Silicate based coolants with phosphate/borate or phosphate buffer systems have dominated both factory fill and the aftermarket in North America since their introduction in 1972. A representative silicate coolant (GM 6043M) was chosen as the standard for an evaluation of some aliphatic carboxylic acid coolants. A series of coolants with aliphatic carboxylic acid inhibitors was evaluated in laboratory and fleet tests. Protection of cooling system metals, inhibitor depletion, and mixed coolant effects were investigated. This paper presents the results of these investigations.

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.

Coolant Composition

Two experimental designs were used to determine the composition of monoacid/diacid combinations for future testing. Test coolant compositions are shown in Tables 1 and 2. Coolants A–L used combinations of octanoic acid and 1,10-decanedioic acid. Coolants M–X included nine combinations of 2-ethylhexanoic acid and 1,10-decanedioic acid and three coolants that used only 2-ethylhexanoic acid.

TABLE 1—*Composition of coolants A-L.*

Coolant	Octanoic Acid, wt%	1,10-Decanedioic Acid, wt%	Sodium Tolyltriazole, wt%	Sodium Hydroxide, wt%	Balance, wt%
A	0.38	0.4	0.25	0.24	98.73
B	0.76	0.4	0.25	0.34	98.25
C	1.52	0.4	0.25	0.53	97.30
D	2.28	0.4	0.25	0.73	96.34
E	0.38	0.8	0.25	0.39	98.18
F	0.76	0.8	0.25	0.49	97.70
G	1.52	0.8	0.25	0.68	96.75
H	2.28	0.8	0.25	0.87	95.80
I	0.38	1.2	0.25	0.53	97.64
J	0.76	1.2	0.25	0.63	97.16
K	1.52	1.2	0.25	0.83	96.20
L	2.28	1.2	0.25	1.02	95.25

NOTE: Balance includes ethylene glycol, water, dye, and antifoam.

TABLE 2—*Composition of coolants M-X.*

Coolant	2-Ethylhexanoic Acid, wt%	1,10-Decanedioic Acid, wt%	Sodium Tolyltriazole, wt%	Sodium Hydroxide, wt%	Balance, wt%
M	0.5	0	0.1	0.13	99.27
N	2.0	0	0.1	0.55	97.35
O	3.5	0	0.1	0.97	95.43
P	0.5	0.2	0.1	0.21	98.99
Q	2.0	0.2	0.1	0.65	97.05
R	3.5	0.2	0.1	1.03	95.17
S	0.5	0.8	0.1	0.44	98.16
T	2.0	0.8	0.1	0.87	96.23
U	3.5	0.8	0.1	1.26	94.34
V	0.5	1.4	0.1	0.69	97.31
W	2.0	1.4	0.1	1.10	95.4
X	3.5	1.4	0.1	1.49	93.51

NOTE: Balance includes ethylene glycol, water, dye, and antifoam.

The composition of coolants 1 and 2 were developed based on results obtained with coolants A-L and M-X, respectively. Table 3 shows the composition of coolants 1, 2, and GM 6043M.

Laboratory Tests

Laboratory tests included ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384), ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat Rejecting Conditions (D 4340), and ASTM Test Method for Cavitation Erosion-Corrosion Characteristics of Aluminum Pumps With Engine Coolants (D 2809). 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. ASTM D 2809 was run once for each fluid.

The high lead solder specimens were coated with a heavy deposit after ASTM D 1384 when monoacids were present in the coolant. Since the standard solder cleaning procedure did not remove all of the deposit, a modified cleaning procedure was used. The samples were heated

TABLE 3—*Composition of Fleet test coolants.*

Inhibitor, wt%	Coolant 1	Coolant 2	GM 6043M
(85%) Phosphoric acid	...	...	0.15
Sodium tetraborate	...	...	0.40
Sodium Silicate	...	...	0.30
(50%) Sodium tolyltriazole	0.50	0.46	0.20
(50%) Sodium mercaptobenzothiazole	...	...	0.50
Sodium nitrate	...	...	0.10
Sodium molybdate	...	...	...
Octanoic acid	1.5	...	...
2-Ethylhexanoic acid	...	3.5	...
1,10-Decanedioic acid	0.8	0.2	...

in toluene for 2 h at 100°C, rinsed with acetone, and recleaned according to the standard procedure. This cleaning procedure was not required for high lead solder specimens removed from fleet vehicles. There was no deposit on these specimens.

Linear Regression Analyses

The contributions of the individual inhibitors in coolant A–X to the data obtained in the D 1384 tests were evaluated by linear regression techniques. The independent variables were initially evaluated by stepwise regression techniques. Stepwise regression is an iterative process. The experimental variables are evaluated individually to determine the best straight line through the data. The effect of the best fit variable is subtracted from the data. The program then fits a line through the remaining variables using the residual data. The variables identified as important in the stepwise regression analysis are used in the multiple linear regression analysis.

The model used in the stepwise analysis was

$$\begin{aligned}\text{specimen weight loss} = {} & \text{constant} + [\text{monoacid}] \\ & + [\text{diacid}] + [\text{monoacid}]^2 \\ & + [\text{diacid}]^2 + ([\text{monoacid}]*[\text{diacid}])\end{aligned}$$

The model accounted for contributions by the individual acids in each array. The squared term accounted for effects of the acids where the contribution changes more rapidly than provided for by the linear term. Interactions between the acids that cause more than additive effects were also examined. The linear regression provided coefficients for each term. These coefficients show whether the variable increased (positive coefficient) or decreased (negative coefficient) specimen weight loss.

Fleet Tests

Selected aliphatic carboxylic acid coolants were evaluated in fleet tests. Coolants 1 and 2 were tested in older vehicles (Series 1). Coolant 2 and GM 6043M were tested as factory fill (Series 2) in new vehicles. Coolants were evaluated by metal specimen weight loss and solution analysis. A description of the fleet test procedures is in Table 4.

A bypass (heater circuit) specimen capsule was used in both tests as in ASTM Practice for

TABLE 4—*Fleet test procedures.*

Fleet	Coolant	Vehicle Type (Number)	Odometer Initial, km	Test Duration, km	Engine Type	Engine Metallurgy	Engine Treatment	Coolant Dilution
Series 1	1	Voyager (2)	48 000	48 000	3.0L V6	1	water wash	yes
Series 1	2	Voyager (2)	96 000	48 000	3.0L V6	1	water wash	yes
Series 2	2	Grand Prix (5)	0	118 000	3.1L V6	2	factory fill	no
Series 2	GM 6043M	Grand Prix (5)	0	118 000	3.1L V6	2	factory fill	no

ENGINE METALLURGY: 1 = Cast iron block, aluminum cylinder head, and brass radiator. 2 = Cast iron block, aluminum cylinder head, and aluminum radiator.

Testing Engine Coolants in Car and Light Truck Service (D 2847). The specimen bundles contained the same seven metals used in ASTM D 1384. 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. Other cooling system components were examined and replaced if necessary.

Series 1 Tests

The fleet tests of coolants 1 and 2 were run consecutively in the same vehicles. The 48 000-km tests took approximately 10 months to complete. Specimen bundles were removed at 8000-km increments between 16 000 and 48 000 km. Solution samples were obtained at 8000-km intervals.

The coolant concentration was reduced during the Series 1 tests from 50 to 25 vol%. ASTM corrosive water was used for coolant dilution. Coolant dilution mimicked consumer neglect. Dilution stressed the coolant and provided an indication of the ability to protect under severe duty conditions.

Series 2 Test—The Series 2 test is scheduled for three years and 116 000 km. The vehicles were factory filled with the test coolant. Coolant dilution will remain at 50 vol% with deionized water throughout the test. Specimen bundles are removed at 19 000-km intervals. Coolant samples are removed at 16 000-km intervals.

Results and Discussion

ASTM D 1384 of Monoacid/Diacid Combinations

Two sets of twelve coolants were used to evaluate the performance of aliphatic carboxylic acids in ASTM D 1384 and to choose combinations of monoacids and diacids for further testing. The weight loss data are shown in Tables 5 and 6. The weight loss data and the results of linear regression analyses are discussed below.

High Lead Solder—There are two weight loss columns presented for high lead solder (Tables 5 and 6). The first column is the weight loss after cleaning according to the procedure for solder in ASTM D 1384, and the second column is the weight loss after the modified procedure described in the Experimental Section. The special procedure was used because the specimens were coated with a layer of corrosion product after the initial cleaning. The removal of the corrosion product resulted in higher specimen weight losses (6 to 282 mg). The alternative cleaning procedure was not the cause of the weight loss. Similar treatment of specimens from tests of traditional North American coolants showed no weight loss change. The weight of untested specimens was unaffected by the alternative treatment.

The use of the alternative cleaning procedure was supported by fleet test results (see below). The corrosion product was never seen on these specimens despite high weight losses. The toluene soluble layer was sufficiently adherent to remain on the specimen in the no flow conditions of a beaker (ASTM D 1384) but did not remain on the specimen in a real cooling system.

No standards have been set for high lead solder weight loss in ASTM D 3306. The data presented here must be evaluated with the standard for ASTM solder of 30 mg and the consideration that approximately 1000 mg of solder was originally coated on the brass specimen. The ASTM solder standard can be used. Our experience is that high lead solder is more difficult to protect than ASTM solder. Therefore, a rule of thumb is that below 30 mg weight loss, high lead solder is well protected, and above 100 mg (10% of available solder) weight loss, a serious high lead solder corrosion problem exists.

Only 3 of the 24 coolants had weight losses less than 100 mg per specimen after the standard

TABLE 5—*ASTM D 1384 weight loss data coolants A–L, mg/specimen.*

Coolant	High Lead Solder (1)	High Lead Solder (2)	Copper	ASTM Solder	Brass	Steel	Cast Iron	Cast Aluminum
A	182	247	2.2	1.2	2.5	0.6	−0.8	123.4
B	262	296	2.6	2.4	3.0	1.2	−1.0	100.2
C	113	229	1.7	1.6	2.4	0.5	−1.2	9.4
D	122	338	1.8	1.1	2.3	0.0	−1.3	48.8
E	86	288	1.8	2.7	3.0	1.1	−0.7	20.1
F	70	306	2.5	2.1	3.4	0.1	−0.6	1.7
G	282	449	2.7	2.7	3.5	0.9	0.1	13.2
H	224	393	2.2	3.1	3.0	0.8	−0.9	4.4
I	154	436	1.1	3.2	1.5	−0.4	−1.8	4.3
J	184	507	2.8	12.0	3.5	0.7	−1.0	2.5
K	166	509	3.0	5.5	3.6	2.3	1.3	11.5
L	162	534	3.1	6.3	3.9	0.6	−0.7	0.0
Upper limit (D 3306)	none	none	10	30	10	10	10	30

NOTE: High lead solder (1)—weight loss after standard cleaning procedure. High lead solder (2)—weight loss after modified cleaning procedure.

cleaning procedure. Only coolant M had a weight loss less than 100 mg after the alternative cleaning procedure. None of the coolants had high lead solder specimen weight losses less than 30 mg. Coolants J–L had weight losses greater than 500 mg. This was approximately 50% of the available high lead solder. None of the test coolants provided good protection for high lead solder.

The contribution of the individual inhibitors to the weight losses was determined using linear regression techniques. The model for high lead solder corrosion derived from this analysis was the same for both sets of coolants

$$\text{high lead solder weight loss} = c_0 + c_1[\text{monoacid}]$$

TABLE 6—*ASTM D 1384 weight loss data coolants M–X, mg/specimen.*

Coolant	High Lead Solder (1)	High Lead Solder (2)	Copper	ASTM Solder	Brass	Steel	Cast Iron	Cast Aluminum
M	73	79	3.2	7.3	3.9	6.6	388	61.9
N	128	138	3.4	4.8	5.0	3.9	238	73.8
O	160	212	3.5	1.0	5.5	1.2	−0.6	39.1
P	112	134	3.6	0.8	4.9	1.4	1.6	10.9
Q	192	223	3.3	1.6	4.6	1.4	−1.1	6.9
R	218	310	3.6	2.2	3.7	1.4	−0.8	12.8
S	163	201	3.7	5.7	5.6	0.8	−1.0	11.9
T	292	337	3.6	4.6	5.2	0.9	−0.5	10.8
U	332	378	3.4	3.3	3.6	1.0	−1.4	8.2
V	193	215	4.3	10.7	4.2	1.1	−0.7	9.5
W	267	324	6.0	3.9	2.5	1.3	−0.1	7.6
X	202	237	4.3	2.8	3.2	1.1	−0.6	12.2
Upper limit (D 3306)	none	none	10	30	10	10	10	30

NOTE: High lead solder (1)—weight loss after standard cleaning procedure. High lead solder (2)—weight loss after modified cleaning procedure.

For coolants A–L this model accounted for 95% of the data, and for coolants M–X the model accounted for 54% of the data (Table 7). The monoacid coefficient was positive. Therefore, increased monoacid concentration was accompanied by increased high lead solder weight loss. There was no effect of the diacid or an interaction between the acids observed for either set of coolants. The effect of the 2-ethylhexanoic acid was clearly seen in coolants M, N, and O where there was no diacid present. The high lead solder weight loss increased from 79 to 378 mg as the 2-ethylhexanoic acid level increased from 0.5 to 3.5 wt%. The monoacids attacked high lead solder in ASTM D 1384.

ASTM Solder—All coolants provided adequate protection to ASTM solder in this test. The weight loss range for coolants A–L was 1 to 12 mg and for coolants M–X was 0.8 to 10.7 mg. This was a large enough range that linear regression techniques were used as above to determine the effect of inhibitors on weight loss. There were no observable effects of either 2-ethylhexanoic acid or 1,10-decanedioic acid on the corrosion of ASTM solder in coolants M–X. There was an effect of octanoic acid on the corrosion of ASTM solder in coolants A–L. The model was

$$\text{ASTM weight loss} = c_0 + c_1[\text{octanoic}] + c_2[\text{octanoic}]^2$$

This model accounted for 73% of the data (Table 8). As the concentration of octanoic acid went up the corrosion of ASTM solder went up. The positive second order term indicated that at higher concentrations of octanoic acid the corrosion losses increased more rapidly than accounted for by the linear term.

The protection of ASTM solder was adequate in the presence of the more active high lead

TABLE 7—*High lead solder multiple linear regression.*

Coolants A–L: High Lead Solder, $N = 12$, $r^2 = 0.951$

Analysis of Variance

Source	Sum of Squares	df	Mean Square	*F* Ratio	Probability
Total	127385.64	11			
Regression	121206.62	1	121206.62	196.16	0.0000
[monoacid]	121206.62	1	121206.62	196.16	0.0000
Residual	6179.02	10	617.90		

Regression Coefficients

Variable	Standard Coefficient	Standard Error	*T* Value
Constant	377.7	7.2	52.64
[monoacid]	137.7	9.8	14.01

Coolants M–X: High Lead Solder, $N = 12$, $r^2 = 0.541$

Analysis of Variance

Source	Sum of Squares	df	Mean Square	*F* Ratio	Probability
Total	62355.43	11			
Regression	33748.02	1	33748.02	11.80	0.0064
[monoacid]	33748.02	1	33748.02	11.80	0.0064
Residual	28607.41	10	2860.74		

Regression Coefficients

Variable	Standard Coefficient	Standard Error	*T* Value
Constant	194.4	15.4	12.59
[monoacid]	43.3	912.6	3.43

TABLE 8—*ASTM solder multiple linear regression.*

Coolants A–L: ASTM Solder, $N = 12$, $r^2 = 0.729$
Analysis of Variance

Source	Sum of Squares	df	Mean Square	F Ratio	Probability
Total	103.15	11			
Regression	75.16	2	37.58	12.08	0.0028
[monoacid]	63.78	1	63.78	20.51	0.0014
[monoacid]^2	11.38	1	11.38	3.66	0.0881
Residual	27.99	9	3.11		

Regression Coefficients

Variable	Standard Coefficient	Standard Error	T Value
Constant	2.3	0.88	2.57
[monoacid]	2.6	0.75	3.51
[monoacid]^2	2.6	1.36	1.91

solder. However, the corrosion of ASTM solder was accelerated by octanoic acid. More testing of these systems needs to be done to demonstrate that the protection of ASTM solder will continue to remain adequate in the absence of high lead solder.

Cuprous Metals—Copper and brass protection was adequate with coolants A–X. All weight losses were 6 mg or less, well below the 10 mg limit is ASTM D 3306-89. Statistical analysis of the weight losses showed no effect of acid concentration for either metal.

Ferrous Metals—Except for coolants M and P the protection of the ferrous metals was very good. Coolants M (0.5%) and P (0.7%) suggest that a minimum acid level (>0.7%) in the coolant concentrate was required to protect cast iron. Protection was very good once that level was exceeded. There were no other effects due to either acid or an interaction between them observed in the linear regression analysis.

Aluminum—Aluminum weight losses ranged from 0 to 123 mg in coolants A–L and 7 to 74 mg in coolants M–X. Nine of the twelve coolants in each array had weight losses lower than the ASTM D 3306 specification (30 mg) for aluminum weight loss in ASTM D 1384. There also seemed to be a minimum acid level required to protect aluminum. The aluminum losses were above 30 mg when there was less than 1.35% acid present in the coolant concentrate.

The effect of the acids and interactions between them was determined by linear regression techniques. For coolants A–X the model that described corrosion was

$$\begin{aligned}\text{aluminum weight loss} &= c_0 + c_1[\text{monoacid}] + c_2[\text{monoacid*diacid}] \\ &\quad + c_3[\text{monoacid}]^2 + c_4[\text{diacid}]\end{aligned}$$

This model accounts for 87% of the data (Table 9) for coolants A–L. The coefficients for octanoic acid and 1,10-decanedioic acid were both negative, indicating that corrosion decreased as the concentration of each acid increased. The positive second order term for octanoic acid indicates that weight losses were higher at higher acid concentrations than accounted for by the linear term. An interaction term between the acids was also present. The coefficient for the interaction term was positive. Therefore, the interaction between the acids resulted in greater aluminum corrosion. Thus, this interaction, if real, represents a negative synergism. This suggests that the acids would be more effective when used alone. A molar ratio [*3*] term was included in the evaluation. It had no significant effect.

The same model describes aluminum corrosion in coolants M–X. The model accounts for 90% of the data (Table 9). The acids protect aluminum by the same mechanism even though

TABLE 9—*Aluminum multiple linear regression.*

Coolants A–L: Aluminum, $N = 12$, $r^2 = 0.867$

Analysis of Variance

Source	Sum of Squares	df	Mean Square	F-ratio	Probability
Total	18888.17	11			
Regression	16377.06	4	4094.26	11.41	0.0035
[diacid]	3718.24	1	3718.24	10.37	0.0147
[monoacid]	7023.68	1	7023.68	19.58	0.0031
$[\text{monoacid}]^2$	2545.38	1	2545.38	7.10	0.0323
[mono*di]	3089.77	1	3089.77	8.61	0.0219
Residual	2511.11	7	358.73		

Regression Coefficients

Variable	Standard Coefficient	Standard Error	T-Value
Constant	7.6	9.5	0.8
[diacid]	−53.9	16.7	−3.22
[monoacid]	−41.0	8.0	−5.09
$[\text{monoacid}]^2$	38.8	14.6	2.66
[mono*di]	67.3	22.9	2.93

Coolants M–X: Aluminum, $N = 12$, $r^2 = 0.898$

Analysis of Variance

Source	Sum of Squares	df	Mean Square	F-ratio	Probability
Total	5880.85	11			
Regression	5285.51	4	1320.63	15.45	0.0014
[diacid]	582.68	1	582.68	6.82	0.0349
[monoacid]	2745.40	1	2745.40	32.12	0.0008
$[\text{monoacid}]^2$	798.11	1	798.11	9.34	0.0184
[mono*di]	1156.33	1	1156.33	13.53	0.0079
Residual	598.33	7	85.48		

Regression Coefficients

Variable	Standard Coefficient	Standard Error	T-Value
Constant	10.6	4.6	2.29
[diacid]	−12.7	4.9	−2.61
[monoacid]	−12.3	2.2	−5.67
$[\text{monoacid}]^2$	7.7	2.5	3.06
[mono*di]	14.6	3.9	3.68

the monoacid has been changed. This is not surprising since 2-ethylhexanoic acid is an isomer of octanoic acid. There did not appear to be any effect of the change in chain length from octanoic acid to 2-ethylhexanoic acid as was postulated [*3*].

Laboratory Testing: Coolants 1 and 2

Two coolants were selected for further laboratory testing based on the ASTM D 1384 results with coolants A–X. Coolant 1 contains 1.5 wt% octanoic acid and 0.8 wt% 1,10-decanedioic acid. Coolant 2 contains 3.5 wt% 2-ethylhexanoic acid and 0.2 wt% 1,10-decanedioic acid. The coolant compositions were selected to give the best balance of metal specimen protection available within the tested concentration range.

ASTM D 4340—The data from ASTM D 4340 testing of these coolants is shown in Table 10. Coolant 1 failed the test marginally. Coolant 2 passed the test. The coolant 2 corrosion rate was slightly higher than that of GM 6043M.

TABLE 10—*ASTM D 4340 data.*

Coolant	Aluminun Corrosion Rate, mg/cm^2 week	Result
1	1.1	fail
2	0.3	pass
GM 6043M	0.1	pass
Upper limit (D 3306)	1.0	. . .

ASTM D 2809—Water pump ratings for these coolants were in the 9 to 10 range. The aluminum surface was discolored but not damaged by coolants 1 and 2. The coolants provided adequate protection for aluminum water pumps.

Compatibility of Coolant Mixtures—Mixing of coolants can occur in several ways. Virtually all cooling systems require makeup at some time because of small leaks. Component failures can lead to large coolant losses. The periodic replacement of coolant also can lead to mixing since it is difficult to remove all of the coolant from the system. Since mixing will occur, it is imperative to assure compatibility between coolants. The corrosion inhibition provided by a mixture of coolants should be no worse than the minimum the performance of the individual coolants.

Mixing effects were examined by combining coolant 2 with two conventional North American coolants. ASTM D 4340 was used to evaluate performance. Representative samples of the North American coolants were obtained in the aftermarket. The North American coolants were phosphate buffered and had both high and low silicate levels. These coolants passed ASTM D 4340 when tested alone (0 vol% coolant 2, Fig. 1). In all cases there was a range of mixtures with corrosion rates greater than the specification for ASTM D 4340 in ASTM D 3306 (1.0 mg/cm^2/wk).

Adding small amounts of the high silicate phosphate buffered coolant caused the corrosion inhibition provided by coolant 2 to break down. At the lowest level tested, 90% coolant 2, the corrosion rate was greater than 4.0 mg/cm^2/wk. The data in Fig. 1 suggest contamination by as little as 2.5 vol% conventional coolant will cause corrosion of heat rejecting aluminum. These levels easily can be reached when topping off a factory fill of organic acid coolant with

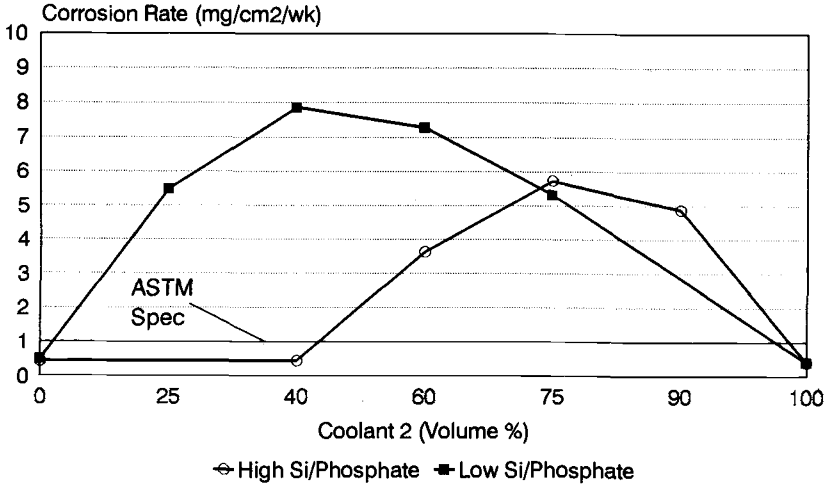

FIG. 1—*Coolant mixture corrosion rates in ASTM D 4340.*

conventional coolant. The corrosion rate continued to increase as the concentration of coolant 2 decreases. The corrosion rate with the high silicate phosphate buffered coolant reached a maximum at 75 vol% coolant 2. A corrosion rate below 1.0 mg/cm^2/wk was not reached until the conventional coolant accounted for nearly 60% of the mixture.

The situation with the low silicate phosphate buffered coolant was worse because the corrosion rate was unacceptably high over the entire mixture range (Fig. 1).

The solution chemistry of the test coolants was adversely affected by mixing. Complete depletion of silicate was observed, and the phosphate buffered coolants had large decreases in the phosphate concentration. There was no inhibitor depletion when the phosphate buffered coolants were tested alone. The solutions above the aluminum test specimens were opaque because of suspended corrosion products. In a vehicle, suspended corrosion products like these are transported to the radiator and deposited, leading to radiator plugging and cooling system failure [*19*].

The exact cause of the corrosion is unknown. It was reported that low levels of some anodic corrosion inhibitors provided worse protection than not having the inhibitor in the formulation [*20*]. Because ASTM D 4340 was run at 25% dilution, the levels of corrosion inhibitors from the conventional coolants were at very low levels in these mixtures. The organic acid coolants can provide acceptable aluminum protection when not contaminated. However, they cannot overcome the aggressive condition caused by the presence of small amounts of conventional corrosion inhibitors. The high silicate coolant is robust enough to protect heat rejecting aluminum when diluted by up to 40% by coolant 2. The low silicate coolants are not compatible with coolant 2 at any level.

Fleet Testing—The fleet tests addressed coolant performance in both used (Series 1) and factory filled (Series 2) vehicles. Coolant 1 was evaluated in used cars only, while coolant 2 was also tested in used vehicles and selected for a longer term test in new vehicles. Coolant 2 was selected for the longer term test because of improved performance in laboratory tests and in the Series 1 fleet test. GM 6043M is the standard factory fill for the test vehicle and so was used as the control. The fleet test data are shown in Tables 11 and 12.

Solder Protection of Series 1 Fleet Tests—Coolants 1 and 2 were unable to protect high lead solder (Table 11). At 16 000 km the high lead solder specimen in coolant 1 had lost approximately 50% (480 mg) of the solder originally on the specimen. At the end of 48 000 km the specimen was almost completely stripped of solder (947 mg). The performance of coolant 2 was better but still unacceptable. The coolant 2 high lead solder weight loss at 16 000 km was 240 mg and increased to 727 mg by the end of the test. In both coolants the weight losses increased throughout the test. The high lead solder specimens removed from the fleet vehicles were free of the corrosion product observed on the specimens following ASTM D 1384.

After the fleet tests, the radiators were removed from the vehicles, sectioned, and individual

TABLE 11—*Series 1 fleet test weight loss data, mg/specimen.*

km	High Lead Solder	Copper	ASTM Solder	Brass	Steel	Cast Iron	Cast Aluminum
			COOLANT 1				
16 000	480	10	4	6	3	−2	32
32 000	521	8	8	12	4	−2	38
48 000	947	6	6	14	1	−1	100
			COOLANT 2				
16 000	239	11	0	8	0	0	32
32 000	356	6	−2	7	0.5	0	42
48 000	727	8	2	7	6	−2	54

TABLE 12—*Series 2 fleet test weight loss data, mg/specimen.*

km	High Lead Solder	Copper	ASTM Solder	Brass	Steel	Cast Iron	Cast Aluminum
Coolant 2							
19 000	194	42	−0.3	12	−0.3	−1.4	2
38 000	865	48	0.6	18	0.4	−0.6	3
GM 6043M							
19 000	11	44	0.4	9	−0.3	3	0
38 000	126	47	−0.8	13	−0.6	2	0

tubes split open for examination. The inside of the coolant 1 and 2 radiator tubes was coated with a deposit identified as a lead carboxylate by infrared spectroscopy and inductively coupled plasma (ICP) emission spectroscopy. The carboxylate has not been identified. However, it is probably the monoacid given the dependence of high lead solder corrosion on monoacid concentration in ASTM D 1384 tests of coolants A–X. Lead carboxylate in the radiator suggests that the lead corrosion product is soluble in the coolant and can be transported to cool areas where it precipitates.

Coolants 1 and 2 protected ASTM solder well. There was no loss higher than 8 mg for either coolant.

Cuprous/Ferrous Metal Protection of Series 1 Fleet Tests—Coolants 1 and 2 protected the cuprous metals and ferrous metals well.

Aluminum Protection of Series 1 Fleet Tests—The coolant 1 aluminum weight loss at 16 000 km was 30 mg and increased to 100 mg by 48 000 km (Table 11). There was a continued increase in weight loss with no signs of leveling out toward the end of the test. The weight loss was due to general surface corrosion. There was no localized corrosion observed.

Coolant 2 performed slightly better. The initial weight loss was 30 mg. The final weight loss was 54 mg and again showed no sign of leveling off.

Solder Protection of Series 2 Fleet Tests—The longer term fleet test shows similar performance (Table 12). GM 6043M provided better high lead solder protection at 38 000 km with a 126-mg average weight loss. Coolant 2 continued to provide poor protection for high lead solder with solder losses greater than 860 mg.

In this fleet, the high lead solder weight losses were accompanied by very high soluble lead levels. Unlike the Series 1 tests where there was no detectable lead in solution, the 40 000 km chemical analysis for the coolant 2 vehicles showed 70 parts per million (ppm) lead in solution. This level exceeds the EPA limit of 5 ppm and means that this coolant must be disposed as hazardous waste. There was no detectable lead in the GM 6043M samples.

Cuprous/Ferrous Metal Protection of Series 2 Fleet Tests—Cuprous and ferrous metal protection by coolant 2 and GM 6043M was equivalent through 38 000 km.

Aluminum Protection of Series 2 Fleet Tests—The Series 2 test has passed the 38 000-km mark (Table 12). There was no aluminum specimen weight loss with GM 6043M. Coolant 2 had a 3-mg weight loss.

The performance of coolant 2 was much better in the Series 2 fleet than in the Series 1 fleet. There were two major differences between the fleets. One was the age of the vehicles. The second was that deionized water rather than ASTM corrosive water was used in the Series 2 test. The use of deionized water means that there was no chloride present to accelerate aluminum corrosion in the Series 2 fleet. It appears that coolant 2 performance may be a function of the condition of the cooling system and will require more care in the selection of water for dilution. The effect of corrosive ions, such as chloride, on the performance of coolant 2 is being examined in our laboratories.

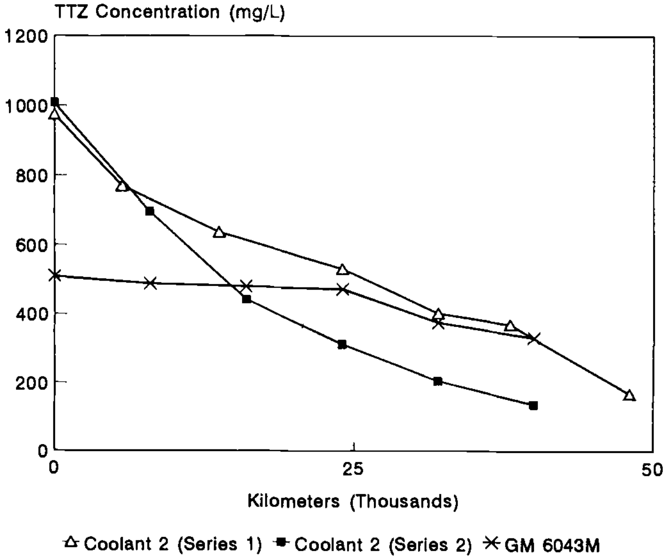

FIG. 2—*Tolyltriazole depletion in fleet tests.*

Inhibitor Depletion—One of the claimed advantages of aliphatic carboxylic acid coolants is that they will have extended service lives compared to current coolants. These claims are based on constant acid levels in solution during testing. It has been confirmed that there is no observable change in the acid concentration during a 48 000-km fleet test. However, constant acid concentration has not meant constant corrosion inhibition throughout the fleet test. Both aluminum and solder weight losses increased throughout fleet tests.

The other major inhibitor in coolants 1 and 2 is tolyltriazole. The tolyltriazole level decreases throughout the course of the test. While a conventional coolant is reported to lose about 10% of the initial charge of tolyltriazole [*21*], organic acid coolants regularly lose 80% of the tolyltriazole in 48 000-km tests (Fig. 2). The depletion rate is higher in factory filled vehicles. In Series 1 tests the coolant 2 tolyltriazole level at 48 000 km was about 21% of the initial level. In the Series 2 tests the coolant 2 tolyltriazole level is below 14% of the original level at 40 000 km (Fig. 2). The tolyltriazole level in the GM 6043M at 40 000 km is 84% of the original level (Fig. 2).

The cause of the tolyltriazole depletion is unknown. One report on tolyltriazole depletion showed that the tolyltriazole lost from solution could be recovered from the metal surfaces or from solid residues [*22*]. The authors concluded that tolyltriazole depletion did occur, but was not due to degradation or chemical reaction. They felt that the tolyltriazole was complexed to metal surfaces or present within residues and corrosion products on the metal surfaces. The observation of depletion only in organic acid coolants suggests that the organic acid plays some role in the depletion.

Conclusion

Selected carboxylic acid formulations have been evaluated in laboratory and fleet tests. The standards by which they have been judged are ASTM D 3306 and comparisons with GM 6043M.

Experimental design sets tested in ASTM D 1384 gave a good overview of the ability of aliphatic monoacids and diacids to protect common cooling system metals. Aggressive behavior of octanoic and 2-ethylhexanoic acid toward solder was observed in these tests. Cuprous metal protection was good. The design sets suggested that minimum levels of the acids must be exceeded before aluminum and cast iron were adequately protected.

Design set results were used to select coolants for further testing. Coolant 1 was a combination of octanoic acid and 1,10-decanedioic acid. Coolant 2 was a combination of 2-ethylhexanoic acid and 1,10-decanedioic acid. Of these two, coolant 2 offered better performance in both laboratory and fleet testing and was selected for further testing. Coolant 1 would not meet ASTM D 3306 standards because it failed ASTM D 4340.

ASTM D 4340 showed that mixtures of coolant 2 and silicate containing aftermarket coolants gave unusually high aluminum corrosion rates. The exact mechanism for the corrosion has not been determined, but it is thought that coolant 2 is not able to overcome the corrosive effects of very low levels of conventional corrosion inhibitors. It is not known whether this corrosion will be observed in vehicles with mixed coolants but mixing effects should be studied in vehicles.

Fleet testing of coolants 1 and 2 showed several interesting effects. There was continued aggressive behavior toward high lead solder. Tolyltriazole depleted from solution prematurely. Despite the loss of tolyltriazole from solution, cuprous metal protection remained good. Finally, a comparison of the aluminum protection by coolant 2 in the Series 1 and 2 fleet tests showed differences. This could be attributed to the age of the vehicle, the type of vehicle, or to the absence of corrosive ions in the Series 2 fleet. All of these have implications in the use of coolant 2 in the aftermarket where vehicle age, type, and water quality cannot be controlled by the coolant manufacturer.

Acknowledgments

The author thanks Angela L. Gelsi for preparing all of the coolants and running the laboratory tests described in this paper. I also thank the Applications Engineering and Analytical Groups of First Brands Corporation for their expert work.

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DISCUSSION

J. M. Burns[1] *(discussion question)*—How many vehicles were used in each fleet test?

W. C. Mercer (author's response)—In the Series 1 test there were two vehicles used to test coolants 1 and 2 and five vehicles for coolant 3. In the Series 2 tests, 5 vehicles were used for coolant 2 and GM 6043M.

J. M. Burns[1] *(discussion question)*—Were the same vehicles used in more than one test?

W. C. Mercer (author's response)—The Series 1 vehicles were used for more than one test. The Series 2 vehicles are used once.

J. M. Burns[1] *(discussion question)*—Were the fleet tests run in parallel or series, if the same vehicles were used?

W. C. Mercer (author's response)—The Series 1 fleet tests were run in series.

J. M. Burns[1] *(discussion question)*—How were the cooling systems prepared? Was oxalic acid used as is recommended in ASTM Practice for Testing Engine Coolants in Car and Light Truck Service (D 2847)?

W. C. Mercer (author's response)—The cooling systems for tests of coolant 1 and 2 were water washed between tests. Series 2 fleet vehicles were factory filled.

J. M. Burns[1] *(discussion question)*—Was the lead carboxylate precipitate that was found positively identified as a product formed by the carboxylic acids used in the formulation, or could it have been composed of the degradation products of ethylene glycol, such as glycolic acid, formic acid, or acetic acid, or a cleaning agent such as glycolic acid?

W. C. Mercer (author's response)—It was not conclusively identified as caused by the monoacid salt. However, coolants using only diacids do not cause high lead solder corrosion. Therefore, there are no precipitates seen in the radiators. It is unlikely that the observed product could be a result of glycol degradation products. For this to be the case, ethylene glycol degradation would have to be much higher in the coolants with monoacids than in traditional coolants. There were no unusual levels of glycol degradation seen with any of the coolants.

J. M. Burns[1] *(discussion question)*—Were any lead solder alloys, other than the two standard ASTM test coupon materials, tested to determine if the acids were actually detrimental to lead in general?

W. C. Mercer (author's response)—No.

J. M. Burns[1] *(discussion question)*—How were the experimental formulations of those tested developed? Were they subjected to any type of strategy of formulation?

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[1] Texaco Chemical Company, 7114 Lamar Blvd., Austin, TX 78752.

W. C. Mercer (author's response)—Coolants 1 and 2 were selected for fleet testing based on the ASTM D 1384 results with coolants A–L and M–X, respectively. The acid levels used in coolants A–L and M–X cover a wide range of the concentrations available to a coolant formulator. The use of an experimental design like that used for coolants A–X allows the formulator to explore many combinations quickly. The chemist can extrapolate from observed performance to expected performance within the range tested.

J. M. Burns[1] *(discussion question)*—Do you have any data from compatibility testing with Japanese engine coolant formulations?

W. C. Mercer (author's response)—Compatibility is assumed based on the absence of reported problems despite extensive mixing in the aftermarket. We do not have ASTM D 4340 results for combinations other than the ones discussed in the paper.

J. M. Burns[1] *(discussion question)*—What was the standard deviation of the losses reported on the lead solder coupons?

W. C. Mercer (author's response)—A maximum standard error (95%) of plus or minus 15% of the mean weight loss was observed for the high lead solder coupons.

J. M. Burns[1] *(discussion question)*—What was the effect of the cleaning method used for the lead solder and aluminum coupons on the weight loss?

W. C. Mercer (discussion question)—Since the alternate cleaning procedure removed corrosion product from the high lead solder coupons, the weight loss was higher following this procedure. This weight loss represents the true weight loss since the layer is a corrosion product and not a protective layer. There was no effect of this procedure on specimens from tests of traditional coolants or on virgin specimens.

All aluminum specimens were cleaned by the same procedure. It is not anticipated that the aluminum cleaning procedure affects specimens from one type of coolant and not another.

J. M. Burns[1] *(discussion question)*—Data were presented that indicated that many consumers neglect their cooling systems. It was stated that as much as 35% of the U.S. fleet have moderate to heavy rust in the engine blocks and heads while up to 41% of the U.S. fleet have heavy to moderate sediment in the cooling systems from corrosion products and inhibitor dropout such as silica gel. In your opinion, would an engine coolant with a longer service life and less required consumer maintenance reduce these problems and provide the consumer with a more reliable product?

W. C. Mercer (author's response)—First, there was no indication in the reference that any of the sediment was due to inhibitor dropout. There were some sources of sediment identified: core sand, corrosion products, water impurities, stop leak particles, and incompatible additives.

Use of coolant beyond its service life was only one of the problems identified in that survey. Others identified included operation with less than 1 in. (25.4 mm) of coolant in the overflow bucket and coolant concentration well below 50%. Neither of these issues will be addressed by a coolant with a longer service life. In fact, coolants 1 and 2 will perform worse than standard coolants under these conditions. This was clearly shown in the Series 1 fleet tests.

There was no indication in the survey that consumers recognize the recommended change interval and ignore it. The more general attitude is that consumers have the freeze protection checked. If acceptable, the cooling system is ignored. I do not think that a longer life coolant would reduce consumer neglect. Education would reduce consumer neglect. Coolant suppliers and the automotive manufacturers need to convince consumers that corrosion protection is important. All coolants have a service life. Use beyond that service life will damage engines.

D. Miller[2] *(discussion question)*—If the formulations were not properly optimized, then this would explain the observation of high aluminum weight losses. Were the formulations optimized? If so, by what method were they optimized?

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[2] Texaco Chemical Company, P.O. Box 15730, Austin, TX 78761.

W. C. Mercer (author's response)—Coolants 1 and 2 were selected for fleet testing based on ASTM D 1384 results with coolants A–L and M–X, respectively. The acid levels used in coolants A–L and M–X cover a wide range of the concentrations available to a coolant formulator. They should give an idea of the chances for optimization of these fluids. I do not think these coolants will provide the balance of properties required for an optimized coolant.

D. Miller[2] *(author's response)*—Was synergism observed between the monoacid and the diacid?

W. C. Mercer (author's response)—Coolants D, H, and K had monoacid/diacid ratios identified in the literature as synergistic. There was no synergism observed with these coolants in the ASTM D 1384 testing. There was a potential interaction between the 2-ethylhexanoic acid and the 1,10-decanedioic acid observed in coolants M–X. The net effect of the interaction was to make aluminum corrosion higher than expected. This could be described as a negative synergism.

D. Miller[2] *(discussion question)*—How many cars were included in the fleet test? What are the statistics (range and standard deviation) for the data obtained from the fleet tests?

W. C. Mercer (author's response)—In the Series 1 test there were two vehicles used to test coolants 1 and 2 and five vehicles for coolant 3. In the Series 2 tests, 5 vehicles for coolant 2 and GM 6043M. Data from coolant 2 tests are presented as examples of the data obtained in fleet tests (Table 1).

D. Miller[2] *(discussion question)*—When comparing tolyltriazole (TT) depletion from the carboxylic acid coolant to GM 6043M, it should be pointed out the GM 6043M contains mercaptobenzothiazole (MBT). Since MBT provides protection to essentially the same metals as TT, the presence of MBT would likely affect the depletion rate of TT. Furthermore, the initial TT concentrations in the two coolants are very dissimilar. The carboxylic acid coolant starts with twice the concentration of TT as GM 6043M. An initially rapid depletion of high TT concentrations is commonly observed in many coolants. Any claims regarding suspected copper and brass protection for these metals was not included in the presentation.

W. C. Mercer (author's response)—It has been our experience that tolyltriazole in traditional North American coolants remains at very high percentages of the initial level. This is true whether mercaptobenzothiazole is present or not. We have not seen traditional North American coolants with high levels of TT show an initial rapid depletion. The rapid loss of TT from solution is a property of the carboxylic acid coolants. As stated in the text, the use of cuprous metal protection has been adequate so far. It is still not clear that coolants with very low levels of cuprous metal inhibitors will protect these metals in the long term. This question has yet to be answered.

D. Miller[2] *(discussion question)*—If the carboxylic acid coolants are corrosive to lead through complexation, then why do they protect 70/30 solder? ASTM D 1384 tests that we have performed show that 70/30 solder is still protected by carboxylic acids even when the

TABLE 1—*Data from coolant 2 test.*

Parameter	High Lead Solder	Copper	ASTM Solder	Brass	Steel	Cast Iron	Cast Aluminum
		SERIES 1 (48 000 KM)					
Mean	727	8	2	7	6	−2	54
High	785	12	6	8	20	−4	71
Low	685	4	−2	6	−3	−1	45
		SERIES 2 (38 000 KM)					
Mean	865	48.3	0.6	17.6	0.4	−0.6	3.3
Std error (95%)	117	5.0	7.4	2.5	0.6	1.0	1.2

high lead solder coupon is not included. ASTM D 2570 simulated service testing of carboxylic acid coolant, meanwhile, even shows excellent protection of high lead solder. Therefore, the conclusion that carboxylic acids attack lead appears to be incorrect. Could there be another reason for high lead solder corrosion?

W. C. Mercer (author's response)—As shown in the text, octanoic acid corrodes high lead solder and ASTM (70/30) solder when both are present in the specimen bundle. 2-ethylhexanoic acid corrodes high lead solder. In our laboratories, high lead solder corrosion with coolants 1 and 2 is very high in all tests except engine dynamometer tests. In the dynamometer tests, high lead solder corrosion is moderate and ASTM solder corrosion is very high. Complexation is the most likely reason as monoacid salts of lead have been identified in fleet vehicle radiators.

D. Miller[2] *(discussion question)*—Although you have stated that existing coolant formulations are fully compatible with each other, no data to support this were presented. What are the ASTM D 4340 results for a Japanese nonsilicate coolant combined with an American silicate coolant? What about other types of combinations? Meanwhile, carboxylic acid formulations have been used in Europe for more than two years without any reported compatibility problems.

W. C. Mercer[2] *(author's response)*—Compatibility is assumed based on the absence of reported problems despite extensive mixing in the aftermarket. We do not have ASTM D 4340 results for combinations other than the ones discussed in the paper. Since the carboxylic acid formulations currently used in Europe are very similar to the coolants already in use, it is not surprising there have been no problems reported.

E. McWilliams[3] *(discussion question)*—Was analysis of voluminous ppt in heat done by aluminum test ASTM 4340? Was analysis of corrosion blacked during testing done?

W. C. Mercer (author's response)—We have generally attributed black aluminum corrosion to oxides, but have seen high carbon levels with auger analysis.

D. Berg[4] *(discussion question)*—What analytical method was used to determine the concentrations of tolyltriazole (TTZ) in your work?

W. C. Mercer (author's response)—We use a Dionex ion chromatograph with an ALC-18 column.

J. A. Lima[5] *(discussion question)*—Bill, you speak as though "long life" coolants are already available using silicone/silicate technology. If this is true, could you comment on any advantages the aromatic carboxylates, as found in many current European formulations, may have over aliphatic carboxylates, or over current North American coolants?

W. C. Mercer (author's response)—We have not evaluated the performance of coolants that use aromatic carboxylic acids.

J. P. Maes[6] *(discussion question)*—Dr. Mercer, can you please comment on the size of the fleet, namely, the numbers of vehicles used in your fleet test?

W. C. Mercer (author's response)—The fleet tests were run in 2 Plymouth Voyagers and 5 Pontiac Grand Prix for each coolant.

J. P. Maes[6] *(written discussion)*—Your presentation alleges concerns about the ability of monobasic/dibasic acid coolant technology to protect aluminum and soldered copper/brass radiators. In Europe, optimized monobasic/dibasic acid coolants that contain the acids mentioned in your presentation have been the subject of qualification testing by a major car manufacturer. The coolants were fleet tested over 100 vehicles, for up to 100 000 miles (160 930

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[3] Caterpillar, 100 N.E. Adams St., Peoria, IL 61614.

[4] Mobay Corporation, Mobay Road, Building 14, Pittsburgh, PA 15205.

[5] Houghton Chemical Corporation, Allston, MA.

[6] Texaco Research and Development—Ghent, John Kennedylann 31, B9042 Ghent, Belgium.

km) and time periods of four years. Included in this fleet were a number of vehicles fitted with copper/brass radiators. The others were fitted with aluminum radiators. At no stage in the fleet testing program were there any reported problems related to radiator corrosion. Likewise, all radiators examined at the end of test were totally compatible with the manufacturers' sign-off criteria. In summary, monobasic/dibasic acid coolants have been qualified by a major European car manufacturer after exhaustive laboratory testing and four-year fleet testing with no concerns on aluminum, solder, or copper/brass corrosion and no reported problems over two years of in-service use throughout all plants of this manufacturer.

Norman C. Adamowicz[1] *and Daniel F. Falla*[2]

Fleet Test Evaluation of Engine Coolants Using Sebacic Acid Inhibitor Technology

REFERENCE: Adamowicz, N. C. and Falla, D. F., "**Fleet Test Evaluation of Engine Coolants Using Sebacic Acid Inhibitor Technology,**" *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 63–82.

ABSTRACT: A three-year, twelve-car municipal fleet test was conducted to compare the relative merits of an extended life sebacic acid coolant and current high silicate alkaline phosphate coolant used in North America. The test was conducted under rigidly controlled conditions in accordance with ASTM Practice for Testing Engine Coolants in Car and Light Truck Service (D 2847).

This paper will show the (1) depletion rates for chemical inhibitors used in the coolants and (2) actual photographs of cooling system component parts removed from the vehicles at the termination of this test.

KEYWORDS: fleet, sebacic, phosphate, corrosion, aluminum, inhibitors, silicate, depletion, radiators

Background

Current high silicate alkaline phosphate engine coolants were developed in the early 1980s to especially protect new aluminum cooling system components against corrosion. These particular components and the type of corrosion are as follows:

1. Cast aluminum:
   - Cylinder head—hot surface corrosion.
   - Water pump—cavitation corrosion.
   - Thermostat housing—cavitation corrosion.
2. Wrought aluminum:
   - Radiator—hot surface corrosion deposits and tube pitting.
   - Heater core—header plate surface corrosion and header plate crevice corrosion.

Continued protection for all other metals previously used in the cooling system is also required. The newly developed inhibitor package was successful in preventing all metallic corrosion in vehicle cooling systems.

Rationale for a World Wide Engine Coolant

There are numerous styles of chemical inhibitor packages used successfully with ethylene glycol world wide. However, the mixing of different styles may accelerate the long-term cor-

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[1] Design engineer, Ford Motor Company, 21500 Oakwood Blvd., Dearborn, MI 48121.
[2] Development chemist, Dow Chemical Canada, Inc., Sarnia, Ontario, Canada.

rosion rate of metals. With the advent of increased trans-oceanic shipment of cars and trucks it became important to find a common coolant inhibitor technology.

Sebacic acid corrosion inhibitor technology (designated as AL-39) [*1*] was developed by the British National Physical Laboratory [*2*] for use by the British Military in a variety of vehicles world wide using a wide range of water quality.

Preliminary confidential test results conducted by the British National Physical Laboratory, the British Military, and by Ford of England, indicated that this new technology had the following potential advantages over high silicate alkaline phosphate inhibitors:

- Reduced hot surface corrosion of aluminum cylinder heads.
- Reduced heat transfer corrosion deposits in radiators.
- Reduced engine hot spot scale deposits that influence heat transfer efficiency.
- Low depletion rate of inhibitors.
- Extended coolant change intervals to lessen the environmental impact and reduce the cost of ownership.

Development Issues

Sebacic acid is made by processing the oils extracted from the castor bean. It is a commodity material controlled by the Brazilian government and other third world countries. As such, the 4.5% concentration defined by the AL-39 formulation is too expensive for commercial use. Formulations were, therefore, developed that substituted other dibasic or monobasic acids for a portion of the sebacic acid. Additives such as these are referred to as extenders or extender acids.

As a further cost reduction it was decided to reduce the number of component chemicals in the inhibitor package to the fewest number required to provide total metallic corrosion protection. The sequence of tests conducted below were conducted satisfactorily and confirmed that these changes were viable.

- ASTM D 1384, Test Method for Corrosion Test for Engine Coolants in Glassware.
- ASTM D 4340, Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat Recycling Conditions.
- Ford Motor Company Simulated Service Corrosion Test for Aluminum Radiator.
- Ford Laboratory Test Method BL 2-2, Engine Dynamometer Test.

The inhibitor package was then made up as follows:

- Total acids (sebacic acid and dodecane dioic acid).
- Tolyltriazole (TTZ).
- Silicate.
- Buffer.

Accordingly, this is a simpler formulation than trying to balance the seven or eight components of a typical alkaline phosphate coolant.

Fleet Testing

Fleet testing is difficult to do (at best) for these reasons:

- Locating a facility that agrees to test parts at no charge to you and allows you to disrupt their work week.

- The knowledge that you may lose 40% of your test cars to accidents.
- Campaigned vehicles that further eliminates test cars.
- Accidental contamination with other coolants.
- Re-assignment of vehicles to other locations.
- Stolen cars.
- Change in fleet management.
- Lost coolant samples.

Before this test, five fleets containing a total of 173 cars were lost for the reasons above. Of these 173 cars, only three cars survived uncontaminated to 60 000 miles (96 558 km).

The fleet test discussed in the paper was headquartered in Martinez, CA. Vehicles were 1986 1.9L Escorts owned and maintained by the municipality of Contra Costa County. This county is northeast of San Francisco Bay, has an arid climate, and is moderately hilly. Each car is assigned to one building inspector who may be required to access remote locations within the county. Consequently, these vehicles undergo severe service. As the vehicles were not new when the test started, the following new parts were installed in accordance with ASTM Practice for Testing Engine Coolants in Car and Light Truck Service (D 2847):

- Cylinder head.
- Cylinder head gasket and bolts.
- Water pump.
- Timing belt.
- Radiator.
- Radiator cap.
- Top radiator hose.
- Bottom radiator hose.
- Radiator hose clamps.

Full flow brass pots capable of holding two ASTM metal coupon specimen bundles were also installed in the top hose of four vehicles: three pots in test coolant vehicles and one in an original equipment manufacturer (OEM) coolant vehicle.

All cooling systems were flushed with a commercial power flush system before filling with a 50% solution of either test coolant or OEM coolant. Small initial samples were taken only to measure glycol content as a function of refractive index. The first check point was at one month for all physical and chemical properties. Thereafter the fleet was visited twice per year whenever it was convenient or appropriate for the Test Fleet, Ford Motor Company, and Dow Chemical Company. At those visits the following evaluations were made:

- Visual check of coolant volume in the radiator.
- Sampled coolant and topped-up the coolant level.
- Checked coolant volume stored in vehicle trunk.
- Pressure tested radiator cap and replaced if necessary.
- Inspected cooling system for leaks.
- Changed coupon bundles as appropriate.

This fleet test was terminated after three years service. At that time cylinder heads, radiators, and water pumps were retrieved from six high mileage vehicles (Table 1, Car Nos. 142, 143, 144, 146, 147, and 152).

The cylinder heads were sectioned to examine the coolant jacket passages. Radiators were wind tunnel heat rejection tested to determine any significant loss in heat rejection capacity and then sectioned to examine the tubes, header plates, and gasket troughs for corrosion.

TABLE 1—*Fleet study data summary (normalized to % inhibitor level).*

Date	Miles	DKP (IC)	Moly	TTZ	SI	RA	pH	Sebacic Acid	Dodec Acid
Car 142									
870522	0	100.0	100.0	100.0	100.0	11.00	10.50	0.0	0.0
870615	1 176	89.2	75.0	89.2	52.0	6.45	9.60	0.0	0.0
880609	23 223	43.9		43.9		5.09	8.30	0.0	0.0
880928	30 298	87.7	76.7	87.7	19.3	4.88	8.00	0.0	0.0
890221	41 062	93.8		93.8		4.50	7.80	0.0	0.0
890724	53 965	61.5		61.5		4.24	7.60	0.0	0.0
	67 410	74.6		74.6				0.0	0.0
900521	72 085	61.5	76.7	61.5	14.0			0.0	0.0
Car 143									
870522	0	0.0	0.0	100.0	100.0	6.00	8.40	100.0	100.0
870615	1 408	0.0	0.0	109.3	45.0	4.68	8.10	140.0	97.9
880610	16 457	0.0	0.0	70.7		3.10	7.30	111.4	89.0
880928	21 216	0.0	0.0	70.0	32.0	3.10	7.10	102.4	91.8
890221	26 168	0.0	0.0	68.0		4.90	7.10	112.9	97.0
890724	33 556	0.0	0.0	62.7		4.40	7.00	109.7	97.0
	47 086	0.0	0.0	68.0				113.7	106.6
900521	58 168	0.0	0.0	62.7	18.7	5.40	6.60	105.2	95.6
Car 144									
870522	0	0.0	0.0	100.0	100.0	6.00	8.40	100.0	100.0
870615	1 227	0.0	0.0	103.3	50.7	4.62	8.10	124.3	97.9
880610	19 738	0.0	0.0	58.7		3.00	7.10	100.6	83.6
880928	26 111	0.0	0.0	56.0	22.7	3.07	7.10	101.9	86.3
890221	33 086	0.0	0.0	66.0		4.70	7.00	112.4	98.3
890724	41 397	0.0	0.0	60.0		4.20	7.00	107.6	96.9
	52 666	0.0	0.0	64.0		5.30	6.60	126.9	113.6
900130					10.7				
Car 145									
870522	0	0.0	0.0	100.0	100.0	6.00	8.40	100.0	100.0
870615	1 130	0.0	0.0	104.0	42.7	4.62	8.10	142.6	98.4
880610	9 524	0.0	0.0	74.0		3.08	7.50	132.5	91.5
880928	11 444	0.0	0.0						
890221	13 410	0.0	0.0	72.0		4.40	7.30	111.5	96.9
890724	15 760	0.0	0.0	72.0		4.30	7.20	113.2	95.8
	18 749	0.0	0.0	84.0	13.2			111.5	112.6
900521	25 470	0.0	0.0	78.0	12.0	5.90	6.90	109.0	107.0

NOTE: 1 mile = 1.6 km.

Water pumps were examined for corrosion damage using an optical microscope having a magnification of X30. The coolant was analyzed using instrumental and wet methods well known in the industry.

The available analytical data were normalized for inhibitor levels and are presented in Tables 2, 3, and 4. This normalized data were also graphed as a function of mileage for all cars (Figs. 1 to 7).

Discussion: Inhibitor Depletion

If we first examine the two OEM coolant control vehicles, two discrepancies are noted. Data from Vehicle 142 (Fig. 1) is very erratic for TTZ throughout the test perhaps because of analytical error. The silicate does not deplete as much as expected during the initial stage but does level off at approximately 20%. The dipotassium phosphate (DKP) depletion is near normal. There is no accounting for these behaviors except to speculate that perhaps this vehicle

TABLE 2—*Fleet study raw data summary (normalized to % inhibitor level).*

Date	Miles	DKP (IC)	Moly	TTZ	SI	RA	pH	Sebacic Acid	Dodec Acid
Car 146									
870522	0	0.0	0.0	100.0	100.0	6.00	8.40	100.0	100.0
870615	1 362	0.0	0.0	97.3	48.0	4.70	8.10	107.4	102.1
880610	14 900	0.0	0.0	...	...	...	...	...	...
880928	27 993	0.0	0.0	55.3	29.3	3.01	7.00	97.5	89.8
890221	35 516	0.0	0.0	66.0	...	4.50	7.00	97.5	88.0
890724	43 447	0.0	0.0	60.7	...	4.30	7.00	103.1	95.0
900521	55 009	0.0	0.0	58.7	...	5.40	6.50	86.7	86.8
Car 147									
870522	0	0.0	0.0	100.0	100.0	6.00	8.40	100.0	100.0
870615	1 063	0.0	0.0	110.0	44.0	4.70	8.10	104.3	101.8
880610	15 589	0.0	0.0	72.4	...	3.20	7.30	112.9	93.9
880928	19 051	0.0	0.0	71.1	16.0	3.20	7.20	106.7	91.1
890221	24 426	0.0	0.0	68.7	...	4.60	7.10	101.4	97.7
890724	30 924	0.0	0.0	63.0	...	4.90	7.10	106.4	99.9
900521	35 524	0.0	0.0	74.5	14.7	...	...	118.6	114.9
...	40 213	0.0	0.0	64.5	...	4.80	6.70	127.4	98.1
Car 148									
870522	0	100.0	100.0	100.0	100.0	11.00	10.50	0.0	0.0
870615	1 399	99.2	76.7	46.2	22.7	6.30	9.20	0.0	0.0
880610	12 767	91.9	...	49.5	...	5.20	8.70	0.0	0.0
880928	19 094	92.7	78.7	41.1	24.4	4.80	8.30	0.0	0.0
890221	26 780	83.1	...	46.0	...	4.40	8.10	0.0	0.0
890724	34 796	89.0	...	32.9	...	4.00	7.70	0.0	0.0
900521	44 181	88.2	62.6	31.4	17.4	3.90	7.30	0.0	0.0
Car 149									
870522	0	0.0	0.0	100.0	100.0	6.00	8.40	100.0	100.0
870615	932	0.0	0.0	96.0	36.0	4.90	8.20	99.7	97.1
880610	15 375	0.0	0.0	66.0	...	2.90	7.10	117.8	93.7
880928	19 085	0.0	0.0	64.2	34.7	2.90	7.00	103.5	87.6
890221	23 822	0.0	0.0	80.4	...	4.10	6.90	100.9	92.6
890724	29 887	0.0	0.0	63.1	...	3.70	6.80	97.6	92.6
900130	37 346	0.0	0.0	63.1	30.7	...	...	104.1	121.6
900516	41 882	0.0	0.0	67.8	28.0	4.60	6.40	97.0	101.6

NOTE: 1 mile = 1.6 km.

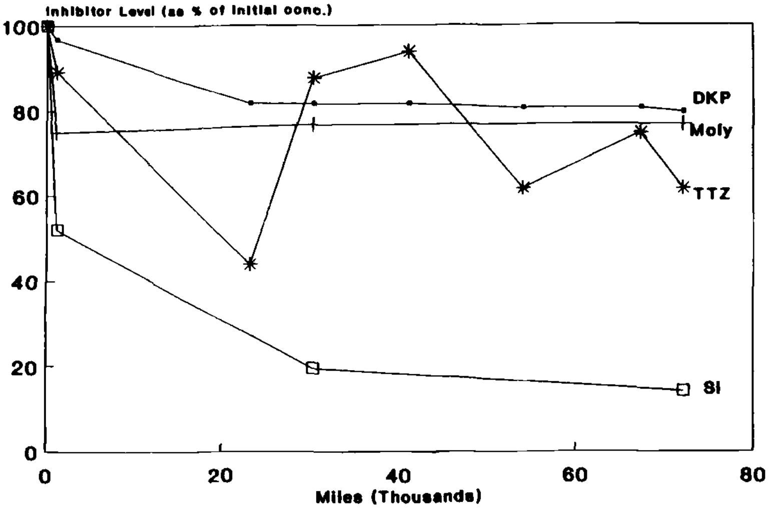


FIG. 1—*Inhibitor depletion versus mileage for Car 0142.*

TABLE 3—*Fleet study raw data summary (normalized to % inhibitor level).*

Date	Miles	DKP (IC)	Moly	TTZ	SI	RA	pH	Sebacic Acid	Dodec Acid
CAR 150									
870522	0	0.0	0.0	100.0	100.0	6.00	8.40	100.0	100.0
870615	715	0.0	0.0	103.2	41.3	4.80	8.10	131.7	113.6
880610	6 352	0.0	0.0	75.8	...	3.20	7.40	103.7	97.1
880928	11 750	0.0	0.0	60.9	29.3	3.00	7.10	106.4	97.0
890221	17 989	0.0	0.0	69.4	...	4.40	7.00	117.3	94.3
890724	26 820	0.0	0.0	57.8	...	5.00	7.00	119.7	96.5
	32 572	0.0	0.0	67.5	18.7	4.80	6.60	106.9	107.6
CAR 151									
870522	0	0.0	0.0	100.0	100.0	6.00	8.40	100.0	100.0
870615	957	0.0	0.0	102.7	49.3	4.80	8.20	133.9	95.1
880610	19 750	0.0	0.0	61.8	...	3.30	7.20	114.7	90.5
880928	25 152	0.0	0.0	60.2	16.4	3.40	7.10	103.2	97.5
890221	31 294	0.0	0.0	60.6	...	5.60	7.10	112.5	90.8
890724	39 576	0.0	0.0	55.5	...	4.70	7.00	111.0	88.0
	47 611	0.0	0.0	51.6	10.3	5.20	6.60	98.4	94.9
CAR 152									
870522	0	0.0	0.0	100.0	100.0	6.00	8.40	100.0	100.0
870615	711	0.0	0.0	103.4	33.3	4.90	8.20	133.8	96.1
880610	18 706	0.0	0.0	58.3	...	3.10	7.10	105.7	89.6
880928	25 362	0.0	0.0	55.8	26.7	3.00	7.00	102.0	90.0
890221	31 103	0.0	0.0	54.3	...	4.40	6.90	125.0	90.7
890724	39 551	0.0	0.0	54.3	...	4.20	6.90	113.3	90.7
...	49 831	0.0	0.0	59.8	19.6	...	...	114.9	110.0
...	54 186	0.0	0.0	58.1	...	4.30	6.40	97.3	90.1
CAR 153									
870522	0	0.0	0.0	100.0	100.0	6.00	8.40	100.0	100.0
870615	1 496	0.0	0.0	...	45.3	4.80	8.10	...	...
880610	2 757	0.0	0.0	...	...	3.30	7.40	...	...
880928	24 229	0.0	0.0	...	14.7	3.10	7.10	...	...
890221	31 950	0.0	0.0	55.3	...	4.60	7.10	112.1	93.3
890724	34 670	0.0	0.0	55.3	...	4.80	7.10	112.9	93.3
...	43 301	0.0	0.0	60.8	20.0	...	...	96.7	100.5

NOTE: 1 mile = 1.6 km.

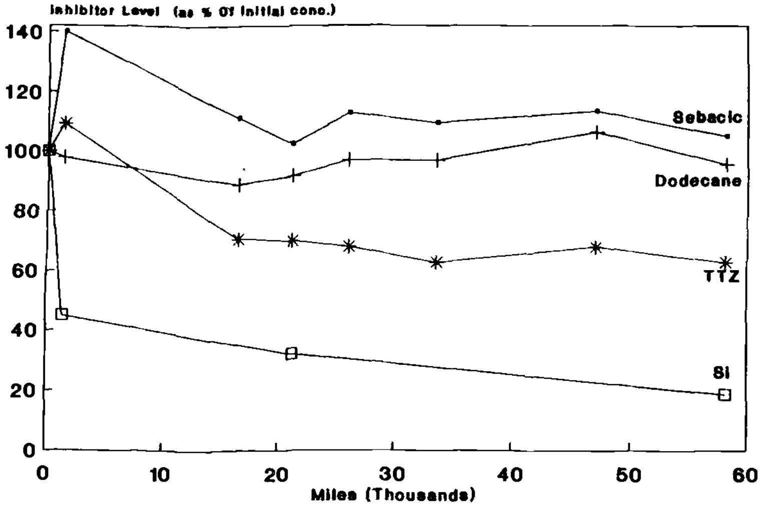


FIG. 2—*Inhibitor depletion versus mileage for Car 0143.*

TABLE 4—*Corrosion data from coupon bundles.*

Miles	Copper	Solder	Brass	Steel	Cast Iron	Aluminum
Car 142						
6889	11.0	1.6	9.7	+0.4	+1.6	3.9
23223	1.0	3.7	2.4	+1.1	+1.9	+0.1
30298	3.5	3.3	6.4	+3.1	+1.5	2.7
60331	1.4	0.7	1.1	+0.9	+1.4	+0.1
73234	1.6	6.4	3.0	+2.5	+5.2	1.2
91354	3.9	5.9	4.3	+6.2	+3.8	+0.6
Car 143						
5832	1.1	1.4	0.8	+0.5	+0.5	0.4
16457	+0.4	0.2	0.3	+1.9	+3.0	+1.8
21216	4.4	3.4	3.6	0.4	0.0	+2.4
47570	1.3	0.0	1.4	+0.7	1.2	0.7
54958	1.7	8.5	1.9	+1.7	+4.3	0.2
79570	5.8	4.6	3.6	1.1	2.3	2.2
Car 145						
5386	1.7	1.6	0.6	+0.5	+1.1	0.3
9524	+1.0	2.2	+1.4	+1.5	+2.3	+2.6
11444	3.4	3.3	2.8	0.6	0.2	3.5
32790	0.8	4.2	0.4	+0.2	+1.7	0.6
35114	1.3	6.1	0.3	+1.9	+3.4	0.2
44850	3.8	6.8	2.6	2.0	2.9	0.7
Car 147						
5433	+0.7	1.6	1.1	+0.7	+0.9	0.2
15569	+0.9	0.7	+1.3	+1.9	+2.6	+1.9
19051	3.6	2.4	3.1	0.7	1.2	2.9
42897	1.3	1.9	4.1	+2.8	7.0	0.8
49395	1.2	18.5	1.1	+1.1	+4.9	1.0
58648	3.3	9.5	2.2	3.2	1.9	1.7
Over Duration of Fleet Study						
Car 142						
72085	25.6	18.7	12.7	1.0	+0.3	4.2
Car 143						
58168	6.6	5.6	8.9	1.3	1.0	4.3
Car 145						
25470	3.0	2.0	3.4	1.2	0.0	0.9
Car 147						
40213	3.1	2.5	4.5	1.2	0.0	2.3

required an addition of coolant during the initial stage. This was not sufficient to disqualify the data for Vehicle 142 as no problems were encountered with it.

Data from Vehicle 148 (Fig. 6) are a near textbook example of inhibitor depletion:

- Rapid silicate depletion during the first 2000 miles (3219 km).
- A 10% depletion of dipotassium phosphate during the course of this test.
- TTZ levels off and remains relatively constant.

Let us note here that when the silicate depletes in this style of coolant, it does not go away [*3*]. Silicate is known to form a molecular film with aluminum and is removed from solution because it has done what it was supposed to do. The remainder of the silicate acts to heal any discontinuities in the film that may occur.

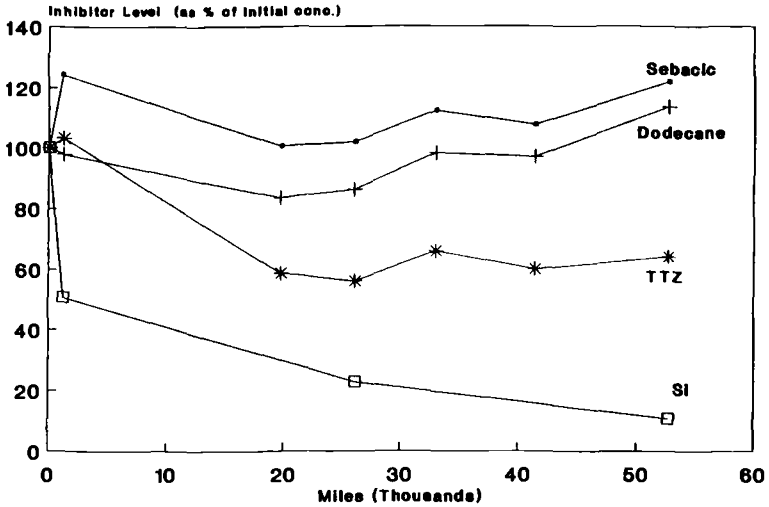


FIG. 3—*Inhibitor depletion versus mileage for Car 0144.*

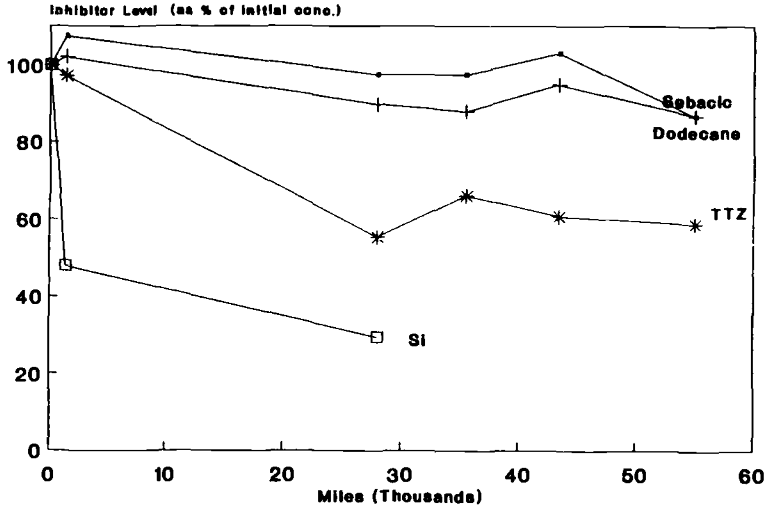


FIG. 4—*Inhibitor depletion versus mileage for Car 0146.*

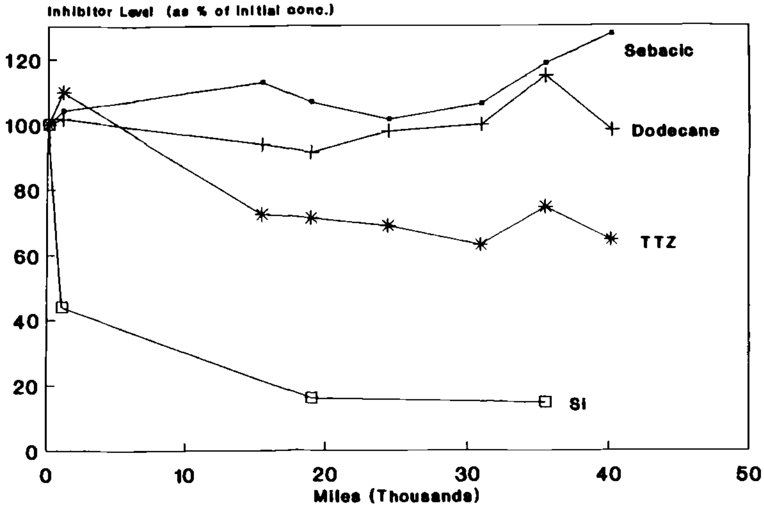


FIG. 5—*Inhibitor depletion versus mileage for Car 0147.*

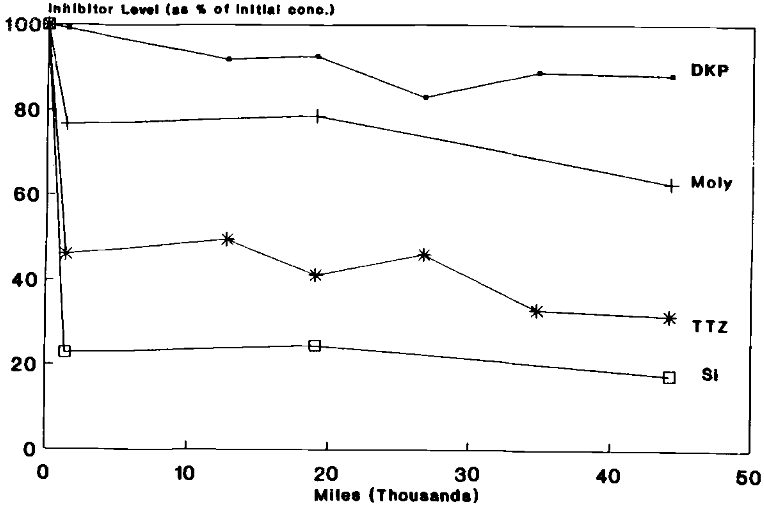


FIG. 6—*Inhibitor depletion versus mileage for Car 0148.*

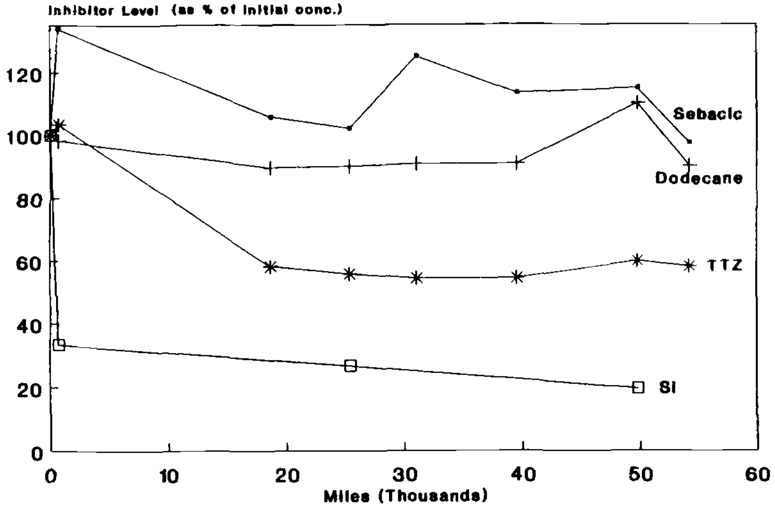


FIG. 7—*Inhibitor depletion versus mileage for Car 0152.*

As to the inhibitor analysis of the test coolant, the author has previously seen examples of a total acids content higher than 100%. What we can infer from this is that the total acids do not deplete significantly during vehicle life. Silicate does again deplete rapidly during the 1st 2000 miles (3219 km) to about 40 to 50% and gradually thereafter. TTZ depletes to 60 to 70% and remains constant thereafter.

Discussion: Metal Coupon Specimen Weight Loss

Let us now judge the metal coupon weight losses against the performance requirements contained in ASTM Specification for Ethylene Glycol Base Engine Coolant, for Automobile and Light Duty Service (D 3306). According to mileage, there is no practical difference between

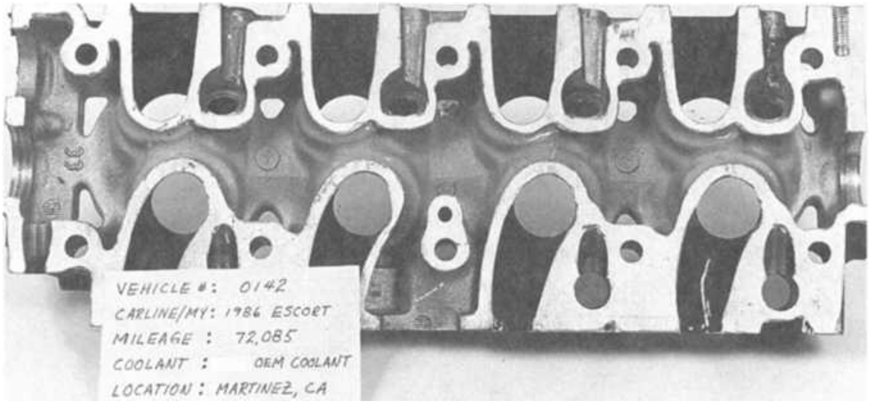
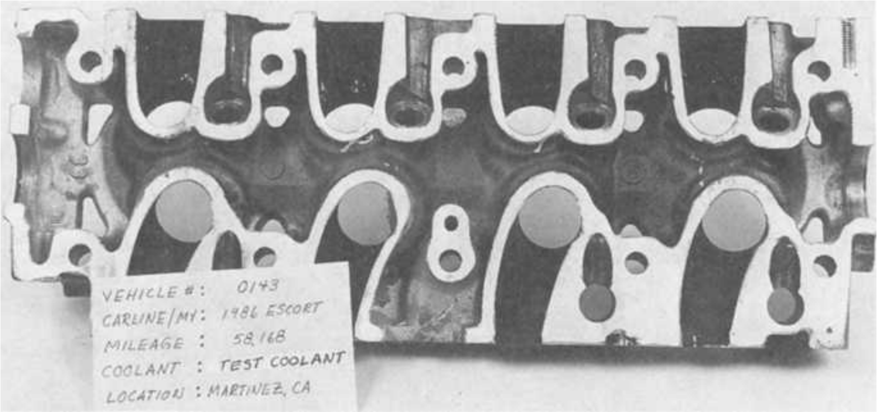


FIG. 8—*Cylinder head cooling jacket of Vehicle 0142.*



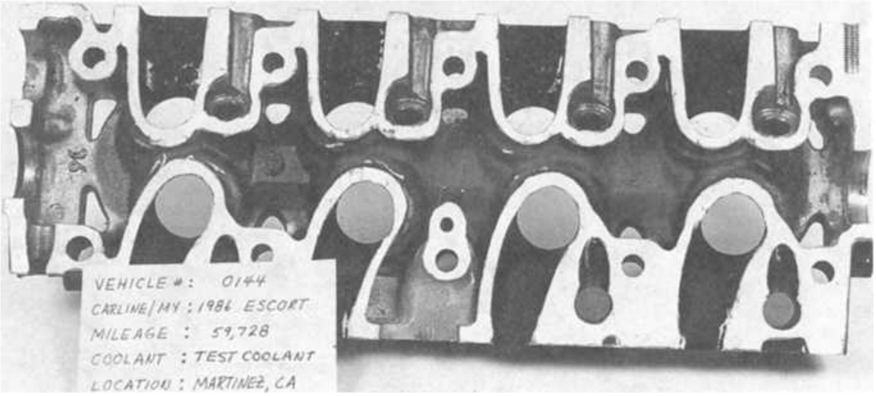
VEHICLE #: 0143
CARLINE/MY: 1986 ESCORT
MILEAGE: 58,168
COOLANT: TEST COOLANT
LOCATION: MARTINEZ, CA

FIG. 9—*Cylinder head cooling jacket of Vehicle 0143.*

the test coolant and the OEM coolant for a loss of aluminum, cast iron, and steel. For solder there is a minor issue that the test coolant may not measure up. For the OEM coolant some slight concern in weight loss occurred during startup for copper and brass but never recurred. With the trend to aluminum heat exchangers that do not use solder, copper, or brass, there is no issue. For the long-term duration, metal coupon weight losses were not considered significant for either coolant.

Cylinder Head Examination

Photographs 8 through 13 show the interior coolant jacket surfaces of the vehicles denoted therein. In Fig. 8 a tan off-white coating covers most of the surface area; this is believed typical of high silicate coolants currently in use. Photos 9 through 13 depict a dark blue black film in the same areas for the test coolant.



VEHICLE #: 0144
CARLINE/MY: 1986 ESCORT
MILEAGE: 59,728
COOLANT: TEST COOLANT
LOCATION: MARTINEZ, CA

FIG. 10—*Cylinder head cooling jacket of Vehicle 0144.*

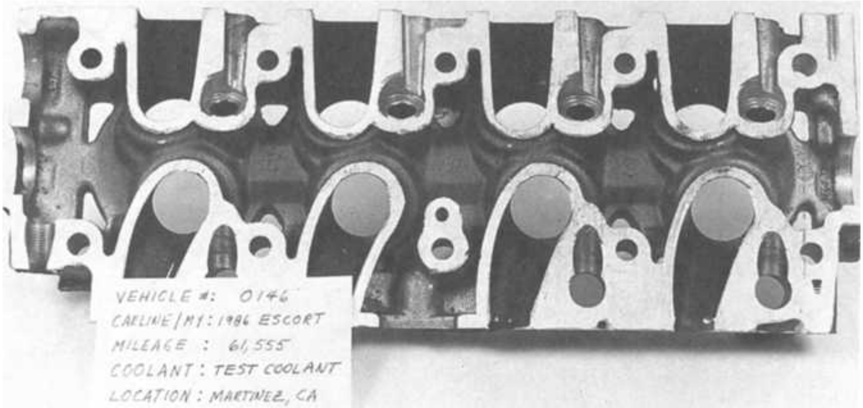


FIG. 11—*Cylinder head cooling jacket of Vehicle 0146.*

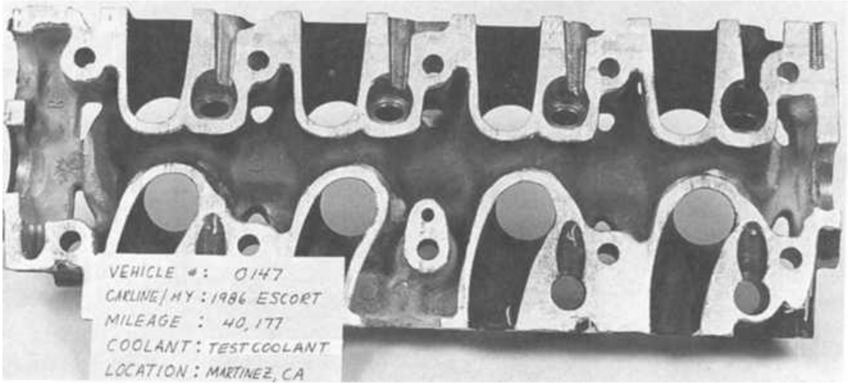


FIG. 12—*Cylinder head cooling jacket of Vehicle 0147.*

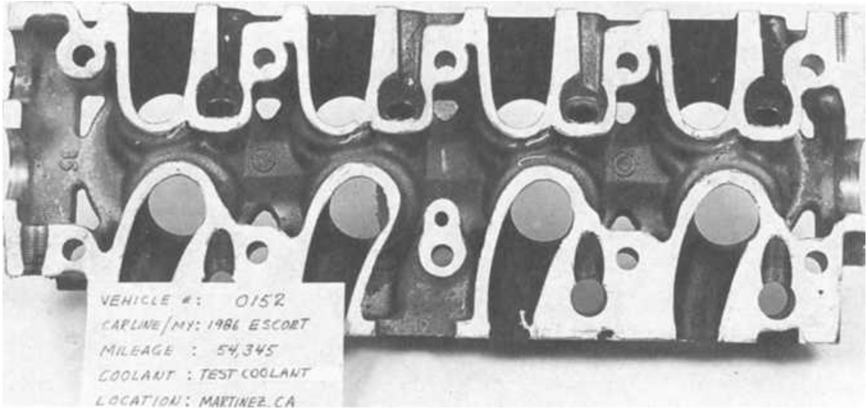


FIG. 13—*Cylinder head cooling jacket of Vehicle 0152.*

TABLE 5—*Chemical analysis of the coatings inside two cylinder head cooling jackets.*

Component	Vehicle 142	Vehicle 146
Aluminum	20	20
Silicon	5	5
Iron	5	0.2
Zinc	3	0.5
Calcium	2	2
Copper	2	0.5
Phosphorus	5	0.2
Potassium	1	0.1
Magnesium	1	0.1
Sodium	0.5	0.2
Manganese	0.5	0.01
Boron	0.2	0.2
Lead	1	0.5
Tin	0.5	0.1

NOTE: *Elemental Composition of Deposits,* approximately % by weight (Emission Spectrographic Analysis of Insolubles).

Emission spectrographic analysis (Table 5) of the coatings from vehicle 0142 and 0146 were composed primarily of aluminum and silicon. Metallographic analysis indicates that the tan off-white coating is particulate in form and unevenly deposited on the surface with a maximum thickness of 0.006 mm. The blue black coating adheres to the surface like a film and extends below the surface with a maximum thickness of 0.002 mm. There is no difference in the microstructure of both cylinder heads in all regions: surface to core in an area with deposit, as well as surface to core in an area without deposit.

Radiator Examination

Figures 14 through 19 depict the interior surfaces of the aluminum radiator cross-flow tubes. All surfaces show a yellow deposit/film, which is likely caused by the presence of TTZ as a corrosion inhibitor. In no case was there any significant deposit worth measuring. The deposits from the OEM coolant appeared heavier. No perforation was noted. Figures 20 through 25 depict the inside surfaces of the aluminum radiator header plates. Again the deposit from OEM coolant appeared heavier. The remaining radiator heat rejection capacity was measured by Climate Control Division of Ford Motor Company and found to above 90% for all radiators.

Water Pump Examination

Visual examination using a X30 optical microscope showed no evidence of erosion or cavitation on interior surfaces. The interior surfaces all evidenced protective coatings that appeared to be of various thickness; pumps from #142, 147, and 152 were thought be to thicker.

Summary

The intent of fleet testing is to evaluate the effect of customer usage upon the durability of a part or a material in comparison to some standard. We believe that this was a good test, well

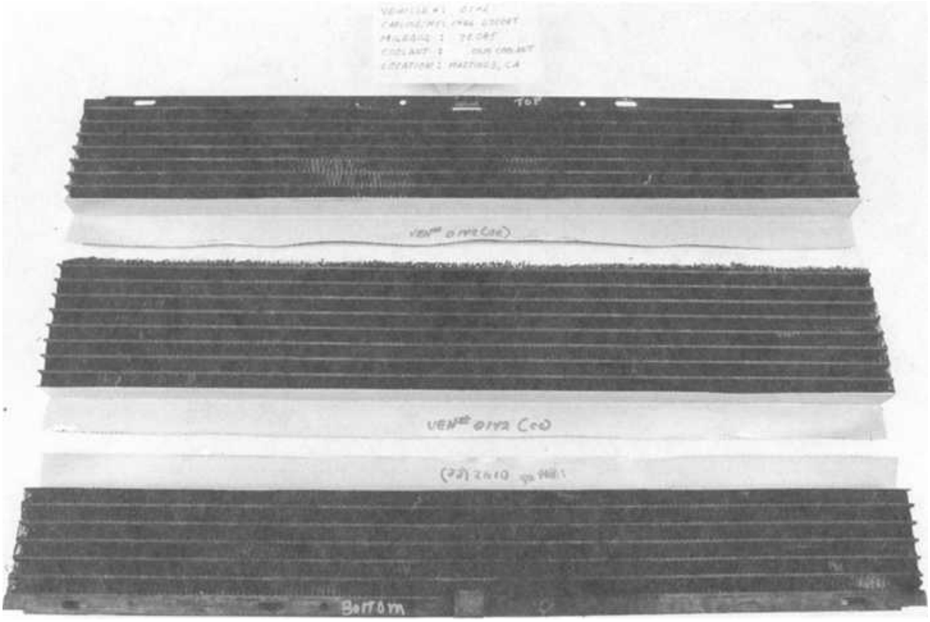


FIG. 14—*Radiator crossflow tubes from Vehicle 0142.*

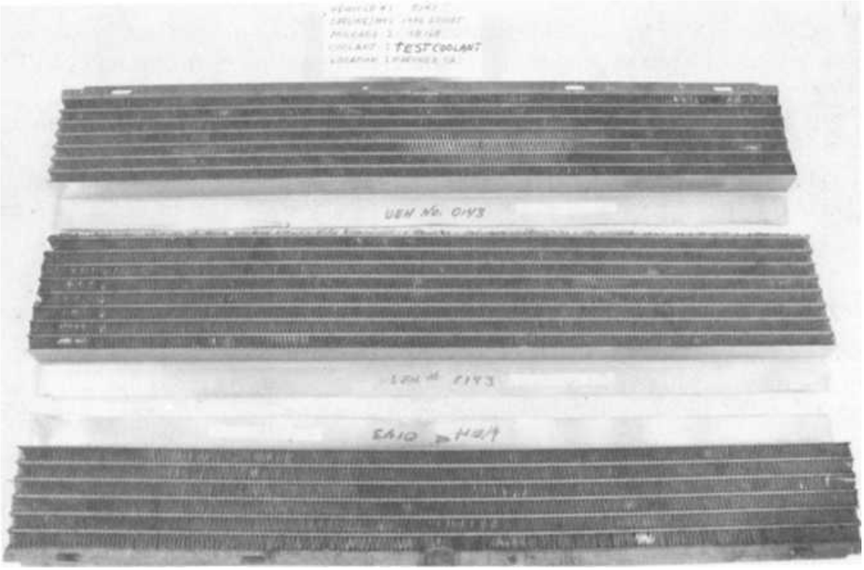


FIG. 15—*Radiator crossflow tubes from Vehicle 0143.*

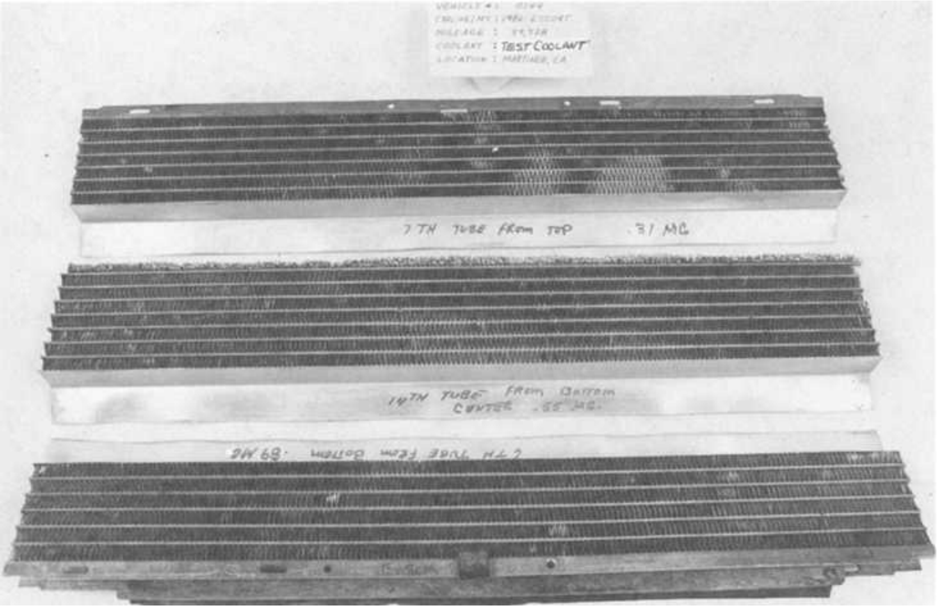


FIG. 16—*Radiator crossflow tubes from Vehicle 0144.*

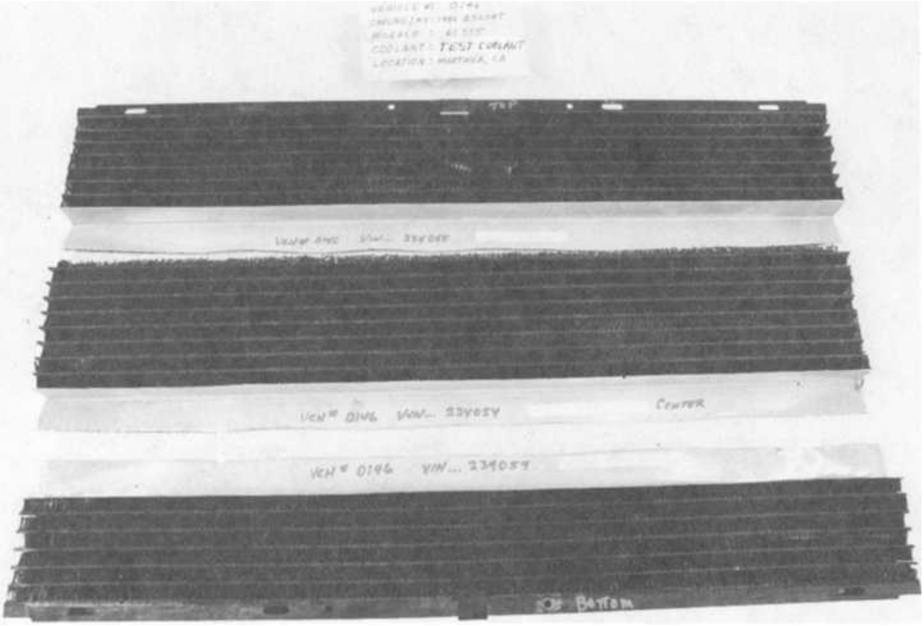


FIG. 17—*Radiator crossflow tubes from Vehicle 0146.*

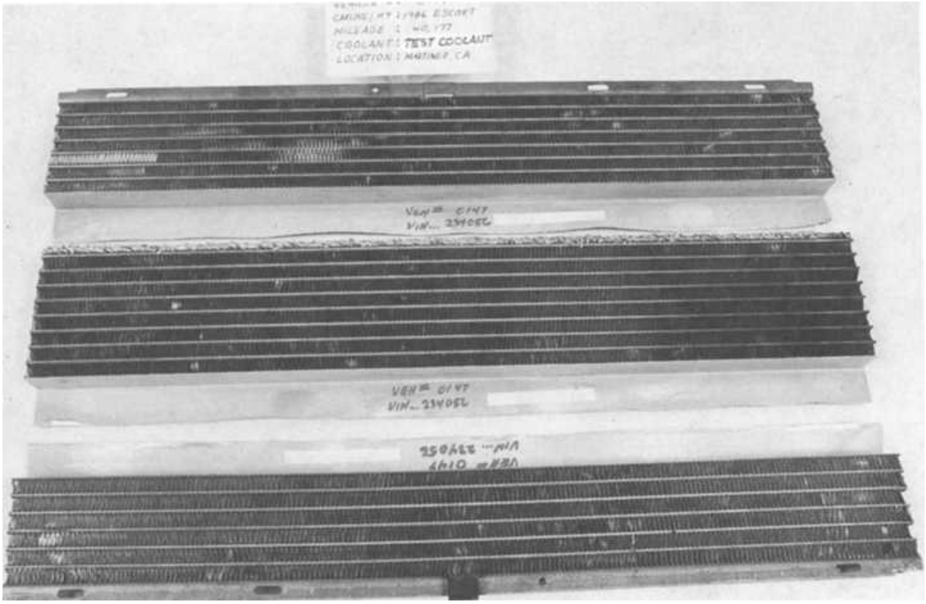


FIG. 18—*Radiator crossflow tubes from Vehicle 0147.*

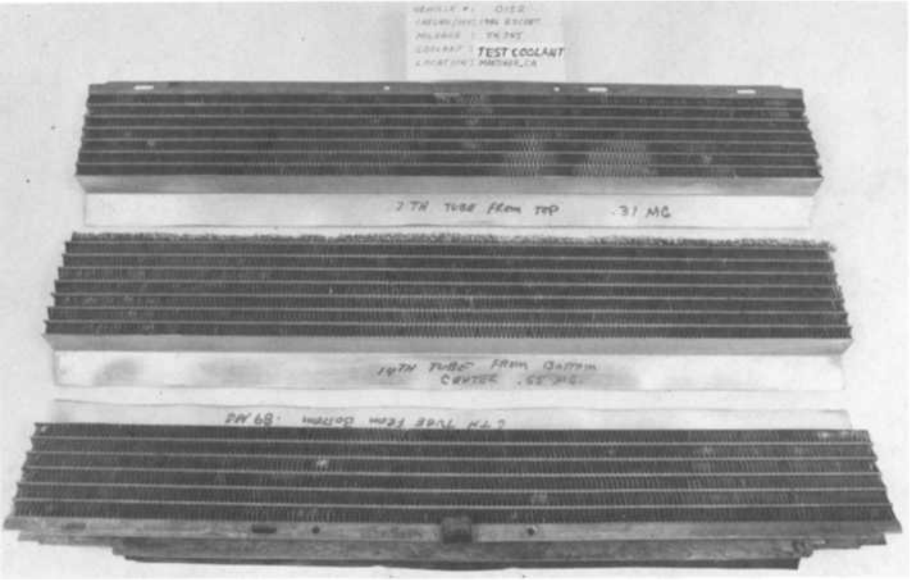


FIG. 19—*Radiator crossflow tubes from Vehicle 0152.*

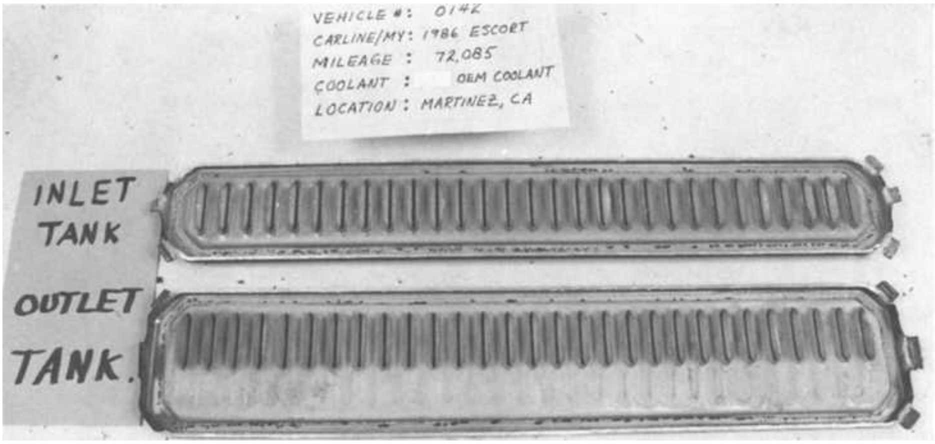


FIG. 20—*Radiator header plates from Vehicle 0142.*

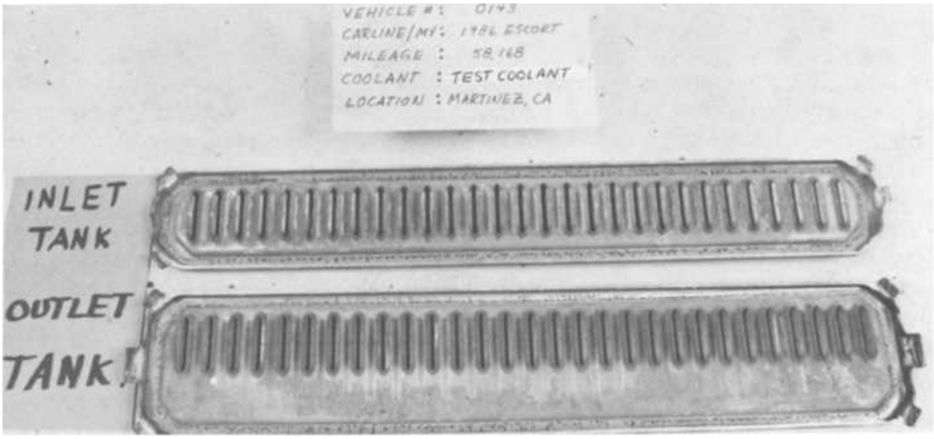


FIG. 21—*Radiator header plates from Vehicle 0143.*

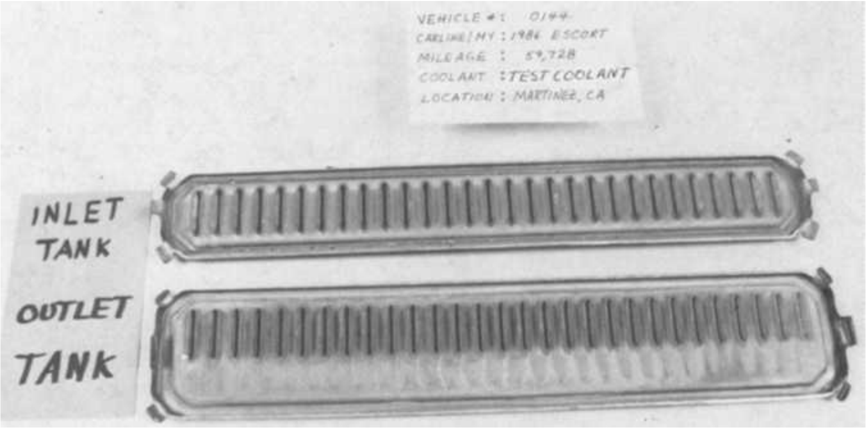


FIG. 22—*Radiator header plates from Vehicle 0144.*

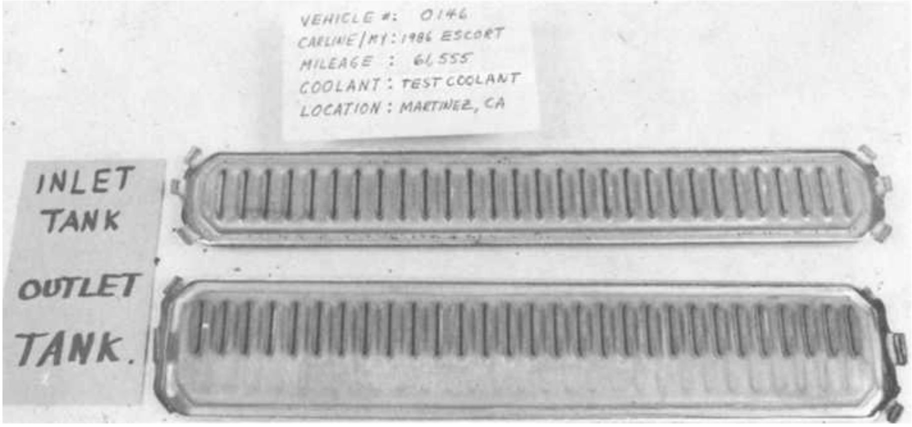


FIG. 23—*Radiator header plates from Vehicle 0146.*

controlled over a three-year period. What we learned was not unexpected and confirmed prior beliefs.

Certainly it showed that low silicate sebacic acid coolants do not suffer as rapid a depletion rate for chemical inhibitors as do high silicate alkaline phosphate coolants. We do not know if the test coolant has a longer life because the coolants were not run to failure. We can say that the test coolant is no worse than high silicate alkaline phosphate coolants. However, this new style of coolant does not offer any significant advantages for the consumer over current North American coolants.

Coolant change intervals vary greatly with the needs of the vehicle manufacturer. Mileage accumulation of the two cars that used standard OEM fill coolant far exceeded our recommended 3 year/30 000 (3 year/48 279 km) mile interval. In a modern car with a well-maintained cooling system, current OEM factory fill corrosion protection can be extended far beyond the current coolant change intervals.

In cars with aluminum radiators and heater cores, no lead solder contamination of the

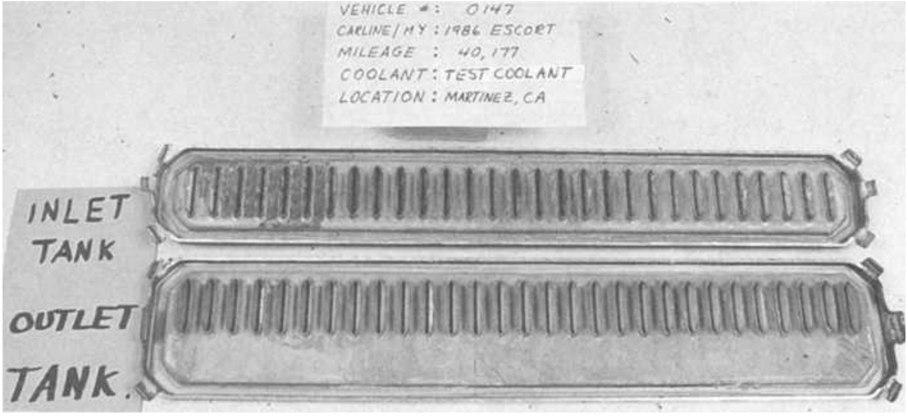


FIG. 24—*Radiator header plates from Vehicle 0147.*

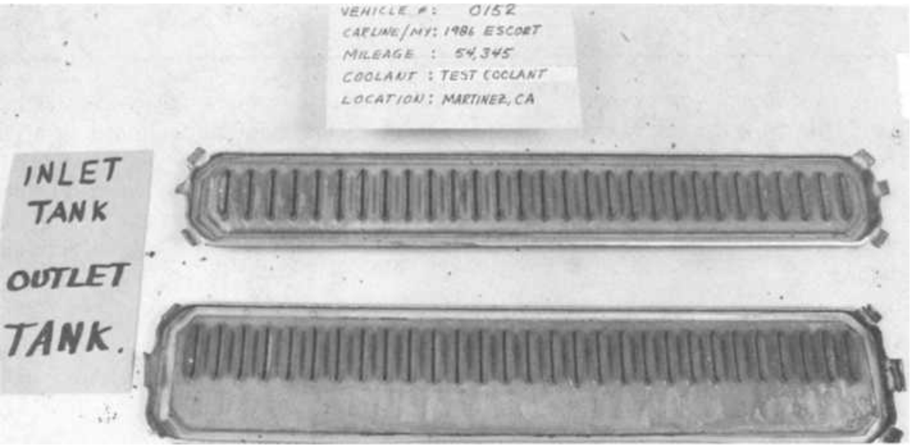


FIG. 25—*Radiator header plates from Vehicle 0152.*

engine coolant occurs. Coupled with an extended coolant change interval the environmental push for recycled coolant may be delayed until proper re-inhibitors can be developed.

One of the issues we have not addressed in this paper is cost. At the time this fleet test began, it was estimated that the added cost for OEM sebacic acid inhibitor technology would be 10 to 15%. When the estimate became a reality in 1989, the cost increase for Ford of North America to replace OEM alkaline phosphate coolants with OEM sebacic acid coolants was 26%. If the actual dollar cost increase due to the 1989 sebacic acid coolant use in Ford of England is added to today's Ford of North America OEM coolant price, the cost increase becomes 66%. In today's economics, such a significant cost increase is not acceptable for a product that offers no distinct advantage.

Conclusions

1. Low silicate sebacic acid coolants do not offer any significant advantages for the consumer over current North American coolants.
2. In a modern car with a well-maintained cooling system, current North American and OEM factory fill coolant corrosion protection can be extended far beyond previous expectations.
3. In modern cars with aluminum radiators and heater cores, no lead contamination of the engine coolant occurs. This may reduce the eminent need/cry for recycled coolant until such time as proper re-inhibitors can be developed.

References

[*1*] British Specification TS 10177, *Antifreeze Inhibited Ethanediol, AL-39,* The Director of Materials Quality Assurance Headquarters Building, Royal Arsenal East, London SE18 6TD.

[*2*] Butler, G. and Mercer, A. D., "Inhibitor Formulations for Engine Coolants," *British Corrosion Journal,* Vol. 12, No. 3, pp. 171–174.

[*3*] Beard, L. K., Jr., Conville, J. J., and Wilson, J. C., "A Demonstration of Aluminum Transport Deposition," *STP 887, Engine Coolant Testing: Second Symposium,* American Society for Testing and Materials, Philadelphia, 1986, pp. 44–60.

DISCUSSION

Joseph A. Lima[1] *(written discussion)*—I agree that use of aluminum radiators is preferable and will reduce the amount of lead in spent coolant, but what about the continued use of copper/brass heater cores? When do you think they will be eliminated?

N. C. Adamowicz and Daniel F. Falla (authors' response)—Ford Motor Company Climate Control Division planning volumes for both OEM aluminum radiators and heater cores exceeds 95% by 1998. There will probably always be a small need for copper/brass heat exchangers.

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[1] Houghton Chemical Corporation, Allston, MA.

Roy E. Beal and Refki El-Bourini[2]

Corrosion Testing for Aluminum Alloy Selection in Automotive Radiators

REFERENCE: Beal, R. E. and El-Bourini, R., "**Corrosion Testing for Aluminum Alloy Selection in Automotive Radiators,**" *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 83-106.

ABSTRACT: Durability of aluminum alloy automotive radiators in service depends on the alloy selected and the expected engine coolant environment. The challenge is to find testing methods that correlate with service experiences that allow for comparative evaluation of competing materials without resort to long-term vehicle exposure at initial selection stages. Design, manufacture, and processing affect radiator performance and must be taken into account in corrosion testing. Aluminum alloys AA3003 and AA7072 are used to illustrate the test program.

Electrochemical corrosion test methods were used for screening purposes in alloy selection and corrosion test environment studies. A simulated service test method is used with selected corrosion media to provide accelerated corrosion data in full sized radiators. The importance of relating corrosion test media to ultimate engine coolant use and abuse is covered. Methods have been correlated with field tests to prove the approach used.

KEYWORDS: engine coolants, corrosion, aluminum alloys, automotive radiators

The automotive market is very much a leader in globalization of the world's economies. Unification of design approaches, standards, and servicing requirements is becoming regular practice. Radiator materials are under constant review and change by all manufacturers with a view to utilizing a single material worldwide. The engine coolant area is very important to this goal, and yet very diverse coolant formulations are prevalent on the major continents and in industrial countries.

Manufacturers of radiators have generally considered a primary market with a particular coolant and tried to have a universal radiator material for wider markets, where coolant condition and quality vary widely. A three layer aluminum alloy with AA7072 clad on AA3003 with a 4343 braze filler on the opposite side has been used on a worldwide basis by one manufacturer. This approach has had a good field record in conjunction with an amine based coolant.

Other manufacturers have preferred to use a two layer AA3003 material as an alternate radiator alloy for the U.S. market. This radiator material has a good performance record with a North American style coolant.

Radiator materials in the engine circuit are selected for cost, fabrication capability, and durability in service. Manufacturers have adopted various national and private standards, such as Japanese Industrial Standard (JIS), British Standards Institute (BSI), Deutsches Institut fuer Normung (German Standards Institute [DIN]), American Society for Testing and

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[1] President, Amalgamated Technologies, Inc., Suite 208, 13901 N. 73rd St., Scottsdale, AZ 85260.

[2] Engineering manager, Calsonic Technical Center America, Arizona Branch, 10232 S. 51st St., Phoenix, AZ 85044.

Materials (ASTM), and Society of Automotive Engineers (SAE) for the development and application of radiator materials and engine coolants.

Durability of aluminum alloy automotive radiators in service depends on the alloy selected and the expected engine coolant environment. The challenge is to find testing methods that correlate with service experiences that allow for comparative evaluation of competing materials without resort to long-term vehicle exposure at initial selection stages.

No single test can be taken as a reliable guide for radiator material and engine coolant selection. Comparison of material and coolant candidates by electrochemistry and a simulated service test was performed in addition to field tests. Various corroding fluids designed to evaluate complete radiators were included in the test series. Results were correlated with field studies of aluminum alloy radiators in service by retrieval and examination.

Technical Background

Aluminum Alloys and Coolants

There are many tests that are performed in the evaluation of engine coolant for automotive use. When considering new alloys for automotive cooling circuit components, similar considerations are necessary. However, it is now important to examine the influence of the materials in question against the approved engine coolants. An examination of tests available suggested that the best approach was to use electrochemical techniques for basic information and then proceed directly to simulated service testing.

Engine coolant tests in the United States have used ASTM corrosive water comprising 100 ppm of chlorides, sulfates, and bicarbonates to accelerate corrosion. An extension of this technique by Alcan to reduce the amount of coolant to very low levels and increase the percentage of ASTM corrosive water has shown discrimination between different candidate aluminum radiator alloys on internal corrosion.

Some Japanese companies have used the Oyama water test regimen for determination of adequate life characteristics of aluminum alloy radiators. Ethylene glycol based engine coolants are likely to maintain importance and be the major coolant component in the foreseeable future. Accordingly, all efforts at radiator design and material improvements should, it was felt, relate to ethylene glycol engine coolant. The amine type coolant, largely used in Japan, is gradually being replaced, because of compatibility problems. In addition, nitrite free formulas are becoming more popular, and phosphates have generally been eliminated in Europe. Organic acid type formulas with fairly neutral pH values are finding increased favor.

All the changes in coolant technology are designed to meet modern vehicle specifications for improved service. However, changes are also taking place in the materials used and manufacturing methods for aluminum radiators. Therefore, developments are involved with a moving target making it important to develop a testing routine that can allow for the changes and give valid results.

Radiator Material Galvanic Effects

Corrosion and design cannot be separated. Design affects the type of corrosion that can occur in the radiator through material and process selection. Technical factors in corrosion include open circuit potential, polarization, resistivity of the electrolyte, area ratios, and the direct and indirect galvanic couplings between materials and fluids.

Radiator manufacturers of aluminum alloy product have long recognized the problem of galvanic relationships and how the effects can be utilized to benefit corrosion resistance. The 7072 clad aluminum alloy is a good example. The clad material is sacrificial to the core, will corrode preferentially, and for some time protect the underlying alloy. However, if the coolant environment is too aggressive to the clad material itself, then many corrosion sites will be developed and the degree of galvanic protection effectively reduced. The potentials of the clad and the underlying core alloy are therefore preferentially balanced to optimize the protection afforded in a specific environment. This is the main point. Compromise is necessary to try and cover a wide range of environmental protection, and optimization will only occur with one radiator and engine coolant combination. Not surprisingly, therefore, by using the sacrificial layer approach, results will vary between very good, a large middle ground of no problems with slight corrosion, and occasionally identifiable difficulties where the clad layer is simply too sacrificial for reasonable protection.

Influence of Fluid Flow

The type of protection is important under fluid flow conditions. If the corrosion resistance is obtained by creating a film or passivated layer by interaction between the fluid and the material, there usually is a critical flow rate, above which the passive film cannot adequately form or is scrubbed from the surface. Galvanic effects can also be exaggerated under these conditions because the scrubbed area generally becomes anodic to the rest of the exposed surface. In time corrosion can be accelerated even below known levels of potential erosion effects.

Radiator Alloys

Some years ago, a major program was executed by Ford Motor Company to evaluate aluminum alloys for radiators. At the time, Ford was vacuum brazing all their radiators. Alloy 7072 clad tubes with AA 6951 header material was brazed into radiator form and subjected to field operations. Corrosion of the 7072 clad tubes was found to be a significant problem, whereas a comparable radiator series made with 3003 unclad tubes revealed negligible corrosion after many miles and years of service. Ford was using vacuum brazing. Radiators were tested in a variety of North American style coolants. Engine coolant composition was also found important to good durability [*1*].

A widely produced standard production radiator is a 7072 clad on 3003, joined using the Nocolok® process. This radiator has shown very good corrosion resistance and is currently in large quantity production and used throughout the world.

The 3003 two layer radiator material is less expensive and is used widely in the United States. There are several alternate three-layer materials used in radiator construction supplied by Kaiser and Reynolds that are also widely used by some aluminum radiator manufacturers.

The decision regarding aluminum radiator material cannot be made in isolation from engine coolant technology with any hope of arriving at the correct solution, either economical or technical.

An example of a new material is a nonvolatile aluminum-tin cladding that was developed by Kaiser. This material is labelled K805 and is especially made for vacuum brazed radiators and heater cores. The clad layer proved valuable in providing cathodic protection to a 3003 core in simulated service testing. During this development effort various electrochemical tests were performed as part of the program. Particularly, galvanic tests, polarization, and potentiodynamic tests were used as part of the screening experiments in alloy development.

In a separate development, a new material designated K319 was found superior to road splash external corrosion. Again, the importance of galvanic relationships is exemplified by the development of a subsurface layer that is anodic to the core alloy that is developed during the vacuum brazing process.

® Alean International Ltd., Canada.

Process selection does influence choice of material. The Alcan Nocolok process can be used with two- or three-layer aluminum radiator alloys. Specific alloys are used for vacuum brazing. The European chloride brazing process is a very forgiving system.

The lesson from these and other aluminum alloy radiator developments is clear. Investigation of a new alloy or selection of an existing one for radiators involves knowledge of radiator material, radiator braze processing, radiator design, other materials in proximity, and engine coolant formulations. The progression of change with alloys and coolants should therefore involve the most complete knowledge of all these factors.

Corrosion Properties

Both internal and external corrosion of aluminum radiators are important and directly affected by material selection and brazing process. Kaiser has observed that the SWAAT test (ASTM Practice for Modified Salt Spray (Fog) Testing (G 85), Method G 43, using synthetic sea salt water with acetic acid at a pH of 2.8 to 3.0 is best for external corrosion simulation. This test program concentrated upon internal corrosion evaluation, using 3003 and 7072 clad materials as examples of the investigative process.

Aluminum alloys are very reactive, especially in aqueous environments. The metal is reasonably resistant to corrosion because of its affinity for oxygen and the protective nature of the aluminum oxide film that develops on the aluminum alloy surface. The aluminum oxide surface is penetrated by the corroding medium, and because of surrounding protection tends to fail by pitting action.

Pitting is considered to be the most commonly encountered form of aluminum radiator alloy corrosion. The problem is accelerated by chlorides, traces of copper forming electrolytic cells, or very high or low pH levels. Where perforation is the criterion for failure, statistical analysis may be judiciously applied to the distribution and depth of pits. Maximum pit depth can be related to practice if the sample size is large enough. However, in practice the best approach is to use probability paper so that data with random probabilities can be plotted to give straight line relationships.

A corrosion rate increasing with time is rarely encountered with aluminum [*2*]. Corrosion volume is linearly related, and several authors have demonstrated that maximum pitting depth extends as the cube root of time as illustrated in Fig. 1 by example [*3*,*4*].

Examination of the radiator tubes should therefore be handled statistically over a period of time and a number of tests in order to achieve reliable pitting data and an understanding of the probable life times of radiators in service.

Engine Coolant and Water Quality in General Usage in the United States

In order to understand the levels of engine coolant percentage, contamination, and water quality generally faced by the aluminum radiator in service, and to assist in development of suitable testing media, a survey was carried out.

A total of 130 used coolant samples was obtained from all regions of the country. Examination of these samples revealed a very wide range of engine coolant quality in actual usage. The percentage ranges of glycol found in vehicles from all regions is presented in Fig. 2. The majority of vehicle users had either lower or higher percentages of glycol than that designated by the automotive manufacturers. Twenty of the samples had less than 20% glycol. This demonstrates that any test program should be carried out with lower percentages and quality of engine coolant than the 50% coolant and water optimum.

Water quality is also very important. Most vehicle owners use tap water with coolant when

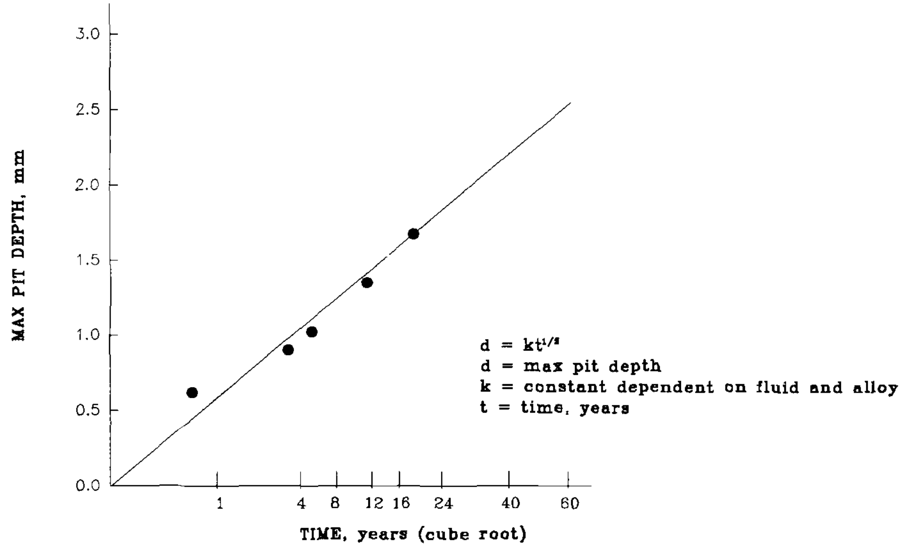

FIG. 1—*Pitting data on aluminum alloy showing pit depth increases with cube root of time* [4].

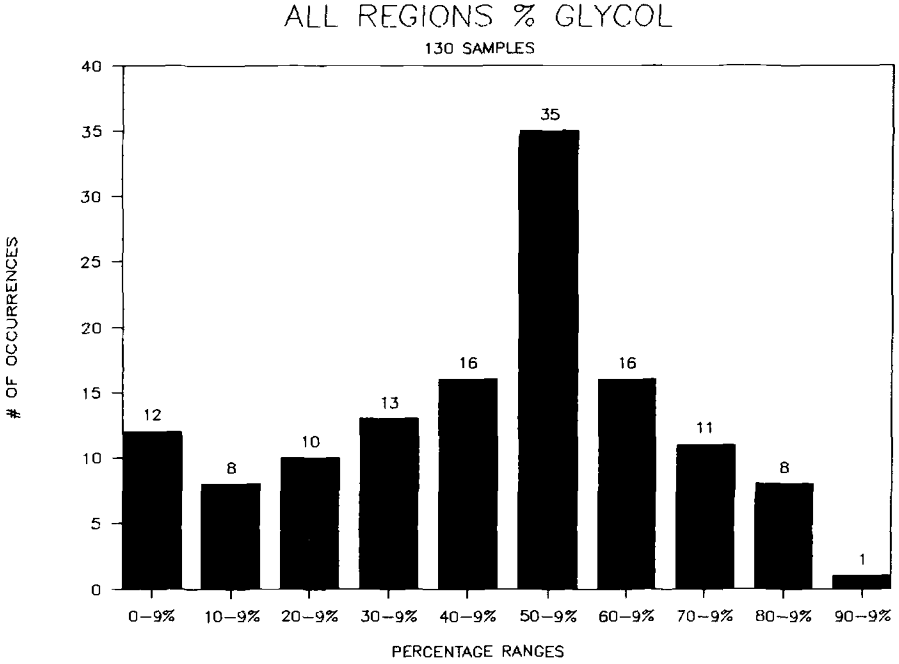

FIG. 2—*Percent glycol found in random sampling of vehicles in the United States.*

additions are required to the engine cooling system. A series of water analyses taken from all regions of the United States revealed a wide range of water quality.

Four waters had high alkaline values outside the Environmental Protection Agency (EPA) limits for drinking water. The worst condition was in St. Louis, MO, with a pH of 9.7 and high sulfates. Florida also showed poor water quality with high chlorides. In Houston, TX, and in Indianapolis, IN, very high chloride levels were recorded. ASTM has defined acceptable water quality in Manual MNL 6 [*4*]. Most areas of the country have satisfactory water. Some problems could be expected from the areas mentioned if the aluminum alloys used for radiators are somewhat susceptible to general corrosion.

Evaluation of Suitable Fluids for Accelerated Radiator Tests

Following a review of engine coolants in use and water quality, it was determined that test fluids for accelerated evaluation of aluminum alloys for automotive radiators should reflect used coolant conditions.

The question is to define how much coolant depletion is acceptable to produce accelerated corrosion effects without compromising the integrity of the corrosion mechanisms involved. It is recognized that a corrosion medium that is too severe can produce unrealistic results that would not place materials under test in their order of merit.

A number of coolant and water conditions were examined to investigate a satisfactory corroding fluid for standardized test purposes.

Two types of water condition were selected for the study. ASTM has developed and defined a corrosive water medium that contains 100 ppm chlorides, 100 ppm sulfates, and 100 ppm bicarbonates. The ASTM water composition is widely used in radiator and coolant testing and is the designated accelerant in several ASTM standards. The second type of water used is known as Oyama water (OY) (Calsonic Company Standard) and has been adopted by some in Japan as a corroding test fluid for the evaluation of aluminum alloy radiators.

Two types of engine coolant were included in the study. A normal North American style phosphate-nitrate formula and a Japanese amine based formula for corrosion protection were used. The North American coolant was used at the 2% and 17% level in conjunction with ASTM water and at 2% in deionized water. The amine coolant was used at the 17% level in ASTM water. A separate test was undertaken with Oyama water only.

Electrochemical Evaluation of Radiator Materials

Electrochemical corrosion testing is an approach to understanding the mechanisms and amount of corrosion that are likely to occur in a coolant system. Several basic techniques can be adopted for measuring corrosion rates. Selection of the appropriate method is carried out by the corrosion engineer, depending on the problem involved.

Metals and alloys tend to corrode over the entire surface or in specific locations producing pits. Corrosion reactions of both anodic and cathodic type are simultaneously occurring on corroding surfaces. When general corrosion occurs, these areas move quickly across surfaces; when pitting occurs, they remain localized.

Corrosion potential depends on material composition and the proximity of other materials of similar or dissimilar compositions. Materials involved can direct the process of corrosion depending on the relative sizes of cathodic and anodic areas. Smaller anodic areas rapidly increase corrosion conditions. Increased corrosion per unit area can therefore be developed in this situation. When two dissimilar corroding metals are involved by direct contact, the problem is generally referred to as galvanic corrosion.

The principal electrochemical methods used for radiator corrosion studies were as follows:

(1) Tafel,
(2) galvanic, and
(3) potentiodynamic.

Tafel

The Tafel technique is the most widely used electrochemical method for the determination of average corrosion rates of metals. Corrosion rates are generally expressed as rate of metal loss per unit area. This can be mils per day or year.

To obtain this information, a combined cathodic and anodic polarization curve is run with the material and environment of interest. The intersection of the slopes of these curves produces a corrosion current density figure at the natural corrosion potential of the system. Using the density of the metal, the corrosion rate can be calculated in any desired units.

Galvanic

Electrochemical techniques for predicting galvanic corrosion are based on three types of measurement. These are mixed potential, galvanic current, and polarization measurements. Each of these techniques have advantages and allow the development of useful information. Usually, more than one technique is necessary to obtain the required confidence in the study.

The use of potential measurements for predicting galvanic corrosion is based on the measurement of E_{corr} for the metals involved. Metals arranged into rank order according to their potential measurement in a given environment are known as the galvanic series for that system.

There are drawbacks that prevent this simple approach being adequate. Formation of films, the effect of time, polarization of specific metals, and distance between corroding species are all important factors.

The measurement of galvanic currents between coupled metals is based on the zero resistance meter. Galvanic current is measured by an ammeter, adjusting voltage, or resistance so that the potential difference between the two elements of a circuit indicated by an electrometer is zero. This allows continuous monitoring of galvanic currents with time.

The measured galvanic current is not always the true situation. When cathodic currents are appreciable at the mixed potential of the galvanic couple, the measured galvanic current is lower than the true value. Mixed potential theory of corroding systems is important to galvanic couples. Using polarization measurements, the corrosion potential of the galvanic couple is determined for each metal individually. When coupled together, the corrosion rate for one metal can be increased, and for the other, decreased. The use of polarization measurements in conjunction with mixed potential of a galvanic couple provides precise information regarding their behavior.

Potentiodynamic

Potentiodynamic polarization experiments are generally used as a qualitative technique to fingerprint a material in a given medium, to identify tendencies to passivate, isolate any multiple reactions, and indicate some idea of stability. Several features of the potentiodynamic curve are important. The curve is obtained by scanning potential values of the specimen over a wide range and measuring the current densities observed in the fluid of concern.

The potentiodynamic scan is commenced on the cathodic branch of the Tafel slope by selecting a sufficiently low potential at which to begin the experiment. The scan proceeds through the change over from cathodic to anodic current. This can be used also for a quick corrosion rate measurement. The next important area is E_{pp}, which is the passivation potential of the material and coolant. At potentials higher than this figure, current density is reduced until the stable passive region, if present, occurs. The next most important point is the breakdown potential from passive to active corrosion at which current level is measured.

Material and Coolant Evaluations

Different engine coolants are used in North America and Japan. North American coolants are generally phosphate-nitrate based, and Japanese coolants have been largely based on amine additives.

An electrochemical study was carried out to compare aluminum alloy 7072 clad material to aluminum alloy 3003 in five different coolant conditions:

Aluminum Alloy:

(1) AA7072 clad on AA3003 and
(2) AA3003.

Coolant:

(1) 2% North American in ASTM water,
(2) 17% North American in ASTM water,
(3) 17% Amine coolant in ASTM water,
(4) Oyama water, and
(5) 2% North American coolant.

Note: ASTM water was prepared according to details in ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384).

FIG. 3—*Princeton 273 computer operator electrochemical testing apparatus.*

TABLE 1—*Results of TAFEL analysis: AA3003 alloy.*

Solution Type	Corrosion Rate, mm/year	*I*-CORR μA/cm^2
2% North American[a]	2.0117	184.00
17% North American[a]	0.0836	7.66
17% Amine Coolant[a]	0.0402	3.68
Oyama water	3.4544	318.00
2% North American	0.508	48.00

[a] Remainder of solution: ASTM D1384 type corrosive water.

Electrochemical Test Apparatus

The electrochemical test apparatus comprises a Princeton 273 potentiostat/galvanostat, the experimental test cell, and the computer and program that runs the experiments, as illustrated in Fig. 3. A working electrode, neutral electrodes, and a standard calomel electrode for reference are enclosed in a glass container in which the specimen to be tested is exposed. The test cell is heated by a standard hot plate. Potential or current scans are automatically ramped according to the required test. A specimen exposure area of 1 square cm was used. A ±250 mV range about E_{corr} was utilized at a 0.2-mV/s scan rate.

Test Results from Tafel Corrosion Method

Results from the Tafel analysis with both aluminum alloys and the five corroding fluids are presented in Tables 1 and 2.

The AA3003 alloy shows relatively slow corrosion in the 17% amine or 17% North American coolant in ASTM corrosive water. The 2% North American style coolant without corrosive water showed similarly low corrosion rates. Two percent North American coolant in ASTM corrosive water results in a considerable increase in material attack as measured by the corrosion current and the calculated corrosion rates. In rank order, the 17% amine coolant corroded the least followed by 17% North American coolant both in conjunction with ASTM corrosive water. The 2% North American coolant was next followed by 2% North American coolant in ASTM corrosive water. Oyama water caused the most severe corrosion.

The data for AA7072 aluminum alloy are presented in Table 2. Some differences are noted from the above results. With AA7072 aluminum alloy, the 17% North American coolant in ASTM water is slightly more protective and essentially equivalent to 17% amine coolant in ASTM water. The Oyama water demonstrates a higher corrosion rate than the above fluids.

TABLE 2—*Results of TAFEL analysis: AA7072 clad.*

Solution Type	Corrosion Rate, mm/year	*I*-CORR, μA/cm^2
2% North American[a]	6.5532	601.00
17% North American[a]	0.0134	0.33
17% Amine coolant[a]	0.0198	0.82
Oyama water	0.4343	39.7
2% North American	1.5494	140.00

[a] Remainder of solution: ASTM D 1384 type corrosive water.

A further increase in corrosion of AA7072 aluminum alloy over Oyama water was found with 2% North American coolant. The most corrosive fluid for this aluminum alloy was the 2% North American coolant with ASTM corrosive water.

These results show that specific aluminum alloy materials respond differently in selected corroding fluids. This is very important. When designing an accelerated corrosion test, care must be taken to select a fluid condition that can be correlated ultimately with service performance. Merely adopting an enhanced corroding condition does not ensure that the expected corrosion can be accelerated without influencing decisions to be made in radiator material selection.

Results from Galvanic Corrosion Tests

The AA3003 and AA7072 clad materials were coupled together under galvanic conditions and tested with the five coolants used for the program.

The Oyama water revealed the greatest galvanic currents in the series at approximately 400 μA as shown in Fig. 4. The 2% North American coolant in ASTM corrosive water was generally lower in current differential. A current of <200 μA depending on which alloy was used as the working electrode on the test was measured as presented in Fig. 5. Both the Amine based coolant and North American coolant at 17% in ASTM corrosive water did not show any effective galvanic currents as shown in Figs. 6 and 7. These results show that from a galvanic standpoint the Oyama water is the most aggressive of the fluids examined.

Results from Potentiodynamic Tests

Potentiodynamic electrochemical tests were carried out with both AA7072 material clad on AA3003 and on unclad AA3003 alloy. The same five environments used for other tests were utilized.

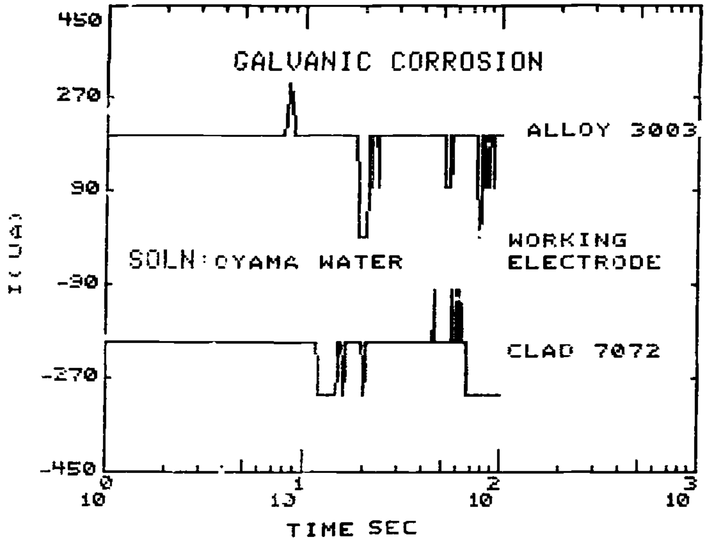

FIG. 4—*Oyama water galvanic test.*

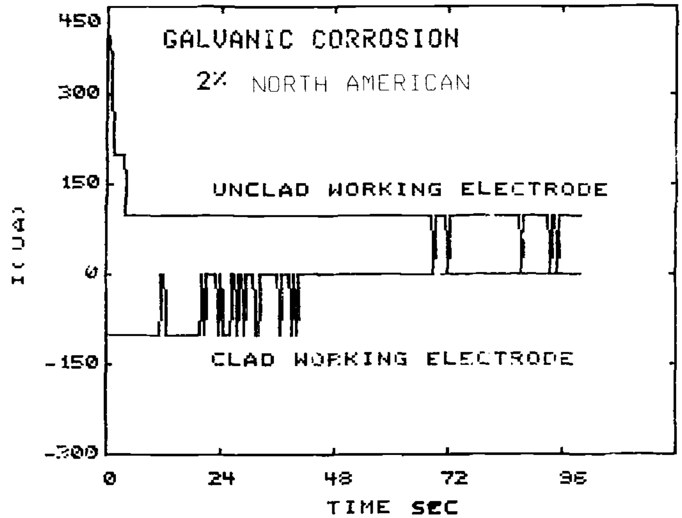

FIG. 5—*Galvanic corrosion in 2% North American and ASTM corrosive water.*

Summary graphs of the AA7072 clad material and the unclad AA3003 are presented in Figs. 8 and 9, directly comparing these materials in four of the environments. In each case, the most severe corrosive condition is demonstrated by the Oyama water. There is no evidence of any passivity, and at very low potentials, a very high corrosion current is observed. Corrosion in the AA7072 is more general with some pitting evident. The unclad AA3003 shows pitting attack at relatively low potentials above E_{corr}.

The next most severe condition was obtained with 2% North American coolant in ASTM

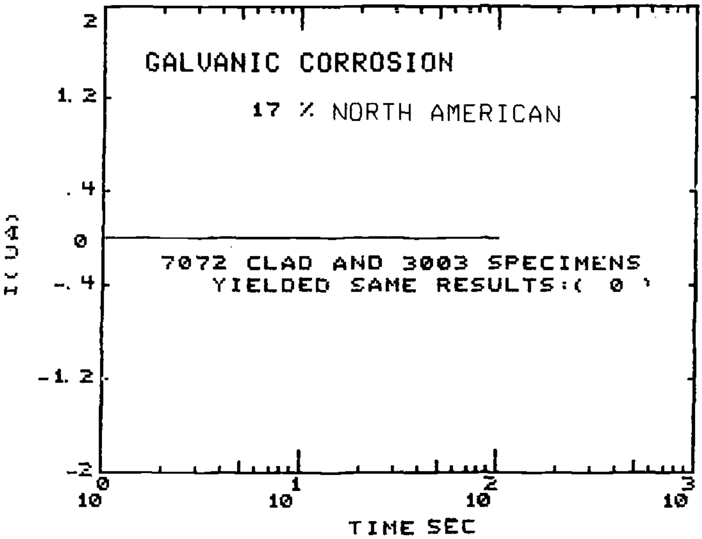

FIG. 6—*Galvanic corrosion in 17% North American and ASTM corrosive water.*

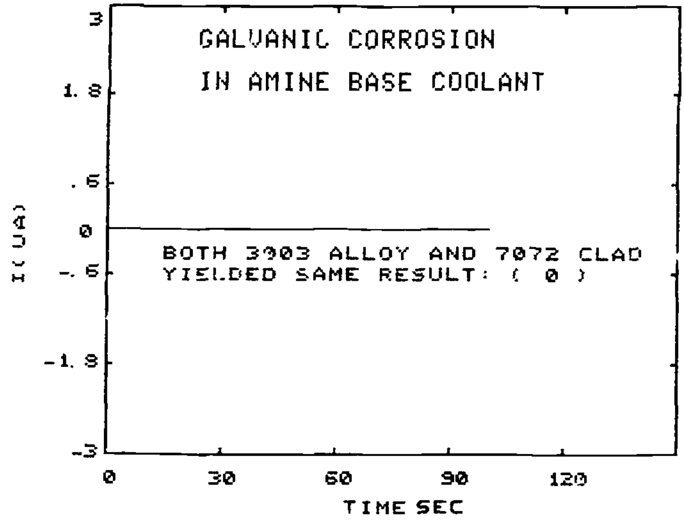

FIG. 7—*Galvanic corrosive in 17% amine base coolant and ASTM corrosive water.*

corrosive water. Overall, corrosion rates are less. An approximate 800-mV range is obtained where passivity is measured, although the corrosion rate is still higher than desirable and does not show protection of these materials.

The 17% North American and amine coolants in ASTM water environments indicated less corrosion as measured by the potentiodynamic technique. Both of these coolants lowered the corrosion rate but only showed slight passivity.

A comparison was made between the North American and Japanese coolants at the 17%

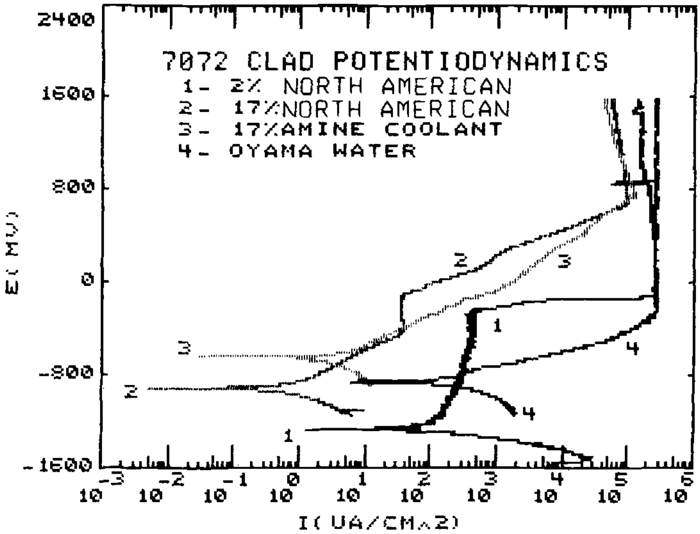

FIG. 8—*Potentiodynamic data plot with clad AA7072.*

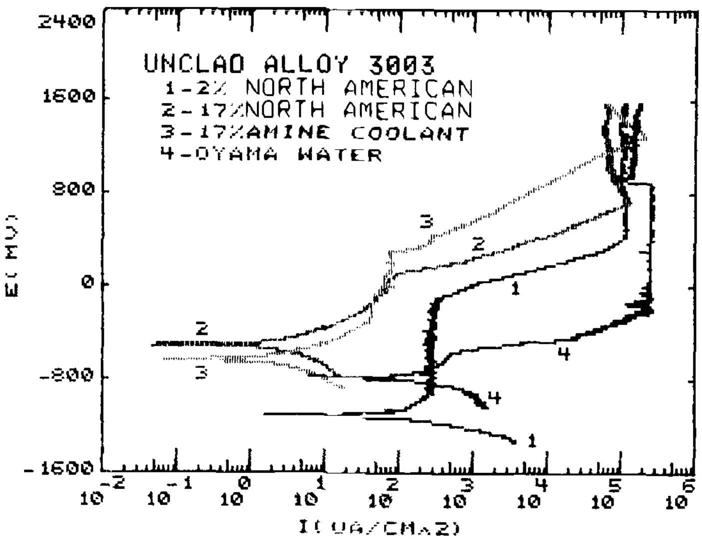

FIG. 9—*Potentiodynamic data plot with unclad AA3003.*

dilution level in ASTM water in Fig. 10. Clad material in North American coolant has slightly better protection, and unclad was slightly better in amine coolant.

Summary of Electrochemical Work

The Tafel, galvanic, and potentiodynamic corrosion studies provide very useful laboratory type corrosion data that can be utilized for material or coolant ranking purposes. The tech-

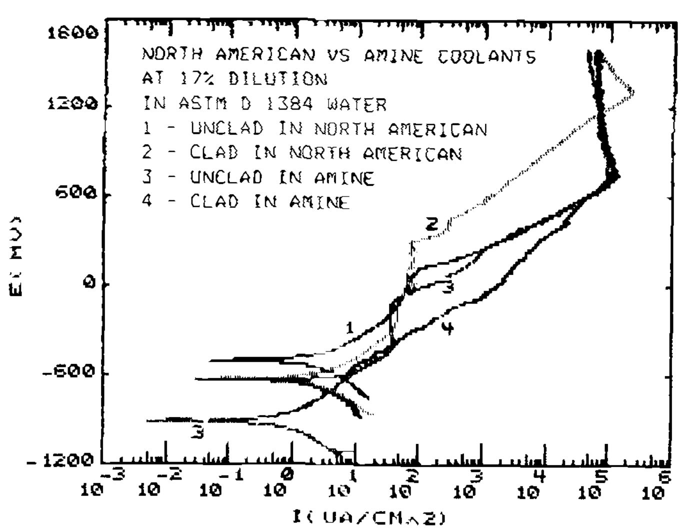

FIG. 10—*Potentiodynamic data plot of North American versus amine at 17% dilution in ASTM corrosive water.*

niques are not infallible, but when used with supporting data, provide an increased confidence level that the true corrosion picture is being observed.

The experimental work in the study demonstrates the viewpoint that North American coolants are aggressive towards AA7072 clad AA3003 alloy. This material does not provide any significant benefit over AA3003 alloy alone that has shown good service experience in U.S. radiators.

Japanese studies[3] on radiator comparisons revealed more rapid corrosion with the AA3003 aluminum alloy in Oyama water than with AA7072 clad material. Mainly, it is understood that this occurs because of the sacrificial nature of the zinc containing aluminum surface alloy that provides cathodic protection to the underlying core material. Results of the electrochemical Tafel work confirm this expectation. Electrochemical data also show that aluminum alloy AA3003 will corrode more in Oyama water than in the Japanese amine type coolant or North American coolant with ASTM corrosive water mixes.

Simulated Service Testing

Test Equipment

Two radiator test stands were utilized that have a capability of operating at up to 125°C and at pressures up to 210 kN/m^2. The test stand is built to operate at a range of temperatures and pressures and to be pressure cycled if necessary.

The thermal cycle is related to the heating system used and normally takes 15 to 20 min to heat up depending on the temperature and size of radiator. The pressure cycle is operated independently by means of an air to fluid pressurization cell that allows a reasonable rise and fall in the rate of pressure in the stand. A timer is used to operate the pressure cycle. The test stands are capable of continuous running or timed periods of operation. An adjustable flow of 0 to 80 L/min is available. The radiator capacity is 2 units at up to 0.9 m wide by 0.75 m high. Safety equipment is included that will operate with loss of fluid, over pressure of the unit, or over temperature. The unit operates quietly, and easy access is available to the radiators. A NEMA enclosure is used for all electrical controls.

Experience with operating similar units on a prescribed pressure and temperature cycle of 0 to 140 kN/m^2 and 80 to 115°C has allowed correlation with on-the-road service.[4] Using an 8-min pressure cycle in conjunction with the above program, 1000 h on the test unit is equivalent to approximately 80 000 km on the highway. A flow rate of 32 L/min was used throughout this test program, which was related to actual service flow rates for the radiators used.

The simulated service test frames are shown in Figs. 11 and 12 with a schematic diagram of engine coolant flow depicted in Fig. 13.

Selected Corroding Test Fluids

2% North American Coolant in ASTM Water—The accelerated corrosion rate coolant used for radiator simulated service tests was 2% North American style coolant with ASTM D 1384 corrosive water. ASTM corrosive water is composed of 100 ppm chloride, 100 ppm sulfate, and 100 ppm bicarbonate ions. This corrosive water is used to simulate a U.S. tap water. Coolant was changed every 3 months.

OYAMA Water—Work in Japan has resulted in the adoption of OY(Oyama) water as a testing fluid for the evaluation of aluminum alloys for automotive radiators by some manufacturers.

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[3] Private communication, Calsonic, Phoenix, AZ, Oct. 1989.

[4] Private communication, Amalgamated Technologies, Scottsdale, AZ, 24 April 1991.

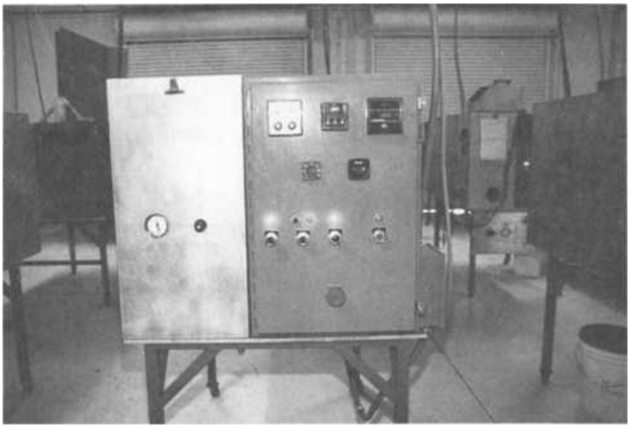

FIG. 11—*Simulated service test frame.*

The engine coolant is replaced by this aggressive water formulation that produces failure of aluminum alloy radiators in 3 to 6 months. This test system is also used by the Japanese to evaluate the rate of pitting formation on the internal surfaces of the tubes in the radiator cores.

Radiators were run continuously in this water at 88°C for up to 90 days. The water was changed every 4 weeks.

Radiators

The radiators used in this particular test were as follows:

1. Calsonic standard production radiators with AA7072 internal cladding, AA3003 base material, and AA4343 braze alloy.
2. Radiators with no internal cladding using AA3003 base material, and AA4343 braze alloy.

FIG. 12—*Installation of radiators in radiator test frame.*

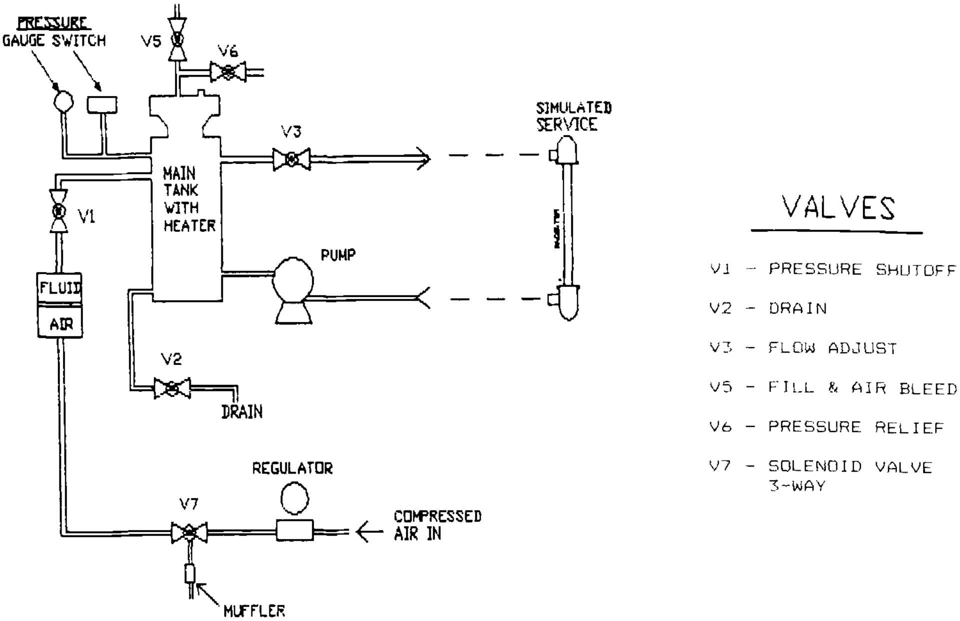

FIG. 13—*Schematic drawing of coolant flow.*

Simulated Service Test Results in North American Coolant

Simulated service tests were carried out using equipment and conditions already described with the above radiators and testing fluids. Pitting examinations on this program were carried out by direct microscope comparator depth measurements and occasionally by metallurgical cross section to verify direct measurements.

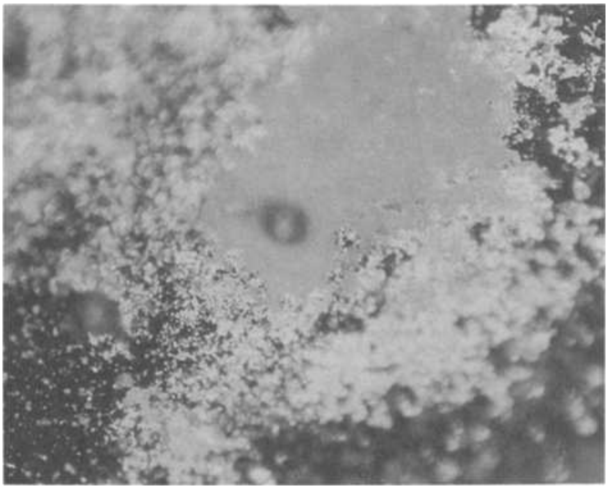

FIG. 14—*Surface nodule on unclad alloy.*

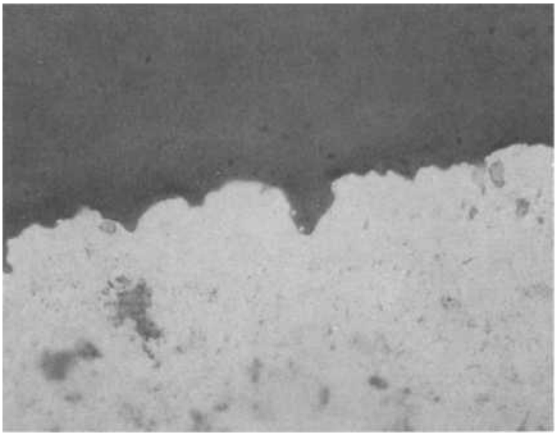

FIG. 15—*5-μm pit on unclad in coolant.*

AA3003 Radiators—Monthly examination of the unclad radiators revealed very little pitting (<1 pit/mm^2) throughout the course of the test. A single 15-μm pit was found after 9 months of testing; however, no other pits were found with a depth greater than 5 μm. Some of the pits were found underneath nodules that had formed on the tube surfaces. Examples of a nodule and a cross section of a tube pit are shown in Figs. 14 and 15. The pitting observed in Fig. 15 was general with several smaller pits than the one measured.

Examination of the header plates after 9 months revealed very little pitting. Maximum pit depth found was 5 μm. An example is shown in Fig. 16. There is some residual braze filler metal material that acted as a cathodic site and tended to promote pitting.

7072-Clad Radiators

Monthly examination of the clad radiators revealed severe pitting ($\gg$ 1500 pits/mm^2) occurring as early as 4 weeks after test initiation. Maximum pit depth steadily increased until a pla-

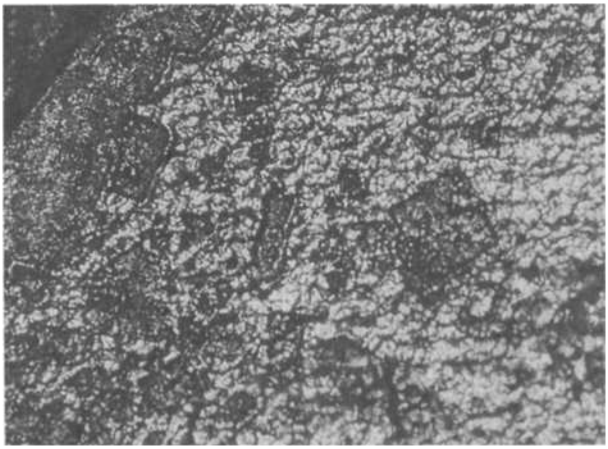

FIG. 16—*Pits in header plate of clad radiator.*

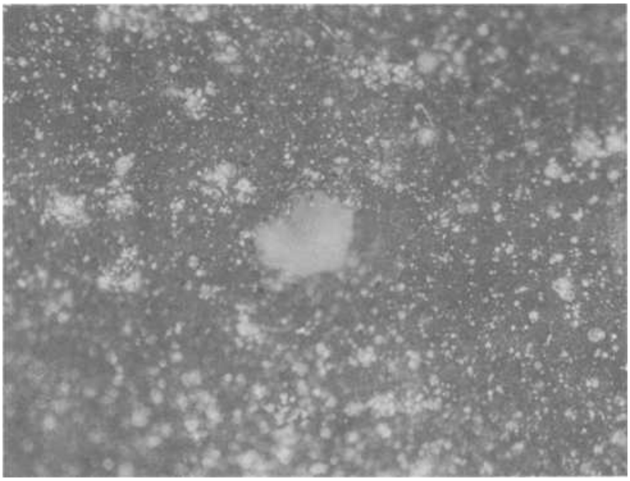

FIG. 17—*131-μm deep pit in clad radiator tube.*

teau of 96 μm after 4 months, where the clad material showed protection of the underlying core alloy AA3003. Maximum pit depth did not rise above this level until after 8 months into the program, when clad protection finally broke down and a pit was found with a depth of 115 μm. Final maximum pit depth after 9 months was 131 μm, well into the AA3003 core material. Examples of these deep pits are shown in Figs. 17 and 18. Figure 19 is a cross section of a 58-μm pit that penetrated the clad layer. At this point the clad layer then becomes protective of the core material slowing down the rate of pitting attack. Additional examples of pitting are shown in Figs. 20 and 21.

Pitting Summary

The pitting mechanism in the standard AA7072 clad alloy radiator begins as a shallow depression in the sacrificial clad, which then spreads along the surface of the AA3003 second

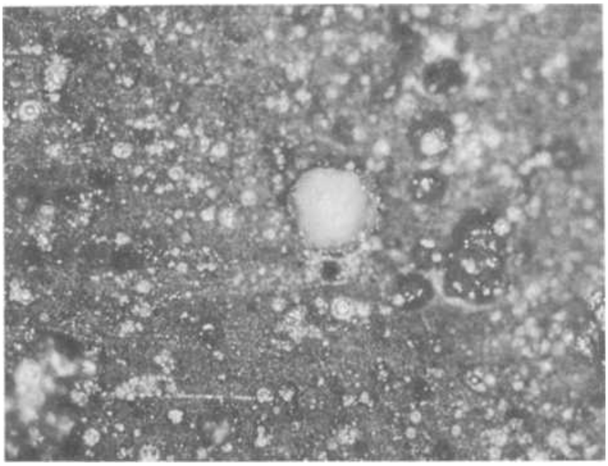

FIG. 18—*114-μm deep pit in clad radiator tube.*

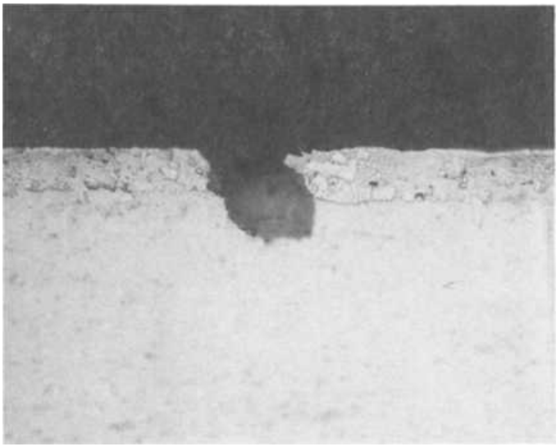

FIG. 19—*58-μm deep pit penetrating clad layer.*

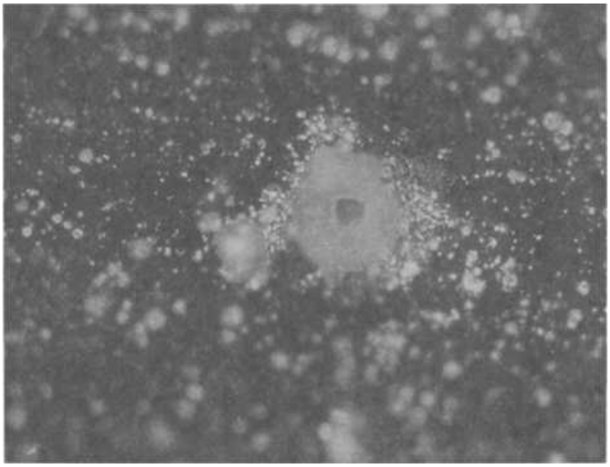

FIG. 20—*71-μm deep pit in clad tube.*

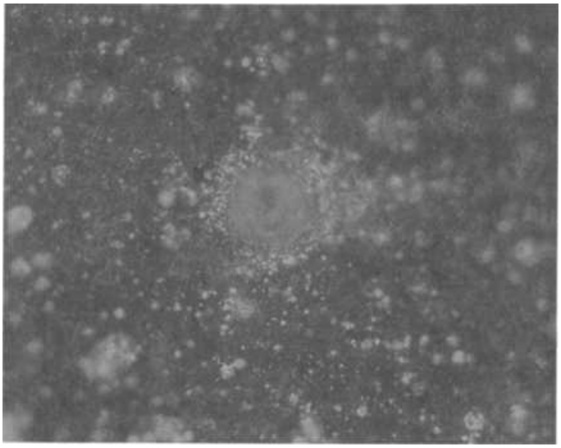

FIG. 21—*65-μm deep pit in clad tube.*

layer in the AA7072 clad material. Galvanic protection takes place. After a period of time, pitting attack occurs in the second layer, more rapidly penetrating the tube material.

In the unclad radiators, no such pitting attack develops initially in this coolant condition. Passivation occurs, producing surface protection. After extended exposure time, pitting attack results in isolated instances. Results are graphically presented in Fig. 22.

No failures of radiators were noted after 9 months of simulated service testing.

Simulated Service Test Results in Oyama Water

AA3003 Radiators—Two unclad AA3003 radiators were used in exposure to Oyama water at 88°C. Very different results were obtained with these two radiators. After 8 weeks of testing, one of the radiators revealed serious tube pitting with a pit depth of 110 μm. This radiator was removed from the test in order to examine the header and other tubes. The deepest header pit found was 115 μm. No deeper pit was found than the original tube examined, although several other pits almost the same depth were identified. An example of tube pitting is shown in Fig. 23. A tube removed from the other radiator after 8 weeks revealed very little pitting (Fig. 24).

A maximum pit depth of 5 μm was found in the tubes when the second radiator was removed from testing after 12 weeks. It is not unusual to have such wide variations in pitting attack with an aggressive corroding fluid. The header plate of this radiator revealed a maximum pit depth of 200 μm. Results of tube pitting for each of the two radiators tested are graphically presented in Fig. 25.

AA7072-Clad Radiators—Tubes removed from the AA7072 clad radiator reveal very small pits even after 12 weeks of simulated service. The maximum pit depth measured was 5 μm.

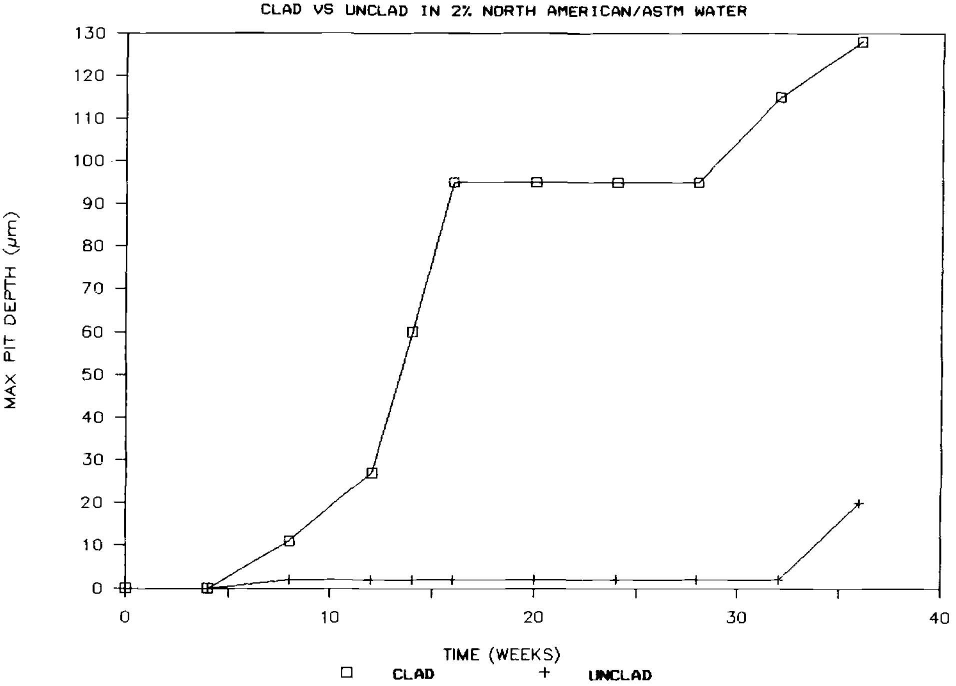

FIG. 22—*Pit depth measurements in 2% North American coolant and ASTM corrosive water.*

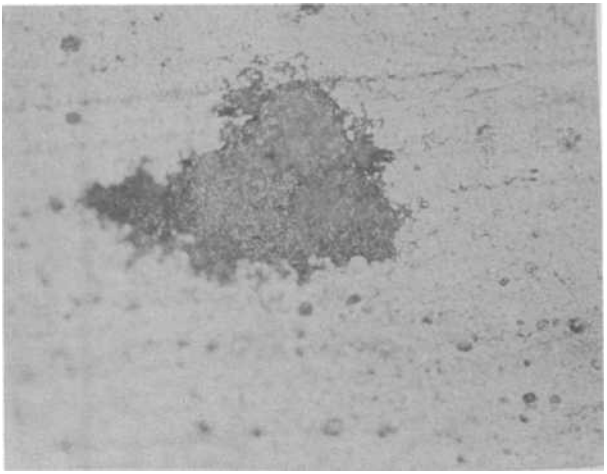

FIG. 23—*100-μm pit in unclad tube after 8 weeks in Oyama water.*

Some pitting was found in the header plate with a maximum depth of 60 μm. Pits in the header had formed adjacent to residual surface braze filler material and were obviously galvanic attack due to braze filler presence. This is illustrated in Fig. 26. No radiator failures were noted after 3 months of simulated service testing.

Pitting Summary—Results of simulated service testing in Oyama water clearly show that AA3003 is subject to pitting attack in this fluid. Under the same conditions, AA7072 showed much less pitting attack. Both materials would pass the Oyama water criteria for testing.

Correlation of Lab Test and Field Data—Success of a simulated service testing program depends upon adequate correlation with actual results obtained in vehicle service. A program of controlled testing was performed with known radiator alloys and engine coolants. Ten vehicles were involved in the field study. Radiators were removed from service after a number of years and miles of operation. The test program is continuing with a new series of evaluations

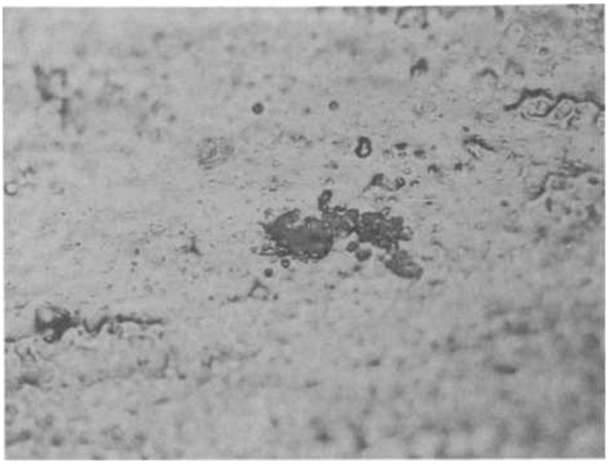

FIG. 24—*Shallow pit in unclad tube after 8 weeks in Oyama water.*

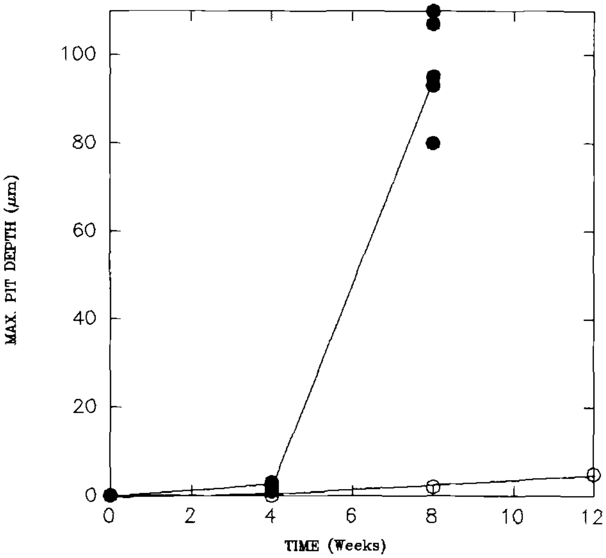

FIG. 25—*Pit depth measurements in unclad radiator material in Oyama water.*

and is expected to be a continuing effort for some time as both radiator alloy materials and engine coolants evolve.

Results for simulated service testing of four different aluminum radiator alloys in a selected corroding fluid are presented in Fig. 27 as an illustration. None of these radiators leaked during the tests. Depths of pitting measured were from radiator tubes after removal from the tested radiators at intervals during the testing program. The maximum pitting depth obtained for each radiator was used for evaluation. Alloy 3 was tested in both field service and simulated service.

Controlled field survey data of Alloy 3 are shown in Fig. 27. Again maximum pit depth found in radiators removed from service are shown. A good correlation is seen between the maximum pit depth obtained by simulated service testing and pit depths found from vehicle

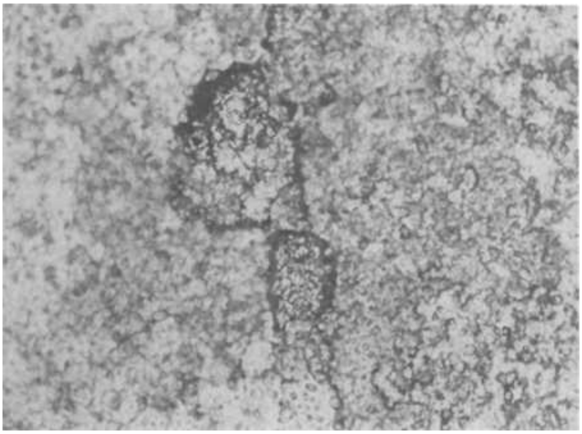

FIG. 26—*Clad header with 56-μm deep pit adjacent to braze filler metal.*

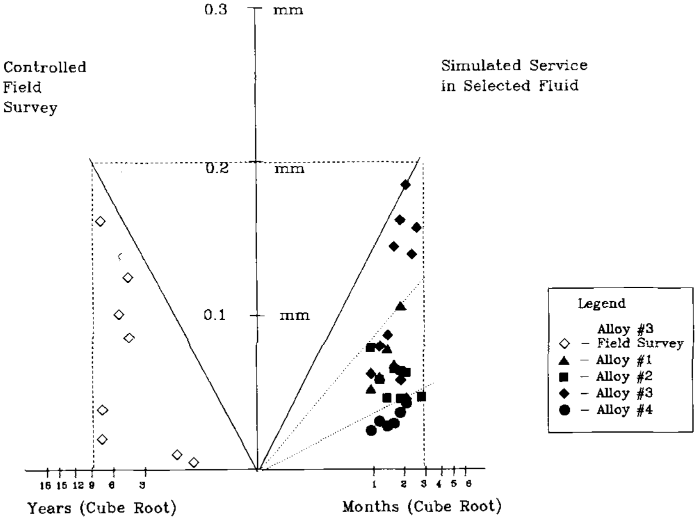

FIG. 27—*Correlation of pit depth from test and field data.*

operation with Alloy 3. Further testing will be used for validation, but presently 3 months of simulated service approximates 8 years vehicle usage. We have noted a direct aluminum radiator alloy dependency for a given corroding fluid as shown by the results of the other three alloys in simulated service in the same test fluid. No obvious universal relationship between each alloy and its service durability in engine coolants was observed. Careful data interpretation is needed in reaching conclusions from accelerated testing with selected coolants.

Discussion

Using the Oyama water test fluid as a measure of acceptability or selection of a radiator material, the AA7072 alloy would be adopted. A Japanese radiator manufacturer has found that the Oyama water test does give credible results that can be correlated with service when using the amine type Japanese engine coolant [*6*].

Very different results are obtained when a North American coolant is employed. Under these fluid coolant conditions, the AA3003 aluminum alloy radiator material is found to perform better than the AA7072 clad AA3003 core aluminum alloy radiator material.

It can be readily discerned, therefore, that preference will be given to a particular aluminum alloy radiator material depending upon the corroding test fluid used. The objective of a testing program is to identify which aluminum alloy material is best suited to service in a particular country, continent, or even worldwide. Dangers in specific test criteria become clear. It could be fatal to be adamant about the accelerating corrosion test media that is most applicable to a development program, unless some understanding of the engine coolant types to be used in service has been ascertained by a correlative field survey study.

The Oyama water concept does not appear to be applicable to the North American coolant situation from electrochemical and simulated service radiator tests carried out on this program. The work has shown that it is better to use a corrosive water medium with a percentage of the engine coolant that is appropriate.

This test program did not include any European style formula evaluation, but this will be the subject of further work based on these findings. The purpose of the paper is to demonstrate the need for careful consideration where using accelerated testing to determine material selection.

Conclusions

A study has been performed on the use of accelerating corrosion media to evaluate aluminum alloy radiator materials in engine coolant service. The study has used electrochemical evaluation of materials and simulated service testing of radiators using alloy AA7072 clad and AA3003 as examples of widely used aluminum radiator alloys. Five accelerated corrosion test coolants were used in the program. These were North American and Japanese style coolants at 17% and 2% levels together with Oyama water.

Results showed that aluminum alloy selection can directly depend upon the test fluid chosen. Data confirmed other studies on aluminum radiator alloy choices and highlighted the problem of test coolant preference.

Unless related to the particular engine coolant environments common to the country or continent of concern, serious mistakes can be made by manufacturers if selection of aluminum alloy radiator materials is based on some form of accelerated test without sufficient corroborative evidence.

Unclad alloy AA3003 performed better in simulated service compared to a AA7072 clad AA3003 material using a diluted North American coolant with ASTM corrosive water. This result is consistent with field experience with these two materials, and electrochemical tests in this study.

A successful accelerated test for radiator service life requires removal of tubes during the test for evaluation of internal pitting depth after certain exposure periods. Reasonable correlation between simulated service and field experience is obtained by these pitting depth measurements.

At the present time, it does not appear feasible to have an accelerated test that causes radiator failure by leaking in a short time period that can be realistically related to field service experiences.

Simulated service tests and field survey work continues with efforts to find improved test correlation for both pitting and radiator failure.

Acknowledgment

The authors wish to acknowledge Mr. Masashi Iwasaki of Calsonic Corporation for his valuable guidance throughout this evaluation program.

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Richard D. Hercamp[1]

An Overview of Cavitation Corrosion of Diesel Cylinder Liners

REFERENCE: Hercamp, R. D., "**An Overview of Cavitation Corrosion of Diesel Cylinder Liners,**" *Engine Coolant Testing: Third Volume, ASTM STP 1192,* Roy E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 107–127.

ABSTRACT: Cavitation corrosion (liner pitting) became a major problem for wet sleeve diesel engines in the 1940s. For most engines, generous use of supplemental coolant additives (SCAs) adequately controlled pitting. In the mid 1980s, problems of SCA overtreatment such as silicate gelation, water pump seal seepage, and solder bloom raised awareness that too generous usage of SCAs was undesirable. This new awareness caused a general shift toward lower average SCA concentration.

In addition, engine power densities increased and load factors increased as speed limits increased. These factors increased the work load of the engine, resulting in a greater potential for liner pitting.

All these factors have resulted in an increased incidence of liner pitting in recent years. This paper is an overview to help place all the various factors related to liner pitting in perspective. The effects of engine design and materials, cooling system hardware, maintenance practices, and coolant composition are discussed.

KEYWORDS: engine coolants, heavy duty, cavitation, corrosion, cylinder liner, cavitation corrosion, liner pitting, additive, SCA

The intent of this paper is fourfold:

1. To serve as a quick review for anyone wanting to learn about the various factors that may affect the degree of cavitation in any specific case. This background should enable one to do a better job of problem solving and getting at the real causes of failure.
2. To provide appropriate literature references to guide serious researchers to pertinent previous work.
3. To present some previously unpublished data.
4. To suggest approaches that could reduce the incidence of cavitation corrosion of diesel engine cylinder liners.

Description of Cavitation Corrosion of Diesel Cylinder Liners

Figure 1 shows a section of an engine block with a replaceable wet cylinder liner. As the piston moves vertically, it also moves a small amount horizontally due to inertia and combustion loading and impacts the cylinder liner causing it to vibrate. When the vibration is severe, the coolant cannot "follow" the rapid motion of the liner wall. Vapor bubbles form due to creation of an instantaneous low pressure in the coolant as the liner moves away from the coolant. Immediately after the vapor bubbles form, the liner surface movement reverses

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[1] Consultant, Fleetguard, 55E 1100S, Columbus, IN 47201.

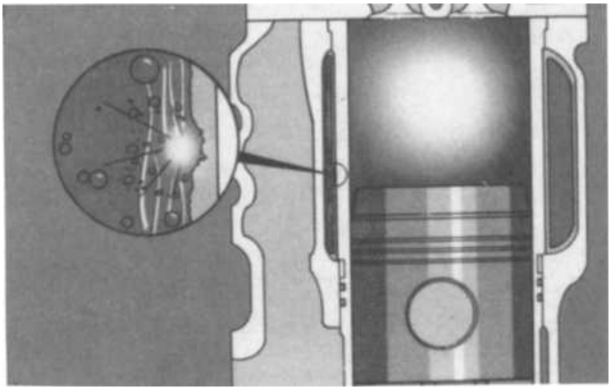

FIG. 1—*Schematic of cylinder liner cavitation corrosion.*

direction creating a localized high pressure in the coolant causing the vapor bubbles to collapse. The resulting forces from the collapsing bubbles act on the liner surface, along with corrosion, to remove metal in a pitting fashion (Fig. 2).

Just as it is important to know what cavitation corrosion is, it is equally important to know what it is not. Figure 3 shows a liner with some cavitation corrosion, but it failed at 59 715 miles due to another reason. The cavitation corrosion is in the circled center of the liner, but the failure occurred lower at the edge of the crevice seal groove. Figure 4 shows a typical deep pit with rough surfaces from the area of cavitation corrosion. This is in contrast to the smooth surface of the failure hole shown in Fig. 5. The seal was held away from its groove by steel shot

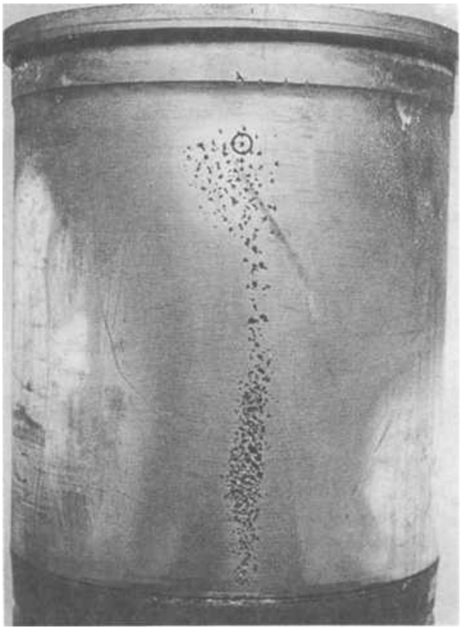

FIG. 2—*Cavitation corrosion on thrust side.*

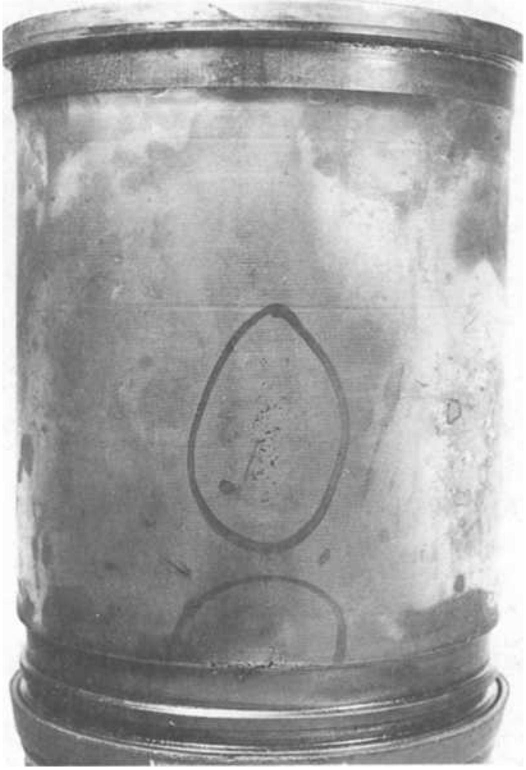

FIG. 3—*Failure at 59 715 miles due to erosion behind the crevice seal.*

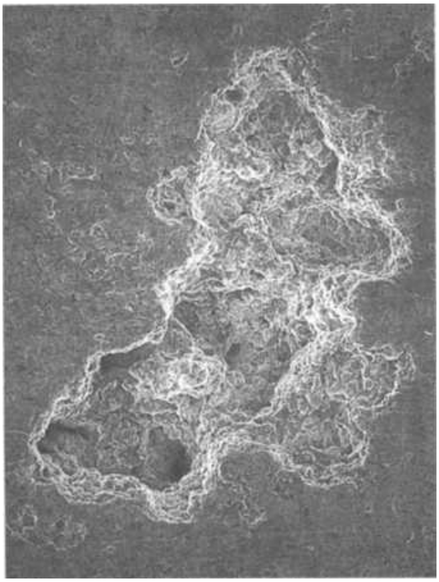

FIG. 4—*Typical pitted area from the circled area of Fig. 3.*

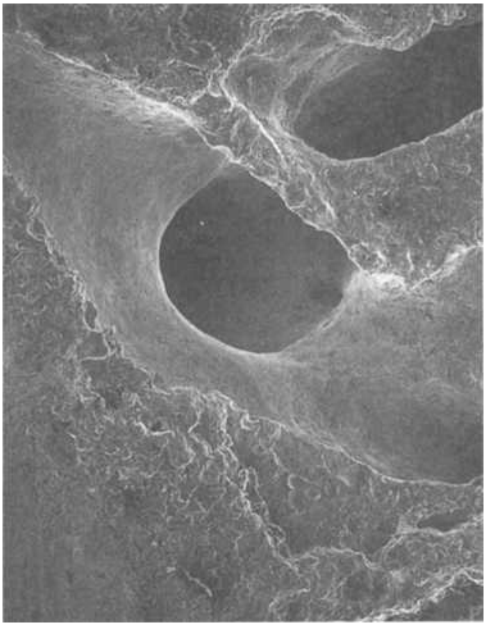

FIG. 5—*Smooth surface of failure hole from crevice seal area of Fig. 3.*

(Fig. 6) found near the failure. The failure resulted from flow erosion due to coolant pumping action behind the rubber crevice seal. The smooth surface of the flow-eroded failure hole is in stark contrast to the rough surface of the cavitation corrosion pit, which is typical of cavitation corrosion. A similar comparison is shown by Leith and McIlquham [*1*] for sand erosion and for cavitation erosion on a Pelton water turbine. The sand erosion surface is smooth compared to the cavitated surface.

Casting defects and stray electrical currents are two other examples of what cavitation corrosion is not. Casting porosity does not routinely occur only on the thrust side of the liner and less frequently elsewhere, as does cavitation corrosion. This rules out casting porosity.

As for stray electrical currents, it is difficult to imagine an external electrical current choosing to flow through the massive cast iron block to only small discrete areas of the liner and create pitting.

Commercial Consequences of Cavitation Corrosion Failure of Cylinder Liners

The cost to repair cavitation corrosion failure of diesel cylinder liners is high. At the least, an inframe engine overhaul is required. At the worst, a hydraulic lock-up at engine start-up due to coolant leaking into and filling the volume above the piston can cause total engine destruction. An inframe engine overhaul can cost about $5000, whereas a new engine can cost $15 000 for an on-highway diesel truck. Furthermore, in severe circumstances, failure can occur in less than 1000 h or 80 000 km of operation.

Cavitation

A paper published in 1982 states, "Since Euler recognized the phenomenon of cavitation in 1754, more than 1000 papers concerning cavitation corrosion have been published and its

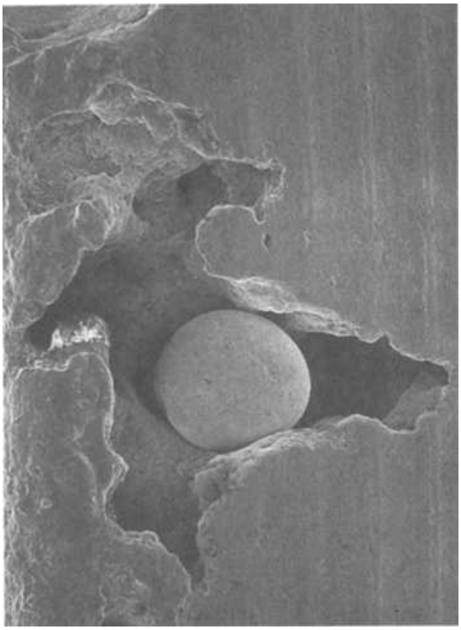

FIG. 6—*Steel shot that held crevice seal away from its seat.*

deleterious effects are often still seen" [*2*]. A useful general coverage of the subject was presented in 1970 in a book entitled *Cavitation* [*3*]. A possibly more useful (from an engineering standpoint) and slightly newer summary is provided in the *Handbook of Cavitation Erosion,* published in 1974 [*4*]. Other books containing compilations of related individual papers are also helpful [*5–9*]. Reference *9* contains an author and subject index for the complete series of Cavitation and Multiphase Flow Forums from 1966 through 1984. Reference *4* lists 243 literature references.

One of the reasons for the large amount of technical literature about cavitation is that the phenomenon is important in many areas. Some of these are liquid film bearings, radial face seals, and synovial joints [*10*]; liquid sodium space power conversion systems [*11*]; liquid sodium pumps for nuclear power stations [*12*]; rain erosion of high-speed aircraft surfaces and liquid droplet erosion in low-pressure stages of steam turbines [*13*]; diesel engine fuel systems [*14*]; ship underwater appendages, ship propellers, hydraulic turbines, pumps, valves, regulators, sluice gates, civil engineering hydraulic structures, underwater sound transmission and detection devices [*15*]; and the subject of this paper, diesel engine cylinder liners. In most of these situations, cavitation tends to be detrimental. However, in some applications, it is useful, such as a cavitating jet used to excavate material more rapidly [*16*], ultrasonic cleaning baths, and as an aid in liquid processing for areas such as biotechnology, chemical catalysis, and the production of colloids and emulsions [*17*].

Cavitation Bubble Dynamics

It is generally agreed that the material damage due to cavitation is caused by repeated mechanical forces acting on the material surface as a result of bubble collapse. It is also generally agreed that some nucleus, either solid or gaseous, is needed to allow vapor bubble growth to occur in most commercial situations where cavitation is observed [*18,19*]. Most recent work has been directed toward determining whether the forces impacting the solid material surface in the area of cavitation is due to shock waves emanating from bubble collapse or from liquid microjets formed near a surface at the end of bubble collapse [*20,21*].

Mechanical versus Chemical Damage

Plesset and Ellis concluded in 1955 that ". . . in so far as the basic process of cavitation damage is concerned, chemical effects are not of primary significance" [*22*]. However, Plesset later proposed a "pulsed cavitation" test method to take into account corrosive effects [*23*]. At about the same time, other investigators were confirming the chemical contribution [*24,25*]. Schulmeister and Chance summarized the situation appropriately: "Chemical and electrochemical actions always have an influence when the mechanical part of the complex stress is relatively low and the attack is directed against materials sensitive to corrosion" [*26*]. "There are two components that contribute to cavitation damage; one is the mechanical component and the other is corrosion. The relationship between the mechanical and corrosion components is complex because the processes involved are frequently interrelated and synergistic" [*27*]. Kallar gives a thorough review of the influence of chemical processes acting in concert with mechanical forces to damage materials [*28*].

Early Work on Cavitation Corrosion of Diesel Engine Cylinder Liners

LaQue and Hergenroether [*29*] first briefly reported on cylinder liner cavitation corrosion in 1949, and Speller and LaQue [*30*] gave a more comprehensive report on the problem in 1950. Several papers were presented at the June 1956 Society of Automotive Engineers (SAE) meeting [*31-35*]. Several more papers were presented in the United Kingdom in 1965 at a symposium on "Cavitation Corrosion and Its Prevention in Diesel Engines" [*36*]. Weigand and Schulmeister [*37,38*] reported in 1967 and 1968 on their work done in Germany at the Internal Combustion Engine Research Association.

Theories of Cylinder Liner Cavitation Corrosion

In 1956, Trock [*31*] listed three principal theories of cavitation erosion: Poulter's, Beeching's, and Crewdson's. (Another reference published by 1955 listed 18 proposed mechanisms of cavitation erosion [*39*].)

Trock described the three theories as follows:

Poulter's Theory—Cavitation-erosion is the result of penetration of a liquid into the pores of metal and its subsequent escape carrying some of the metal with it.

Beeching's Theory—Cavitation-erosion is the mechanical disintegration of surface layers under repeated, highly localized pressure pulses. These pulses are caused by the sudden collapse of cavities in contact with or close to the surface.

Crewdson's Theory—Cavitation-erosion is caused by super-heated steam at extremely high pressure. This steam is the gas or vapor in the cavitation bubbles.

My view of typical cavitation corrosion of diesel cylinder liners has been previously expressed [*40*]:

> It is the authors' opinion that cavitation corrosion could best be described as corrosion accelerated fatigue. Nonetheless, it is in this region where the chemistry of the coolant is exceedingly important

> since the type of oxide formed and its adhesion to the liner surface dictate whether pitting will take place. This is the vibration range where a well formulated coolant corrosion inhibitor can offer excellent liner pitting protection.
>
> At high levels of vibration, coolant chemistry effects are minor because the damage taking place is mainly of a mechanical nature. Bubble collapse has become so violent that base metal is rapidly fatigued making corrosion inhibitors of little, if any, use.

Little has changed since then to alter this view except that coolant passage geometry has been added as a significant factor [*41*].

Some Discordant Notes

Although work in the area of cavitation damage in general and cylinder liner cavitation damage in particular has supported the basic view that material damage is caused by a combination of mechanical damage due to the forces resulting from vapor bubble collapse and chemical damage due to corrosion, not all agree. Some of these other views are as follows:

> Bubbles do most of their damage not when they burst but when they billow, according to a new study by You Lung Chen and Jacob Israelachvili at the University of California, Santa Barbara. In the May 24 *Science*, they conclude that a bubble's birth involves violent stresses that can deform and destroy nearby surfaces. This counters the conventional explanation of how bubbles cause pitting, or cavitation damage, in turbine blades, pumps, propellers and other materials in contact with moving fluids [*42*].

Yakovlev [*43*] felt that cylinder liner cavitation corrosion occurs at areas of high tensile stress rather than areas of greatest vibration levels.

Wall [*44*] felt that cylinder liner pitting could be due to vibration-accelerated corrosion even if the cylinder liner vibration levels were low enough to preclude formation of vapor bubbles in the coolant.

The chemical aspect of cylinder liner cavitation corrosion was discounted by Zhou [*45*] as follows: "It was concluded that chemical corrosion had little effect on forming the honeycombed structure of the eroded surface."

A recent paper [*46*] accepts the chemical/mechanical nature of cylinder liner cavitation corrosion but adds some additional views on the failure mode.

> The failure mechanism can be described in the following form:
>
> - penetration of the cooling liquid into the bulk of the metal along large graphite inclusions and surface defects with subsequent oxidation of the base metal;
> - loosening of the base metal as a result of oxidation and the action of hydrolytic impacts which can cause plastic deformation of microvolumes of the metal;
> - unwedging of the base metal by the impacts and the oxides which leads to its failure;
> - the development of internal stresses in the heterogeneous structure due to thermal and mechanical effects (the microstructural components pose differing mechanical and thermophysical properties) where the structural components with low strength (graphite, ferrite, and the nonmetallic inclusions) are easily damaged and washed out of the cavitation zone which then permits an even higher level of corrosion-erosion attack.

Current Commercial Situation

Liner pitting (cylinder liner cavitation corrosion) became a major problem for wet sleeve diesel engines in the 1940s. For most engine designs, generous use of supplemental coolant additives (SCAs) adequately controlled pitting. In the 1980s, problems of overtreatment such as silicate gelation [*47*], water pump seal seepage [*48*], and solder corrosion [*49*] raised awareness that not only undertreatment but also overtreatment was undesirable. This caused a shift toward lower average concentration of SCA (Fig. 7).

Decreased heat exchanger design capacity margins, increased complexity of cooling systems, and less coolant volume led to many instances of overheating and greater coolant loss rates. In addition to leakage at hose clamps and so forth, overzealous topping up procedures also increased coolant loss. These increased occurrences of coolant loss further aggravated pitting problems by widening the distribution of SCA concentration (Fig. 8).

In addition to this, engine power densities (horsepower per litre) continued to increase and speed limits were increased. These factors increase the work load of the engine, resulting in a greater potential for liner pitting.

Factors Affecting Liner Pitting Severity (see Table 1)

Engine Design and Materials

Liner Vibration Levels—Anything done by design that reduces liner vibration also reduces liner pitting. When liner vibration is at normal levels, liner pitting can be adequately controlled by the proper choice of coolant additive. But not when the liner vibration levels are too high. In the case of one V-12 engine design, Teflon (Teflon is a registered trademark of Dupont) pads were added to the piston skirts to reduce piston slap (and, therefore, liner vibration levels)

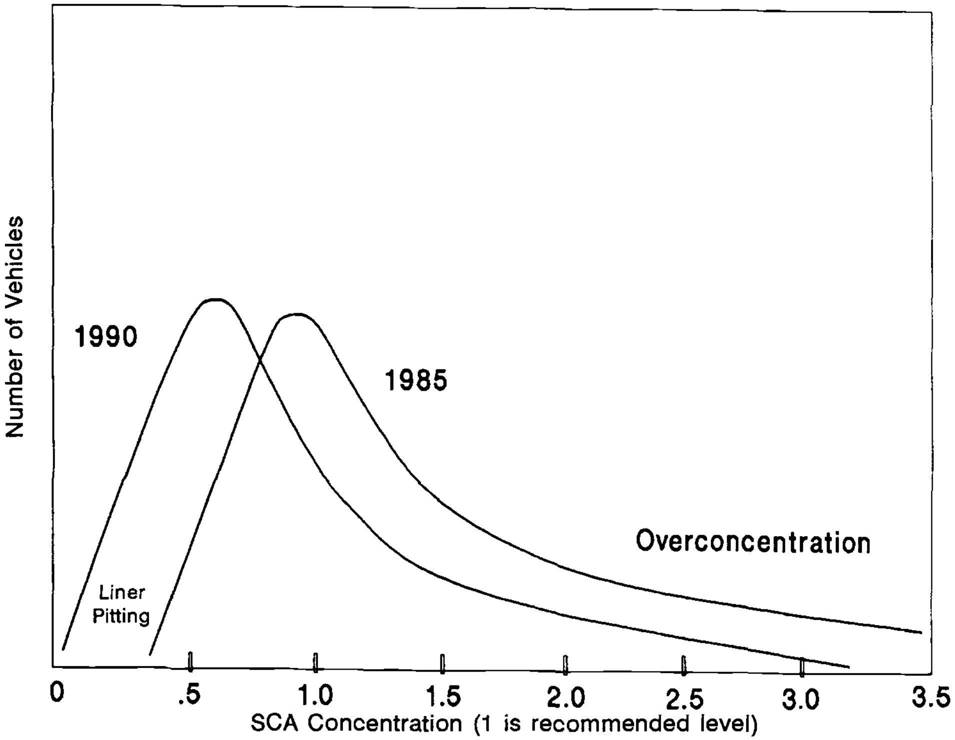

FIG. 7—*SCA concentration 1985 versus 1990.*

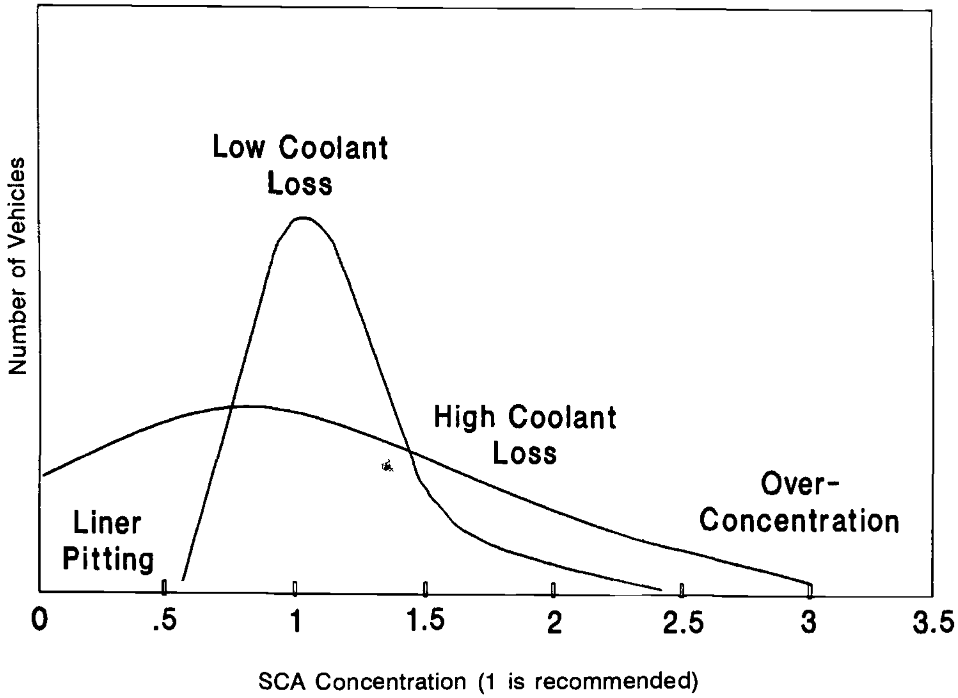

FIG. 8—*Coolant loss effect on SCA concentration.*

TABLE 1—*Summary chart of factors affecting liner pitting.*

A. Engine Design and Material Variables			
Liner Vibration Level	Coolant Passage Geometry	Coolant Condition	Liner Material and Coatings
Power density Design of piston Piston/liner clearance Timing Reciprocating mass Liner stiffness Liner support		Temperature and pressure of coolant in the block	
B. Cooling System Hardware			
Aeration Coolant loss Temperature and pressure of coolant (design, malfunction, misapplication)			
C. Maintenance Practices			
D. Coolant Composition			
Chemical Physical			

because pitting could not be controlled by use of coolant additives alone [*50*]. Some other engine designs have been relatively resistant to liner pitting, even if the coolant was not well-maintained. Some of these have used so-called mid stop liner designs wherein the liner is supported at its mid section [*51,52*]. This design reduced liner vibration levels. Some aluminum piston designs have had large piston-to-liner clearances when running at low piston temperature, so that piston expansion and scuffing would not occur at high piston temperature at high load. These designs were prone to pitting under cyclic loading because of the large piston-to-liner clearance at low temperature [*52,53*]. This allowed high impact loads due to severe piston slap, resulting in high liner vibration levels. Conversely, oil-cushioned [*54*] and some articulated two-piece piston designs have been shown to reduce liner vibration greatly [*52,55*], as well as one-piece gallery cooled [*56*] and "sled runner" type aluminum pistons [*57*]. Back-to-back 200-h engine tests with the same marginal coolant in the same engine using non-sled runner design pistons showed much liner pitting (Fig. 9). In contrast, none of the cylinder liners in the test run using "sled runner" design pistons was pitted. In fact, the lubrite coating was not even removed.

The following factors have also been observed to affect the level of liner vibration:

- In general, as the power density increases and the rated speed decreases, liner thrust loads increase. This tends to increase liner motion on the major thrust side where liner pitting is generally most severe.
- A heavier piston and a thinner, less stiff liner result in greater liner vibration.
- Piston dynamics are complex. In addition to piston design, other variables such as timing, rates of pressure rise, engine speed, and load, can all greatly affect the severity with which the piston impacts the liner [*58–60*].

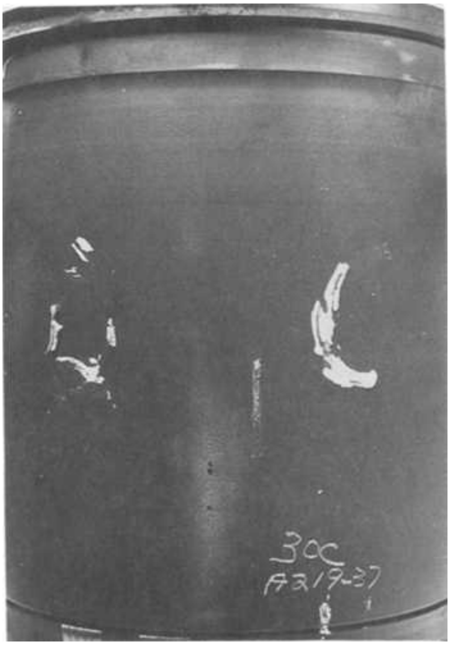

FIG. 9—*Five liners that pitted in a 200-h test using weak SCA.*

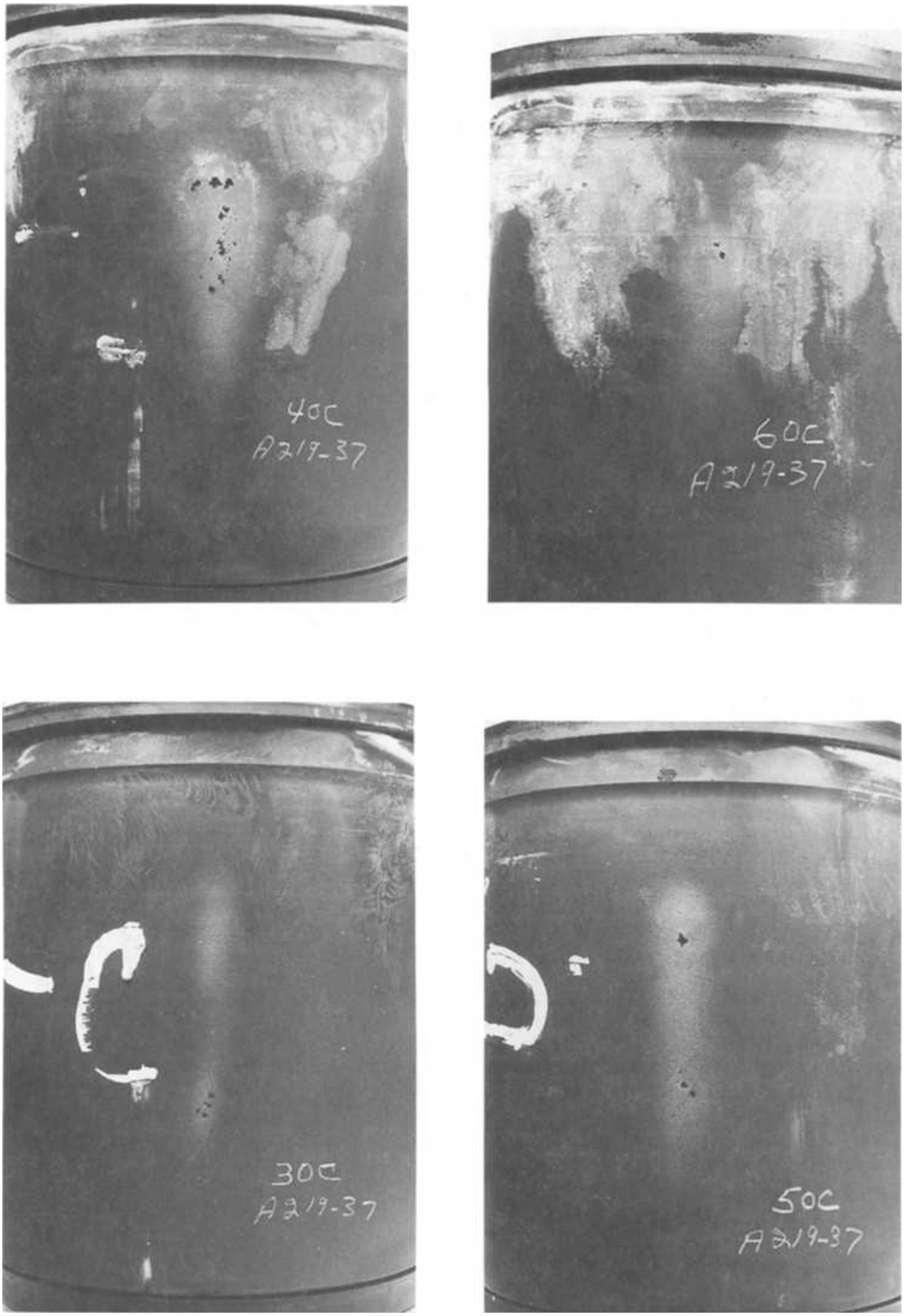

FIG. 9—*Continued.*

Coolant Passage Geometry—Another important design factor is the coolant passage width in the thrust area of the liner most prone to pitting. Generally, the less the width of the coolant passage, the greater the pitting, all other factors being equal [*45,55*]. However, an increase of coolant passage width beyond about 0.4 in. yields little, if any, benefit [*41*].

Coolant Condition—Because bubbles of coolant vapor must form and then collapse to cause liner pitting, the design pressure and temperature in the coolant passage at the thrust side of the liner are important factors. Laboratory tests using a vibrating cast iron specimen in coolant show the nonlinear effects of temperature and pressure (Fig. 10) [*61*].

When the coolant temperature is low, relative to the boiling point, or when the coolant pressure is high, it is difficult to form a vapor bubble. Therefore, the vapor bubble either does not form or the collapse of the relatively small bubble that is formed does not generate a mechanically severe environment. Under these conditions, pitting is not severe. At the other extreme, when the coolant is near the boiling temperature and pressure, vapor bubbles easily form, but they do not readily collapse. The maximum damage rate is obtained at an intermediate temperature and pressure where a significant number of bubbles form and collapse, yielding an intense mechanical attack.

Liner Material and Coatings—Because liner pitting is a physical and also a chemical phenomenon, both the corrosion resistance of the liner and its strength influence its resistance to pitting. The ultimate resilience of materials has been found in bench tests to correlate best with cavitation resistance in the absence of corrosion [*62–64*]. Ni-Resist and other more corrosion-resistant alloys have been reported to improve [*30,33*] or to be of no benefit [*65*] in reducing cylinder liner cavitation corrosion.

Because the liner material has generally been optimized for inside (oil) surface wear performance and producibility, it is difficult to change the liner material to increase its liner pitting performance. Therefore, outside diameter (OD) coatings have been evaluated. OD coatings, such as chrome, have sometimes been reported to be helpful [*32,53,66*], but many times are

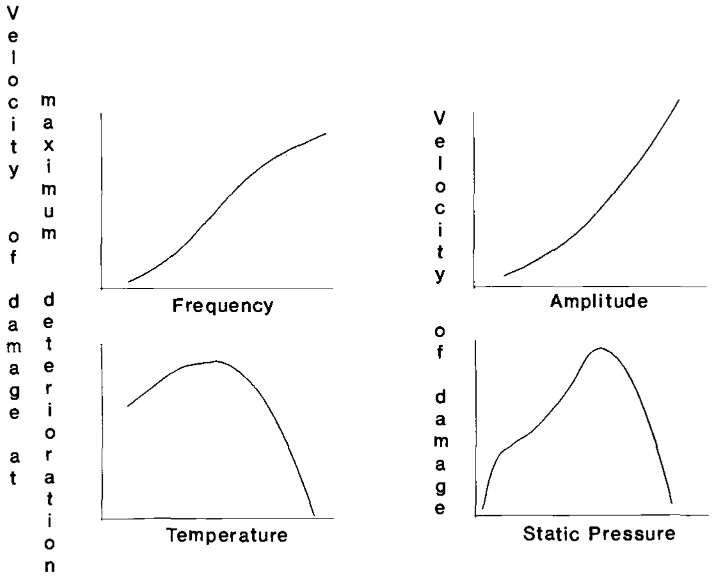

FIG. 10—*Relation between velocity of damage and main influences of test rig (schematic).*

not [*33*]. Coating failures probably relate to the difficulty of applying and maintaining a defect-free surface on the liner before and during assembly. Any coating discontinuity tends to aggravate pitting severity by physically and galvanically focusing the attack.

Cooling System Hardware

Even when the engine design and materials variables described in the previous section are optimized to prevent liner pitting, cooling system hardware and plumbing problems can cause liner pitting. If the cooling system does not de-aerate properly, liner pitting can result [*37*]. The circulating air bubbles serve as nuclei for cavitation vapor bubbles to form when they otherwise might not. Aeration of the coolant can also occur when the design of the cooling system flow circuit results in low coolant pressure at the suction side of the pump. In this case, air will be aspirated past the coolant pump seal faces. Improper installation or design of cooling system hardware can alter the coolant pressure or temperature in the block coolant passages and can result in increased liner pitting. Improper installation of cold starting aids, operation with malfunctioning thermostats, shutter stats, fan clutches, and so forth, or with improper activation temperatures are specific examples of these types of problems.

Finally, any cooling system hardware problem that results in excessive coolant loss will result in liner pitting because the chemical balance of the coolant is upset. Water by itself or a water and antifreeze mix used to replace coolant loss will result in a low SCA concentration (Fig. 11). Liner pitting is the end result. Some examples of field problems with cooling system hardware that result in excessive coolant loss are: silicone coolant hoses leaking at low temperature [*67*]; leaking head gaskets, water pump seals [*68*], oil coolers, radiators, and after coolers; and overheating resulting in boil-over.

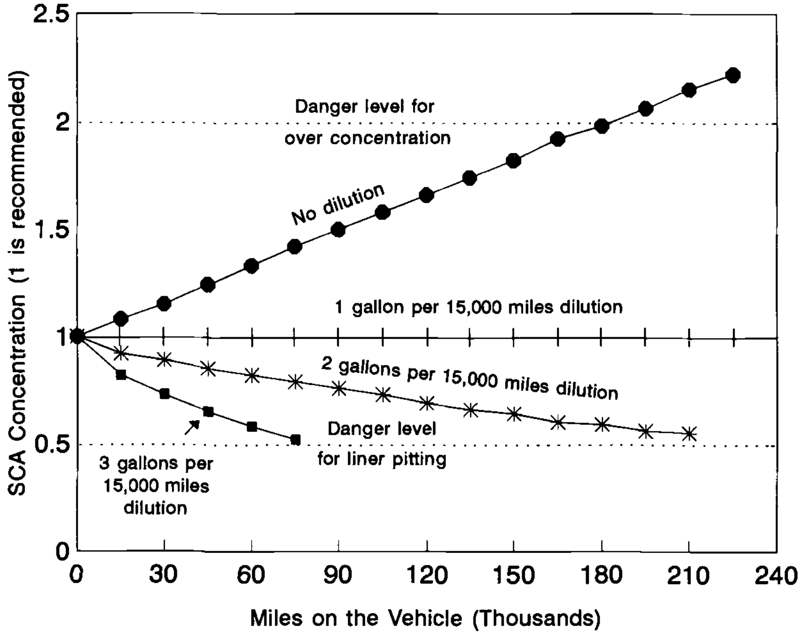

FIG. 11—*Effect of dilution rate on SCA concentration.*

Maintenance Practices

Many maintenance personnel are not aware of two facts: The SCA (not generally the antifreeze) contains the ingredients that control liner pitting. Second, the initial dose of SCA is three to four times the maintenance dose. Therefore, when coolant loss is excessive, the coolant composition gets out of balance because the proper amount of SCA is not replaced at the same time the system is topped up. The following specific practices have been observed to give low SCA levels in the coolant and result in liner pitting:

1. Excessive topping-up of coolant. Even if a 50/50 mix of antifreeze and water is used, the SCA level can be severely reduced if the cooling system is frequently filled to the cap. About 10% of the coolant is lost due to expansion as soon as the unit reaches operating temperature. Low SCA levels result.
2. Refilling the cooling system with a 50/50 mix of new antifreeze and water after repairs, but not adding a precharge of SCA. (The precharge amount of SCA is about three to four times the service charge.) This results in low SCA levels.
3. Skipping the SCA service charge at the oil and filter change interval. The amount of SCA in the service filter is designed for the nominal 16 000 mile (400 h) maintenance interval. Grossly extending the maintenance interval or failing to replace the coolant service filter at this maintenance interval can result in dangerously low SCA levels.

Coolant Analysis and Testing—A test kit should measure the amount of the chemicals used to prevent pitting if the testing results are to be meaningful [*69*]. In most of the world today, these chemicals are nitrite alone or a mixture of nitrite and molybdate compounds. In the past, some test kits have been used that measure pH, mercaptobenzotriazole (MBT), reserve alkalinity, conductivity, and so forth. These chemical ingredients and coolant properties do not relate to the ability of the coolant to protect against liner pitting.

Coolant Composition

Finally, if the engine design, cooling system hardware, and coolant maintenance practices are correct, liner pitting can still occur due to coolant composition. Coolant is composed of water, antifreeze, and SCA. Each is discussed below.

Water—Water with a high chloride or sulfate level aggravates liner pitting. Original Equipment Manufacturer's (OEM) limits on chloride and sulfate levels in make-up water vary, but are in the range of 40 to 100 ppm for each.

Antifreeze—Low silicate antifreeze from a reputable manufacturer is recommended by all heavy-duty engine builders. The purchaser must be careful when selecting an antifreeze because some blenders use off-grade glycol that is full of impurities. These impurities are often corrosive and can cause liner pitting. This problem is much more likely to occur when glycol supplies are tight and antifreeze prices are high [*70*].

SCA—Although few papers have been published on their mechanism of action [*71*], it is known that supplemental additives provided by reputable suppliers generally prevent liner pitting. Two basic types of SCAs are used in North America for heavy-duty equipment, phosphate/molybdate/nitrites and borate/nitrites. The borate nitrites should provide at least 1500 ppm nitrite as $NaNO_2$ in the precharged coolant to protect against liner pitting. The combination of molybdate and nitrite has been found to be more effective than nitrite alone or molybdate alone [*72,73*].

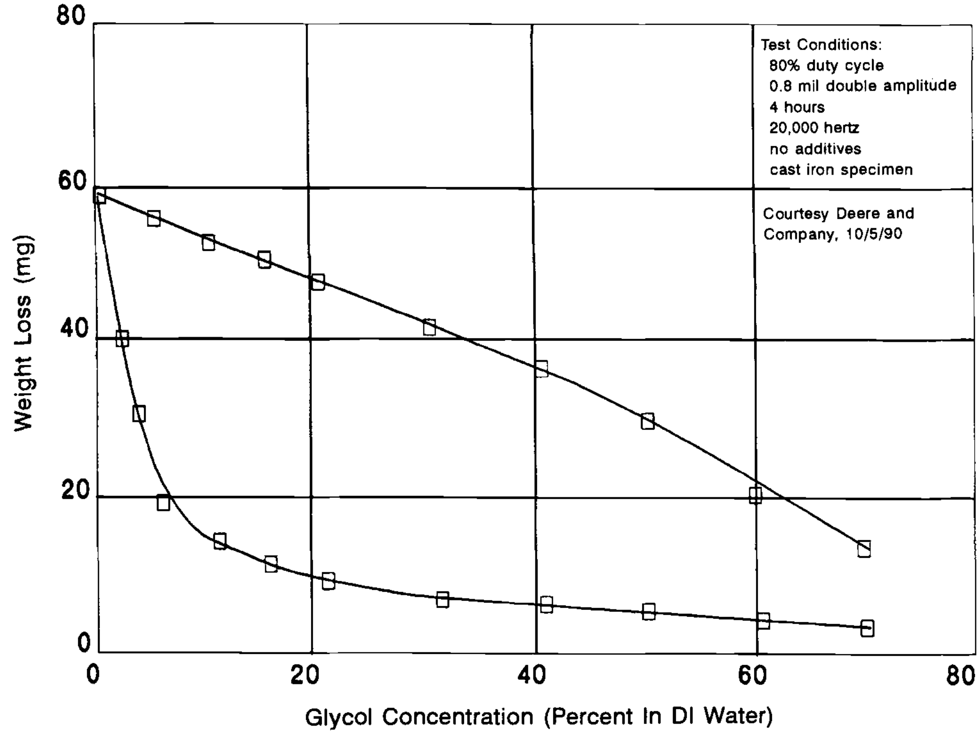

FIG. 12—*Effect of concentration of uninhibited aqueous EG and PG on cavitation corrosion of cast iron.*

Just as the phosphate/molybdate/nitrite SCA has been shown to give superior liner pitting protection, aqueous coolant based on propylene glycol (PG) in place of ethylene glycol (EG) also has been found to give additional protection against liner pitting [*74–76*]. Figure 12 shows the superior performance of PG over EG when no corrosion inhibitor is added.

Although the above coolant variables are the most important, others have been found to affect liner pitting adversely:

1. Entrained air [*37*] and
2. Dirt in make-up water/circulating particulate in the coolant [*77*].

A procedure for troubleshooting liner pitting is as follows:

1. Take a random sample of coolant from 10% of the engines in the fleet. Low SCA levels in many units indicates the potential for liner pitting problems.
2. Check the records for the unit in question for excessive coolant additions, cooling system repairs, excessive maintenance interval length, skipped coolant filter at the maintenance interval, use of maintenance filter after repair work when precharge should have been used.
3. Check for aeration.
4. Check for abnormal block coolant pressure.
5. Check for abnormal block coolant temperature.

Future Work That Can Contribute Toward Reducing the Incidence of Cylinder-Liner Cavitation Corrosion

Coolant

Standards need to be developed for both SCAs for heavy-duty engines and for antifreeze coolants for heavy-duty engines *that include a precharge dose of SCA*. These standards would enable the heavy-duty engine and vehicle manufacturers to specify appropriate coolants, and the coolant suppliers to identify their products as meeting those standards. Use of substandard products would be minimized. Of equal importance, use of antifreeze coolant that contains a precharge dose of SCA would dramatically reduce cavitation corrosion caused by topping up with coolant without SCA.

The increased use of aqueous PG coolants would further reduce cavitation corrosion due to their proven improved performance in the area. Furthermore, if heavy-duty vehicle manufacturers design their product to use nonaqueous PG coolant, cylinder liner cavitation corrosion can be eliminated [*78*].

Engine Design and Materials

Widespread use of new acoustic and liner motion test methods on early prototypes of new engine designs holds much promise to measure quickly the propensity of newly designed engines to pit liners. This quick measurement of cavitation acoustics or liner vibration levels allows time for design revisions before engine production.

Designing the block casting to accommodate proper coolant passage geometry, particularly on the thrust side of the liner, avoids what can be difficult and expensive revisions later during engine development.

Close attention to piston design to minimize liner vibration is required. Articulated piston designs appear to offer distinct advantages.

The freedom to alter liner material to improve liner cavitation is severely restricted due to the fact that the material used has generally been optimized for ID performance. Therefore, liner OD coatings should receive greater attention. Although past experience with coatings has not generally been favorable, possibly newer processes such as ion nitriding, physical vapor deposition, ion implantation [*79*], and so forth should be evaluated.

Cooling System Design

The design of the vehicle cooling system must be controlled so that the coolant pressure and temperature at the cylinder liner are not altered beyond the limits specified by the engine builder. Also, the system should de-aerate rapidly and in all intended vehicle operating angles. A positive contribution might be the addition of an overflow tank containing a rubber bladder plus a coolant level gage. This would minimize coolant composition imbalance due to unnecessary topping up and also would minimize the oxygen content of the coolant to reduce corrosion.

Maintenance Practices

The most important practice to be recommended is use of an antifreeze coolant truly formulated for heavy-duty engines. Preferably the coolant should be PG based. The second is to use appropriate field test methods to check the coolant condition [*69,80*].

Summary

The test tools, the design knowledge, the maintenance practices, and the coolants are available to eliminate cavitation corrosion failures of diesel cylinder liners as outlined above. Continued efforts by all involved will readily reverse the trend toward an increased incidence of cylinder liner cavitation corrosion failures.

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DISCUSSION

Joseph A. Lima[1] *(written discussion)*—First, I am wondering about alternatives for the SCA approach to prevent liner pitting. Many European coolants contain some nitrite, and apparently some of these are in successful use in heavy-duty equipment in Europe without SCAs. Is this a successful approach in Europe, and, if so, why not in the United States?

Second, I note that no "leakage" allows an overconcentration to develop, whereas excess leakage seems to cause a less than optimal SCA level. For a long-term SCA approach, it seems a controlled removal, almost what is done in cooling tower treatments, of some of the coolant could help maintain an acceptable level of total dissolved solids (TDS) and permit addition of SCAs without the attendant overconcentration problem. Comment?

R. Hercamp (author's response)

1. If the coolant contains a minimum of 1500 ppm nitrite (as $NaNO_2$) after being diluted to its recommended usage level (generally 50% glycol), it will control cavitation corrosion in most engines. In this case, an initial charge of SCA would not be required. However, periodic addition of SCA to maintain the protection would still be required. This is necessary to compensate for the effects of additive depletion and dilution with extended use of the coolant, which is typical with heavy-duty engines.

2. A better approach would seem to be that of using coolant that contains additives for reducing cavitation corrosion. Use of this type coolant for both initial fill and for "make-up" would reduce the starting TDS level and would also allow the amount of solids added at the maintenance interval to be reduced. The SCA maintenance dose could be reduced to compensate for only depletion rather than a larger dose to take care of depletion plus some average estimated rate of dilution.

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[1] Houghton Chemical Corporation, Allston, MA.

George R. Otterman[2] *(written discussion)*

1. Does cavitation corrosion occur on all cycles of the engine stroke?

2. In the real world, will good engine design and/or quality SCAs completely eliminate cavitation corrosion, or do you always expect to see and live with the problem?

3. Why phosphate the liner wall?

R. Hercamp (author's response)

1. I don't know, but the normal location of the most severe damage is on the thrust side of the cylinder liner. This would indicate that the corrosion occurs primarily during the firing stroke. Liner vibration measurements and liner vibration models reported in the literature indicate that maximum liner vibration generally occurs very soon after firing.

2. Engines can certainly be designed to eliminate cavitation corrosion. Whether these engines would be economical and practical is a much more difficult question to answer. At the other extreme, some engines have been designed that are so severe that the proper use of quality SCAs is not sufficient to control cavitation corrosion. If liner vibration is too severe, coolant additives are not the answer. The design must be modified to reduce vibration.

I expect that we will need to live with the cavitation corrosion problem for many years to come. Therefore, it is imperative that ASTM D 15 continue its work to develop standards for both SCAs and antifreeze coolants for heavy-duty engines that incorporate additives to reduce cavitation corrosion.

3. Some cylinder liners are coated with a phosphate-rich coating as the last step in their manufacture. The coating generally serves two purposes, that of a rust preventative during storage and as a solid film lubricant for the liner ID during engine operation. The phosphate coating has no effect on the rate of cavitation corrosion damage.

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[2] Electro-Motive Division of General Motors, LaGrange, IL.

R. D. Hudgens[1]

Phosphate-Molybdate Supplement Coolant Additives for Heavy Duty Diesel Engines

REFERENCE: Hudgens, R. D., **"Phosphate-Molybdate Supplement Coolant Additives for Heavy Duty Diesel Engines,"** *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 128–148.

ABSTRACT: Supplemental coolant additives (SCAs) are commonly used in heavy duty diesel service. The SCA boosts the performance of the typical antifreeze coolant and replaces additives lost to depletion and coolant dilution.

In the early 1970s chromate based SCA's were phased out because of chromate's toxicity and adverse environmental impact. Borate-nitrite based SCAs replaced the chromates and are widely used today.

This paper describes the development of a third generation phosphate-molybdate additive package. Relative to the borate-nitrite SCAs, the phosphate-molybdate supplemental coolant additive gives better overall aluminum protection. Furthermore if overtreated, it is less likely to cause solder bloom, silicate gelation, and water pump leakage.

KEYWORDS: supplemental coolant additives, heavy duty diesel, engine coolants, antifreeze-coolants, corrosion inhibitors, corrosion, cavitation

Background

Supplemental coolant additives (SCAs) have been used in heavy duty diesel engine coolants since the mid 1950s. The primary function of the SCA is to stop liner pitting (cavitation-corrosion) as well as prevent deposits and scale buildup in the cooling system. The typical light-duty automotive antifreeze coolant does not provide this type of protection. An SCA is also used to replenish the additives consumed in normal service. This is vital for heavy duty vehicles where the service life of the coolant can range from 200 000 to 500 000 miles (320 000 to 800 000 km) or 5000 to 12 000 h.

The typical supplemental coolant additive is formulated to work in water alone or when used in conjunction with an antifreeze coolant. For this reason there is some overlap between the additive package of an SCA and antifreeze. Both are likely to contain a phosphate and a borate buffer, or both, as well as some of the same corrosion inhibitors (nitrate, silicate, and tolytriazole). Table 1 compares the features or functions of a heavy duty supplemental coolant additive to those of a light duty antifreeze coolant.

Chromate based SCAs were used in the United States from about 1955 to 1975. Chromates were largely phased out in the 1972 through 1975 time frame because of environmental concerns, and to a lesser extent, antifreeze compatibility problems. The chromates were replaced with borate-nitrite based SCAs. Borate-nitrite supplemental additives specifically formulated to protect the cooling system of a heavy duty highway diesel engine first appeared in the late 1950s. Those products were very similar to the borate-nitrites used today.

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[1] Senior staff chemist, Fleetguard, Inc., Cookeville, TN 38502.

TABLE 1—*Comparison of a heavy duty supplemental coolant additive to light duty antifreeze coolant.*

Function	Heavy Duty SCA	Typical Antifreeze/Coolant
Buffer	yes	yes
General corrosion protection	yes	yes
Liner pitting protection	yes	no
Scale/deposit control	yes	no

Development of a Third Generation Supplemental Coolant Additive

In 1980, a Fleetguard/Cummins Engine Company technical group was formed to consider the need for an improved supplemental coolant additive. This group consisted of chemists and technical service engineers from both companies.

The technical group's field survey showed the following problems associated with the use of borate-nitrite based SCA's:

- Solder bloom or corrosion
- Antifreeze compatibility
- Aluminum corrosion (especially with high mineral content make-up water)

The survey also showed that heavy duty cooling systems were often fouled with oil, which can cause heat transfer and corrosion problems. This was a problem not being addressed by the SCAs available at that time.

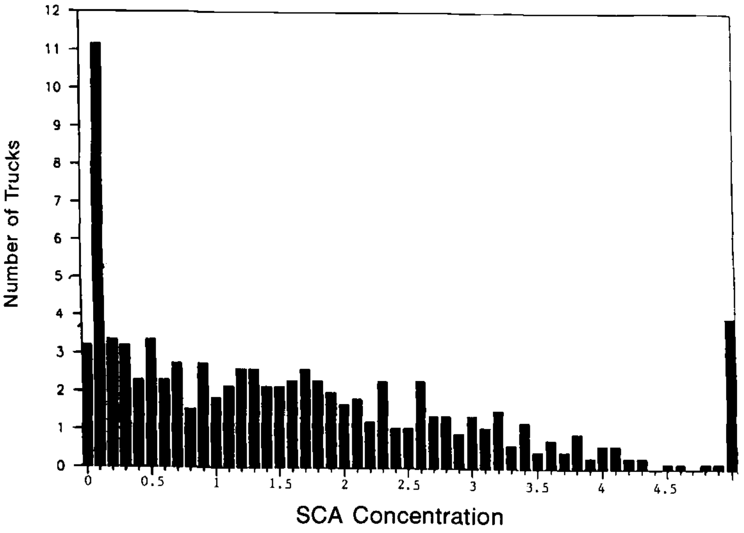
With our field survey as a guide, we began the development of a new supplemental coolant additive. The primary objectives were to formulate a product that gave good aluminum and solder protection under a wide variety of service conditions and minimize the problems that occur when an SCA is overtreated. For many operators of heavy duty equipment it is difficult to control the amount of SCA in the engine coolant.

Figure 1 shows the range of SCA concentration in the coolant of vehicles from one on-highway fleet. Many of the vehicles have 3 to 4 times the recommended concentration of supplemental coolant additive. This overconcentration of SCA can trigger the following problems:

- Silicate gelation
- Solder bloom (corrosion)
- Water pump leakage

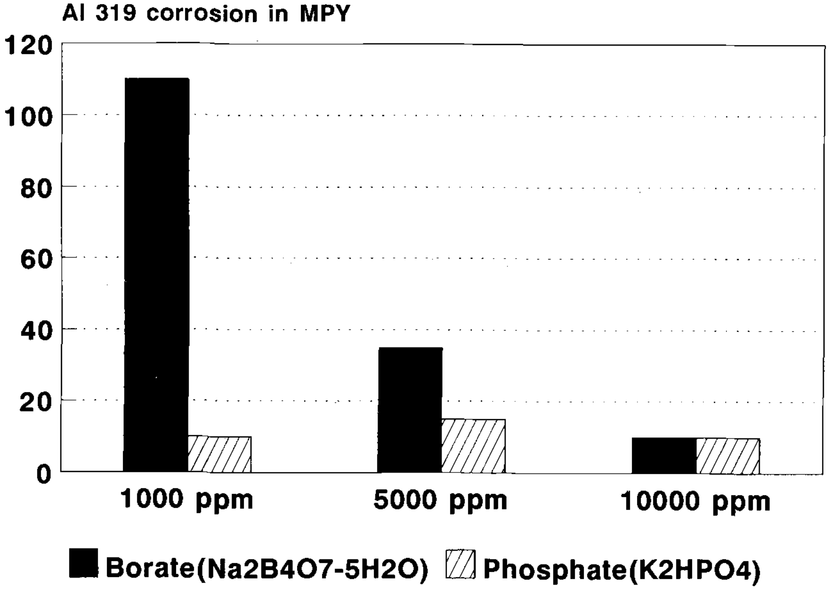
We began our laboratory work by carrying several different additive mixtures through preliminary/screening type tests. In some instances we took the same mix of chemicals and simply interchanged phosphate for borate to understand which buffer made the better foundation on which to build. The bulk of the information generated indicated that a phosphate buffered additive package gave better corrosion protection, especially for aluminum. Figures 2 and 3 compare phosphate and borate as to their aluminum corrosion protection and aluminum cavitation protection. It is clear that in both tests phosphate gives significantly better protection. These results are consistent with those reported by Oakes [*1*]. In addition, Vukasovich and Sullivan of Climax Molybdenum [*2*] and Wiggle et al. of Ford Motor Company [*3*] reported borate to be aggressive to aluminum under cavitation and heat transfer conditions.

Another reason for focusing our development effort on a phosphate buffered product was that it coupled well with molybdate. In the early 1980s, molybdate was being promoted as an effective all around corrosion inhibitor by Climax, General Motors, and Ford Motor Company. We did not observe a strong synergism when we tested borate with molybdate. Our find-



NOTE: Concentration is given relative to the recommended amount. Therefore 1 is the recommended treat level.

FIG. 1—*Variation in SCA concentration from several vehicles in a large on-highway fleet.*



Base solution contains 100 ppm chloride

FIG. 2—*Aluminum corrosion with phosphate and borate buffers.*

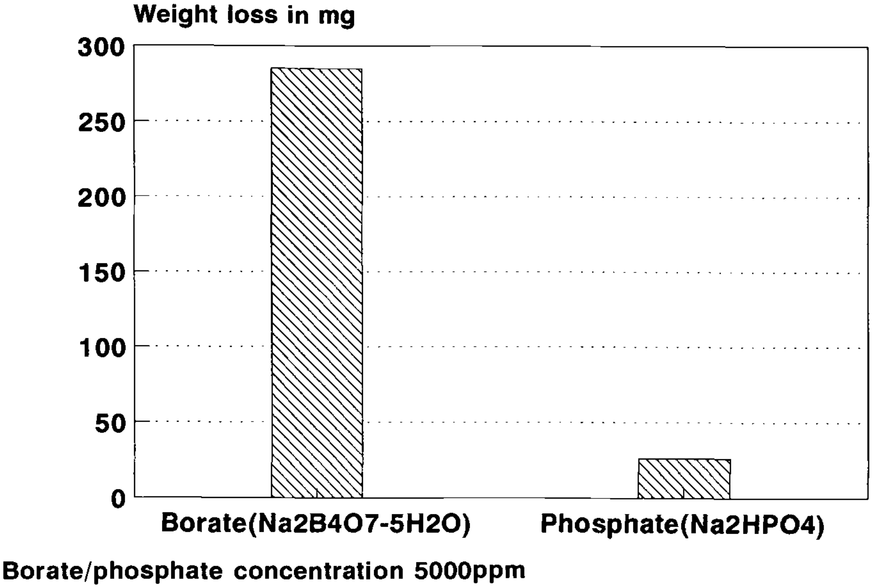


FIG. 3—*Aluminum cavitation-corrosion with phosphate and borate buffers.*

ings were consistent with data reported by Vukasovich [*2*] and Wiggle et al. [*3*], that phosphate-molybdate blends were synergistic when it came to protecting cast iron, high lead solder, and aluminum from corrosion. In addition, our laboratory work showed that molybdate was synergistic with nitrite in protecting cast iron from cavitation corrosion protection. This finding is also supported by the work of Weber et al. [*4*] and Al-Borno et al. [*5*].

Laboratory and Dynamometer Test Methods

The test scheme used in this development work is outlined in Table 2 and the details of the various test methods discussed elsewhere in the literature. Rowe [*6*] in his overview of engine cooling system inhibitors suggests the same glassware to field test progression.

TABLE 2—*Supplemental coolant additive testing scheme.*

Level 1[a]	Level 2[b]	Level 3	Level 4
Glassware corrosion	erosion corrosion	dynamometer test	field test
Electrochemical	German FVV	...	...
Bench cavitation corrosion	water pump leakage	...	...
Aluminum hot surface corrosion (D 4340)	D 2570 simulated service	...	...
Antifreeze compatibility	D 2809 water pump cavitation	...	...
Detergency/dispersency	...	...	...

[a] These tests are more "beaker" or "bench top" test methods that use small quantities of coolant. Test duration is often short, and several tests can be run at the same time so that they make a good screening tool.

[b] These methods are more involved and often longer in duration. The test stands are larger, more complex, and in some ways simulate actual field conditions.

TABLE 3—*Supplemental additive comparison.*

Function	Borate-Nitrite	Phosphate-Molybdate
Buffer	borate	phosphate
Liner pitting protection	nitrite	molybdate and nitrite
Corrosion inhibitors	nitrate and silicate	nitrate and silicate

Glassware tests were run in a mixture of ethylene glycol and corrosive water, corrosive water only, and hard water. Test methods included both ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384) and Case MT-817. Later in the paper as results are presented, more information will be given on the test methods used.

The dynamometer testing was conducted using the Cummins NTC-400 oil consumption test. This test, which runs at rated speed and 5% overfuel, was developed to measure lubricating oil's ability to prevent piston deposits and limit oil consumption. The fact that the engine is overfueled makes it run hot and pit liners. It is an excellent tool to measure an SCAs ability to control liner pitting and prevent hot surface scaling. Hercamp [7] has thoroughly described the test method in an earlier paper.

The field test methods and results will be presented in a later section of this paper.

Chemistry Comparison and Summary of Advantages

Table 3 compares the inorganics present in a borate-nitrite versus a phosphate molybdate SCA. There are several organic components in each (surfactants, scale inhibitors, defoamers, and corrosion inhibitors), but the inorganics still compose 75 to 90% of the additive package.

Borate is replaced by phosphate and molybdate when the chemistry of the two SCA types are compared. The phosphate based system exhibits more synergism among its components, which allows the use of less nitrite and silicate. Lower nitrite levels in the coolant result in less solder corrosion while lower silicate concentration reduces the chance of silicate gelation. Table 4 lists the advantages of the phosphate-molybdate additive package.

Phosphate-Molybdate Versus Borate-Nitrite Performance

The advantages listed for the phosphate-molybdate system will be discussed in more detail in this section. Only data relative to how the two SCAs compare are included. (General test results on the phosphate-molybdate system are included in Table 5).

Aluminum Protection

A borate-nitrite SCA depends heavily on silicate to protect aluminum. This presents a problem when the make-up water contains high levels of hardness (>250 ppm). Calcium and mag-

TABLE 4—*Phosphate-molybdate advantages.*

Better aluminum corrosion protection
Better solder corrosion protection
Improved antifreeze compatibility
Improved liner pitting protection
Lower toxicity
Fewer water pump leaks
More tolerant if overdosed

TABLE 5—*Phosphate-molybdate performance in ASTM tests.*

	Test Results versus ASTM D 3306 Requirements		
Test Method and Conditions		Results, mg	Required, mg
D 1384 glassware at ⅓ recommended dose in 50/50 (v/v) ethylene glycol-corrosive water	copper	4.0	10
	solder	0.4	30
	brass	3.0	10
	steel	0.9	10
	cast iron	1.4	10
	aluminum	3.3	30
D 4340 aluminum hot surface at recommended dose in 25/75 (v/v) ethylene glycol-chloride water		0.5 mg/cm^2/week	1.0 mg/cm^2/week
D 2809 water pump cavitation at ½ recommended dose in 17/83 (v/v) ethylene glycol-corrosive water		8.0	8.0 min
D 2570 simulated service at recommended dose in 44/56 (v/v) ethylene glycol-corrosive water	copper	7.7	20
	solder	22.0	60
	brass	6.7	20
	steel	0.3	20
	cast iron	2.7	20
	cast aluminum	1.0	60

NOTE: Recommended dose of phosphate-molybdate SCA 3% by volume for liquid and 6000 mg/L for solid.

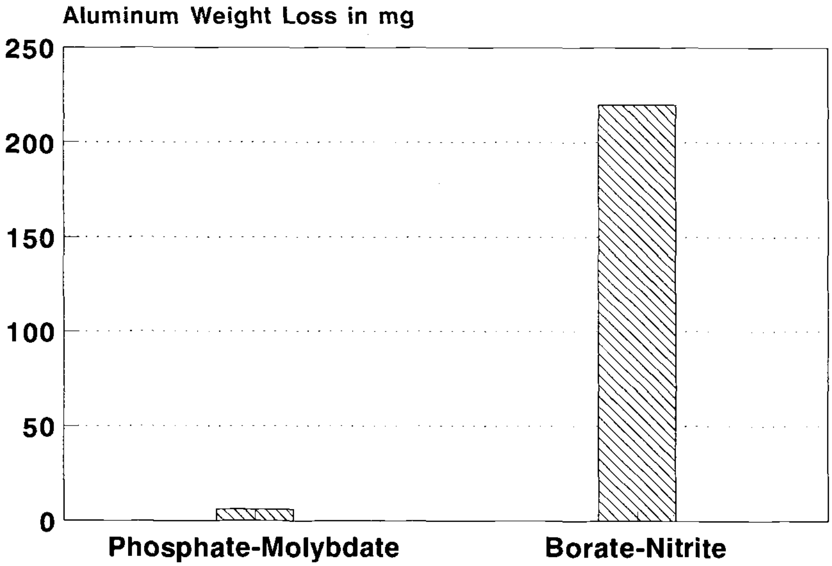
nesium (water hardness) react with silicate to form a precipitate. The precipitated silicate is no longer able to maintain a protective film resulting in aluminum corrosion. Figure 4 presents data obtained from a D 1384 glassware test using hard water.

It is evident that the phosphate-molybdate additive provides improved aluminum protection in hard water. This occurs because phosphate and molybdate help provide aluminum protection even when silicate precipitates from solution. Where aluminum cavitation is a problem and hot surface corrosion protection is needed, phosphate is the buffer of choice (Fig. 3). Wiggle et al. [*8*] recommended against the use of high levels of borate where hot surface aluminum corrosion is a problem (engine block and head). This is shown in Fig. 5 which presents data from the British Standard Recirculating Rig Test (BS 5117), which tests for hot surface aluminum protection. A borate-nitrite SCA fails after only 12 days while the phosphate-molybdate additive provides hot surface aluminum protection for 34 days.

Solder Protection

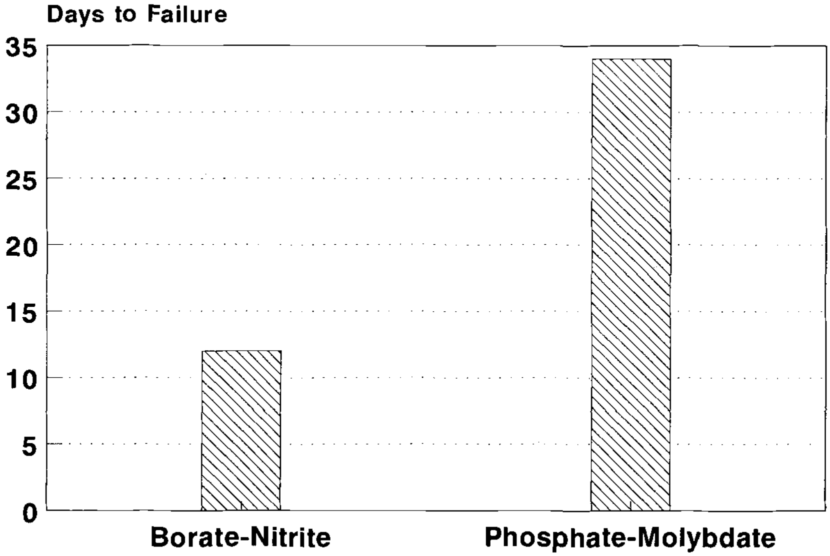
A borate-nitrite SCA uses relatively high levels of nitrite to protect liners from cavitation corrosion or pitting. While nitrite effectively reduces cast iron liner pitting it can be aggressive to solder. Rowe [*6*] warned of this problem several years ago. Our experience shows that solder corrosion can be initiated by sodium nitrite levels in excess of 3000 ppm. This concentration is exceeded with twice the recommended dosage of the typical borate-nitrite SCA; something that regularly occurs in the field. Table 6 presents dynamometer test data which shows the effect of nitrite on solder corrosion based on the soluble lead in the coolant.

ASTM D 1384 glassware corrosion tests were run on a borate-nitrite and phosphate-molybdate SCA at the recommended concentration in a 50/50 by volume mix of ethylene glycol and ASTM corrosive water. The phosphate-molybdate SCA provides superior solder protection as



SCA concentration @ 3000 ppm

FIG. 4—*Glassware corrosion test of SCAs run per D 1384 except hard water substituted for standard corrosive water.*



Loss of temperature control ends test

FIG. 5—*British Simulated Service Test (BS 5117) of borate nitrite versus phosphate molybdate SCA.*

TABLE 6—*Nitrite concentration versus solder corrosion.*

	Borate-Nitrite	Phosphate-Molybdate
Nitrite Concentration (ppm $NaNO_2$)	3500	690
Dosage versus Recommended	2X	1X
Lead in Coolant, ppm	21	1

shown in Fig. 6. This is due in part to the nitrite concentration, which is less than half that found in borate nitrite SCAs.

Silicate Gelation

On occasion, a problem develops with SCA/antifreeze compatibility. Silicate gelation is the most recent problem of this nature. It is formed when silicate polymerizes or reacts with itself. Our investigation of the problem showed that the following coolant conditions promote the formation of gel:

- Silicate concentration (> 1500 ppm)
- Glycol concentration (> 60%)
- Total dissolved solids (> 3%)

The typical field problem involves a high silicate antifreeze at concentrations of 60 to 70% with a double or triple dose of SCA.

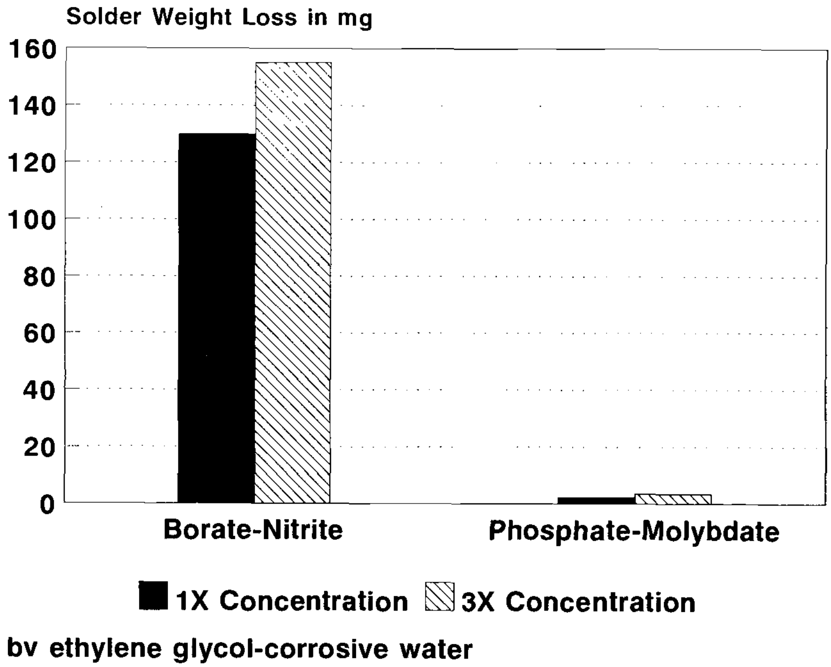


FIG. 6—*Solder weight loss in ASTM D 1384. SCAs run at recommended and 3 times recommended concentration (for liquid SCAs this equals 3% and 9% by volume).*

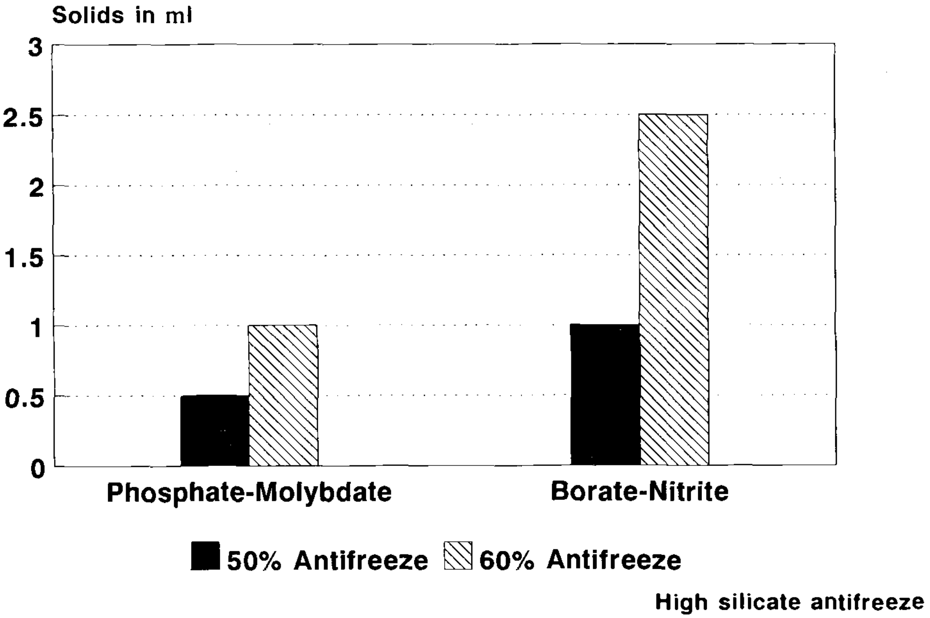


FIG. 7—*SCA compatibility with a high silicate antifreeze. SCA concentration twice that recommended.*

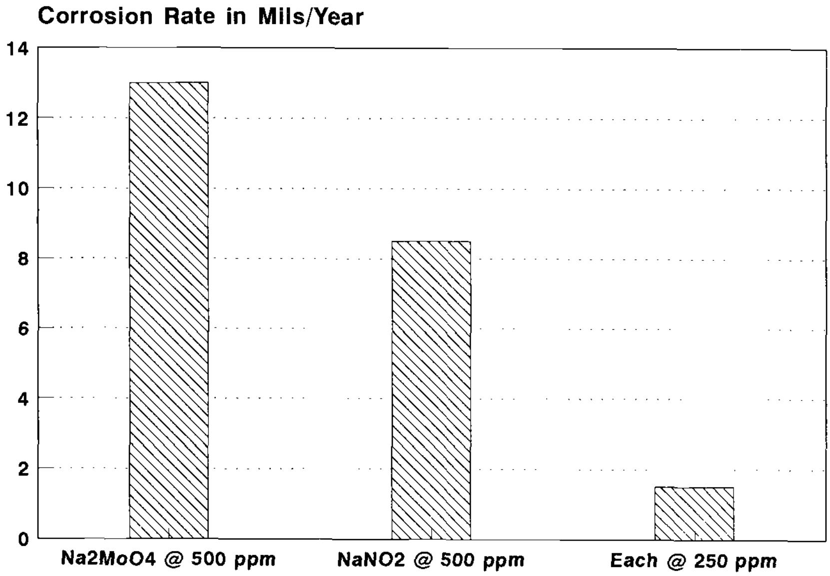
Figure 7 compares the two types of SCA as far as their tendency to form silicate gel. The test was run by heating the mixture of high silicate antifreeze and SCA at 190°F (88°C) for 24 h in a 100-mL centrifuge tube. The tube was removed from the oven, cooled to room temperature, centrifuged at 500 RCF for 15 min, and the volume of solids reported. Because the phosphate-molybdate SCA contains less silicate, it forms less gel.

Liner Pitting

The most important function of an SCA is to prevent the pitting of wet sleeve liners in a heavy duty diesel engine. When pitting penetrates the liner wall, coolant leaks into the crankcase making a rebuild necessary ($4000 to $5000 for a 10- to 14-L engine). Liners can be perforated by pitting (cavitation-corrosion) with a corrosive coolant in as little as 30 000 miles (48 000 km).

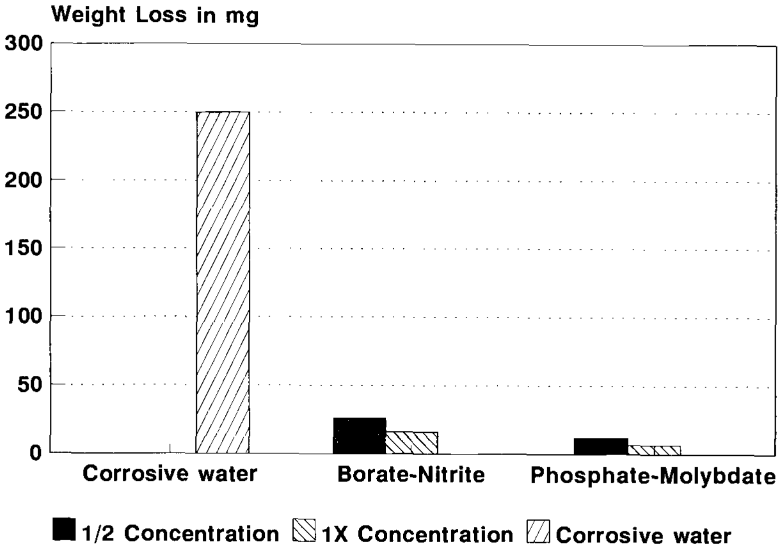
The nitrite in a borate-nitrite SCA provides good liner pitting protection. We wanted to keep the good performance of a borate-nitrite SCA but limit the amount of nitrite. Lower nitrite levels reduce the chance of solder bloom and corrosion when the SCA concentration builds up in the cooling system. Our laboratory evaluation showed that nitrite and molybdate work synergistically to protect ferrous metals. This is shown in Fig. 8 where glassware type tests were run with 1010 steel in water [*3*]. A mixture of 250 ppm of nitrite and molybdate performed much better than 500 ppm of each inhibitor separately. Other data published in the literature confirms this synergism [*4*].

With a mixture of nitrite and molybdate, we found that nitrite could be reduced by 50 to 60% with improved liner pitting protection. Figure 9 shows results from a cavitation-corrosion bench test in ASTM corrosive water. An ultrasonic welding system is used to vibrate a cast iron button in a beaker of coolant at 20 000 cps and an amplitude of 0.4 mils. After 22 h, the



REF:Weber, CORROSION, VOL.42, #9, p542

FIG. 8—*Glassware corrosion tests of molybdate and nitrite alone compared with a molybdate-nitrite mixture.*



SCA's run in corrosive water

FIG. 9—*Liner pitting (cavitation-corrosion) bench test of SCAs at half and recommended concentration.*

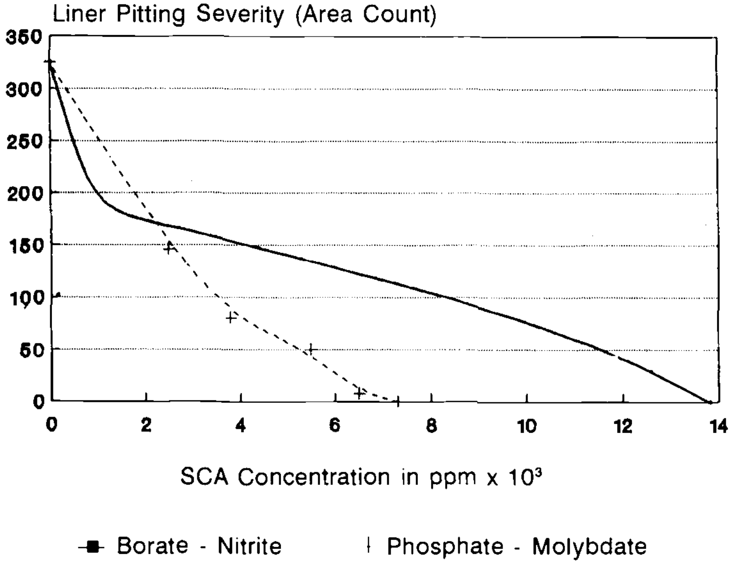


FIG. 10—*Liner pitting dynamometer test of SCAs over a range of concentration.*

button is removed from the apparatus, cleaned, and weighed. The details of the test method are given in the paper by Hercamp and Hudgens [7].

Bench type tests give an indication of how a product will perform, but they cannot guarantee that the product will work well in the field. For this reason and the critical nature of liner pitting, we ran further comparative tests on the Cummins NTC 400 dynamometer test [9]. Figure 10 presents data where both a borate-nitrite and the phosphate-molybdate SCA were tested at various concentrations in a 50% by volume solution of GM-6038 antifreeze. The liner pitting count (*y* axis) is a relative measure of the area of the liner that has cavitation-corrosion damage. In this severe test the phosphate-molybdate SCA required a concentration of 7500 ppm compared to 12 000 to 13 000 ppm of the borate-nitrite SCA to eliminate liner pitting.

Toxicity

The health affects associated with chemical products are of growing concern. Figure 11 presents rat acute oral toxicity data for two SCAs. The lethal dose for half the test group of rats (LD_{50}) is about 4000 mg/kg of body weight with the borate nitrite SCA. The phosphate-molybdate additive is somewhat less toxic with an LD_{50} of 6200 mg/kg of body weight. This lower toxicity is the result of the phosphate buffer and the lower level of the toxic sodium nitrite (LD_{50} 100 mg/kg). See Figs. 12 and 13.

Water Pump Leakage

Water pump leakage may occur when supplemental coolant additives are overdosed or slowly built up in the coolant over time. Our investigation of water pump leakage has shown the following conditions increase leakage:

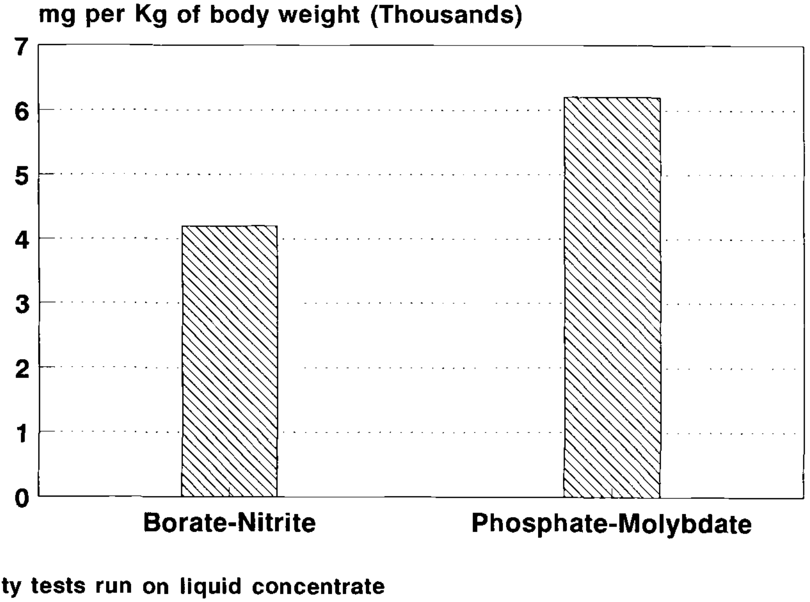


FIG. 11—*SCA oral toxicity in rats* (LD_{50}).

- High glycol concentration (> 60%)
- High total dissolved solids (> 3% to 4%)
- Debris in the coolant
- Excessive silicate concentration

Note that the above conditions are very similar to those that promote silicate gelation.

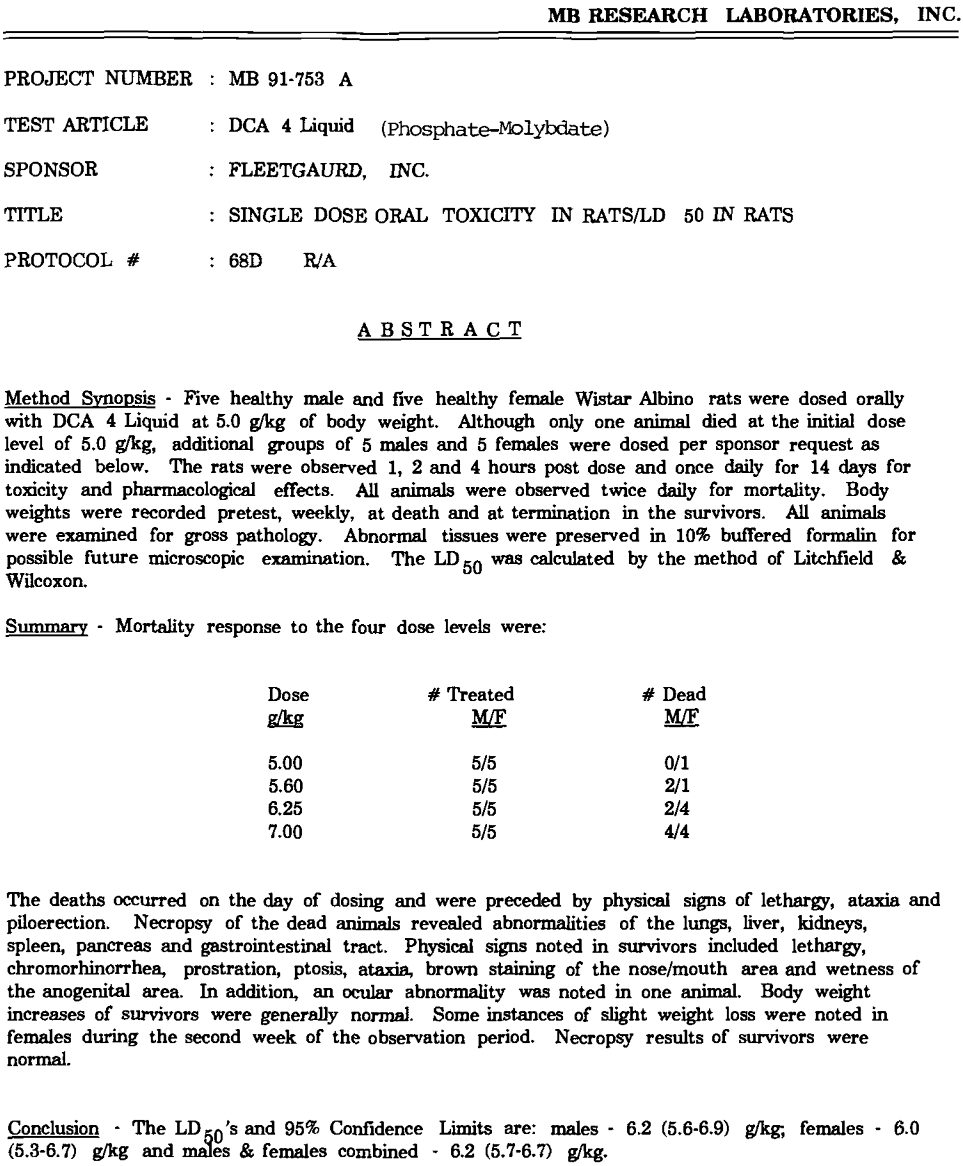
A simulated service type test was set up at Cummins Engine Company where a water pump driven by an electric motor circulated coolant through an engine block. Three times the recommended dose of SCA was added to a high- and low-silicate antifreeze-coolant, and the effect on water pump leakage was monitored. The results of this test are presented in Table 7. The test results show that when SCAs are over concentrated, the phosphate-molybdate SCA was not as likely to cause water pump leakage as the borate-nitrite additive.

Field Test

Before the release of the phosphate-molybdate additive, it was field tested in three locations as outlined below. A borate-nitrite SCA was run as a control or reference at each location.

TABLE 7—*Water pump leakage versus SCA type.*

SCA Type	70% High Silicate	50% High Silicate	50% Low Silicate
Borate-nitrite at 3X	leakage	leakage	no leakage
Phosphate-molybdate at 3X	no leakage	no leakage	no leakage
No SCA added	no leakage	not run	not run



MB RESEARCH LABORATORIES, INC.

PROJECT NUMBER : MB 91-753 A
TEST ARTICLE : DCA 4 Liquid (Phosphate-Molybdate)
SPONSOR : FLEETGAURD, INC.
TITLE : SINGLE DOSE ORAL TOXICITY IN RATS/LD 50 IN RATS
PROTOCOL # : 68D R/A

ABSTRACT

Method Synopsis - Five healthy male and five healthy female Wistar Albino rats were dosed orally with DCA 4 Liquid at 5.0 g/kg of body weight. Although only one animal died at the initial dose level of 5.0 g/kg, additional groups of 5 males and 5 females were dosed per sponsor request as indicated below. The rats were observed 1, 2 and 4 hours post dose and once daily for 14 days for toxicity and pharmacological effects. All animals were observed twice daily for mortality. Body weights were recorded pretest, weekly, at death and at termination in the survivors. All animals were examined for gross pathology. Abnormal tissues were preserved in 10% buffered formalin for possible future microscopic examination. The LD_{50} was calculated by the method of Litchfield & Wilcoxon.

Summary - Mortality response to the four dose levels were:

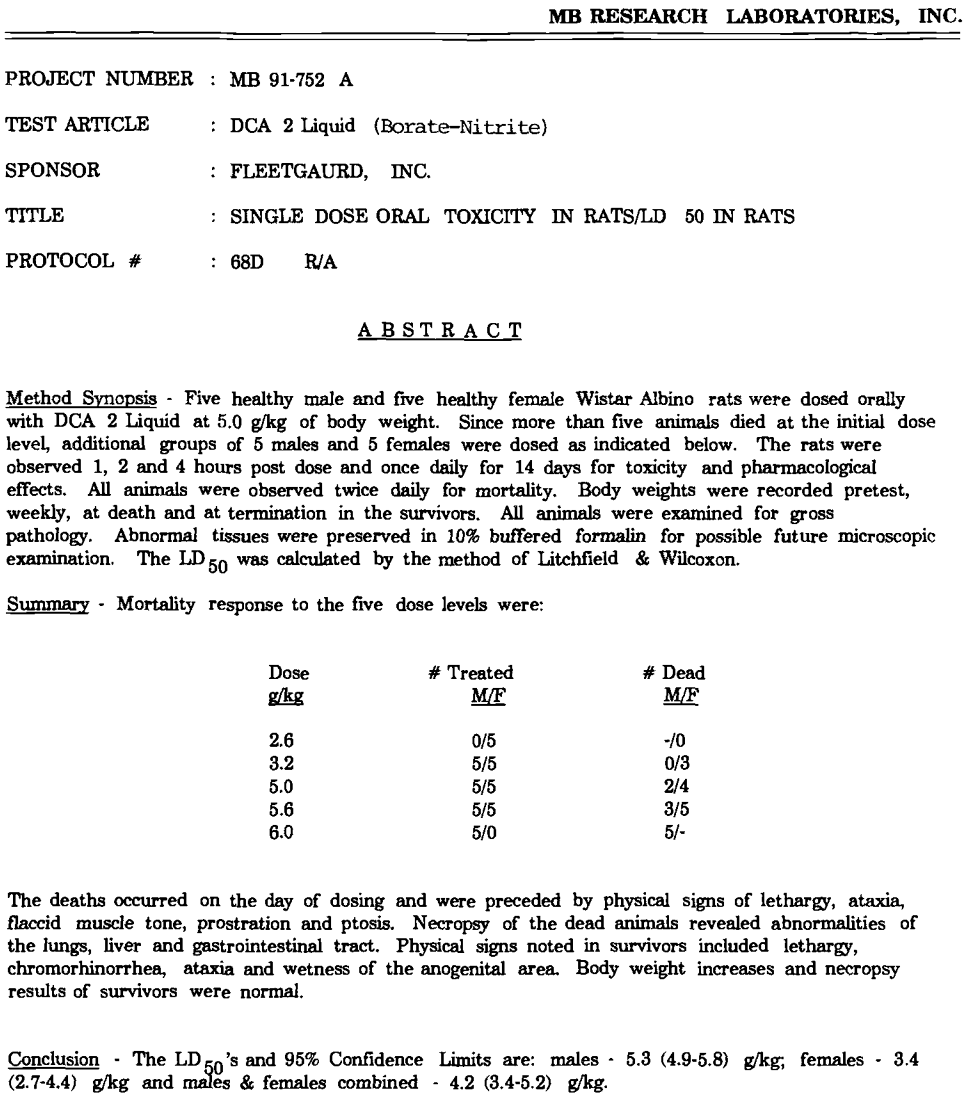
Dose g/kg	# Treated M/F	# Dead M/F
5.00	5/5	0/1
5.60	5/5	2/1
6.25	5/5	2/4
7.00	5/5	4/4

The deaths occurred on the day of dosing and were preceded by physical signs of lethargy, ataxia and piloerection. Necropsy of the dead animals revealed abnormalities of the lungs, liver, kidneys, spleen, pancreas and gastrointestinal tract. Physical signs noted in survivors included lethargy, chromorhinorrhea, prostration, ptosis, ataxia, brown staining of the nose/mouth area and wetness of the anogenital area. In addition, an ocular abnormality was noted in one animal. Body weight increases of survivors were generally normal. Some instances of slight weight loss were noted in females during the second week of the observation period. Necropsy results of survivors were normal.

Conclusion - The LD_{50}'s and 95% Confidence Limits are: males - 6.2 (5.6-6.9) g/kg; females - 6.0 (5.3-6.7) g/kg and males & females combined - 6.2 (5.7-6.7) g/kg.

FIG. 12—*Single dose oral toxicity in 50 rats/LD.*

(1) Strip mine near Bowling Green, KY: 4 bulldozers with Cummins K-6 engines, 1-year duration.
(2) On-highway truck fleet near Cookeville, TN: 18 Cummins NT engines, 100 000 miles (160 000 km) duration.
(3) On highway fleet in Oklahoma City, OK: 6 Cummins L-10 engines, 60 000 miles (96 000 km) duration.



MB RESEARCH LABORATORIES, INC.

PROJECT NUMBER : MB 91-752 A

TEST ARTICLE : DCA 2 Liquid (Borate-Nitrite)

SPONSOR : FLEETGAURD, INC.

TITLE : SINGLE DOSE ORAL TOXICITY IN RATS/LD 50 IN RATS

PROTOCOL # : 68D R/A

ABSTRACT

Method Synopsis - Five healthy male and five healthy female Wistar Albino rats were dosed orally with DCA 2 Liquid at 5.0 g/kg of body weight. Since more than five animals died at the initial dose level, additional groups of 5 males and 5 females were dosed as indicated below. The rats were observed 1, 2 and 4 hours post dose and once daily for 14 days for toxicity and pharmacological effects. All animals were observed twice daily for mortality. Body weights were recorded pretest, weekly, at death and at termination in the survivors. All animals were examined for gross pathology. Abnormal tissues were preserved in 10% buffered formalin for possible future microscopic examination. The LD_{50} was calculated by the method of Litchfield & Wilcoxon.

Summary - Mortality response to the five dose levels were:

Dose g/kg	# Treated M/F	# Dead M/F
2.6	0/5	-/0
3.2	5/5	0/3
5.0	5/5	2/4
5.6	5/5	3/5
6.0	5/0	5/-

The deaths occurred on the day of dosing and were preceded by physical signs of lethargy, ataxia, flaccid muscle tone, prostration and ptosis. Necropsy of the dead animals revealed abnormalities of the lungs, liver and gastrointestinal tract. Physical signs noted in survivors included lethargy, chromorhinorrhea, ataxia and wetness of the anogenital area. Body weight increases and necropsy results of survivors were normal.

Conclusion - The LD_{50}'s and 95% Confidence Limits are: males - 5.3 (4.9-5.8) g/kg; females - 3.4 (2.7-4.4) g/kg and males & females combined - 4.2 (3.4-5.2) g/kg.

FIG. 13—*Single dose oral toxicity in 50 rats/LD.*

In each case the field test vehicles were split between the phosphate-molybdate and borate-nitrite SCAs. Bundles of corrosion test coupons were installed in the upper radiator hose of the on-highway trucks and mounted in the torque converter housing of the dozers. At the Cookeville location, each SCA had 5 units at the recommended concentration and 4 units charged to half the recommended concentration. The conclusions from the field test were as follows [*10*]:

- The phosphate molybdate provided superior solder corrosion protection.
- Both SCAs provided excellent liner pitting protection even when dosed at half the recommended concentration.

- The phosphate-molybdate provided slightly better aluminum protection at the reduced concentration.

Since the release of the phosphate-molybdate additive package, we have continued to field test at an on-highway fleet near Columbus, IN. The test has involved 30 to 34 units with Cummins 14-L engines that accumulate about 5000 miles (8000 km) per week. The SCA concentration is controlled at 0.5 to 1.5 times that recommended (3000 to 9000 mg/L) with the use of coolant filters that contain SCA. Engines in this fleet are pulled from service at 500 000 to 650 000 miles (800 000 to 1 050 000 km) and overhauled because of oil consumption. The results from this test fleet show are as follows:

- No liner pitting or crevice seal failure
- Water pump seal life in the range 450 000 to 650 000 miles (725 000 to 1 050 000 km)

Engine Cleanliness Issues

Heavy duty service with its greater power density and load factor requires efficient removal of large quantities of waste heat from the engine. If an engine is to deliver a half million miles (approximately 804 650 km) or more of service, the cooling system must be free of deposits and fouling. Deposits that build up in the cooling system can cause overheating, lube oil deterioration, and excessive oil consumption. This subject is discussed in detail in a previous paper by the author [*11*]. Some of the reasons that heat transfer problems develop in the cooling system are hard water precipitation, oil fouling, and additive solubility problems. These are discussed in more detail below.

Engine Scaling

Silicate, phosphate, and molybdate can precipitate with water hardness (calcium and magnesium) and form deposits (scale) on hot cooling system surfaces. This usually occurs on the upper portion of the liner and in the head. Scaling in an engine is very similar to what occurs in a tea kettle or hot water heater. The hardness in water is less soluble at high temperatures and tends to drop out of solution and adhere to hot metal surfaces. If this scale is allowed to build up in engine cooling systems, oil consumption and head cracking can occur.

In the 1950s German OEMs experienced scaling problems when phosphate inhibited antifreeze coolant was used with hard water. Since that time there has been a reluctance by some to use phosphate in engine coolants for fear of forming hard water deposits. What is often forgotten is that the carbonate found in make-up water will form scale so that one needs to deal with the scaling issue regardless of whether phosphate, silicate, or molybdate are used in the coolant additive package. Certainly there is the potential for aggravating scale formation when phosphate is used with hard make-up water, but the technology exists to control this situation. Scale inhibitors (water soluble polymers in the 1000 to 5000 molecular weight range) have been developed especially to control hot surface deposition problems. It is a common practice to use phosphate along with a scale inhibitor in high pressure boilers [*12*]. Scale information in this application is far more critical than an engine cooling system.

As part of the development of the phosphate-molybdate SCA, the additive package was checked for its hot surface scaling tendency in hard water. Figure 14 shows results from a scaling bench test rig. In this test a heater is inserted into a stainless steel tube, and coolant is circulated over the surface of the hot tube. The wattage of the heater is chosen to give a heat flux similar to the surface of a diesel engine liner. An automotive antifreeze coolant was tested and then compared to the same coolant with the recommended dose of the phosphate-molybdate

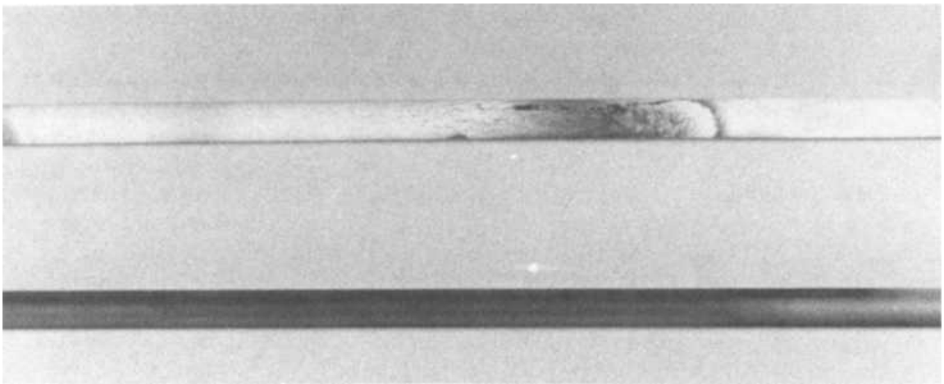


FIG. 14—*Hot surface scaling bench test. Upper tube is a commercial antifreeze alone while the lower tube is the same commercial antifreeze combined with the phosphate-molybdate SCA.*

SCA. There is a significant amount of scale for the antifreeze alone, but the antifreeze plus SCA gave almost no scale at all.

The ability of the phosphate-molybdate additive to control scale was further evaluated using the NTC-400 test. Since the engine is over fueled and runs hot, it is a good tool to evaluate the scaling protection provided by an SCA. The phosphate-molybdate additive was tested at the recommended concentration in 50% by volume GM-6038 antifreeze. The make-up water was Columbus, IN, tap water, which has a hardness of approximately 300 ppm. The GM-6038

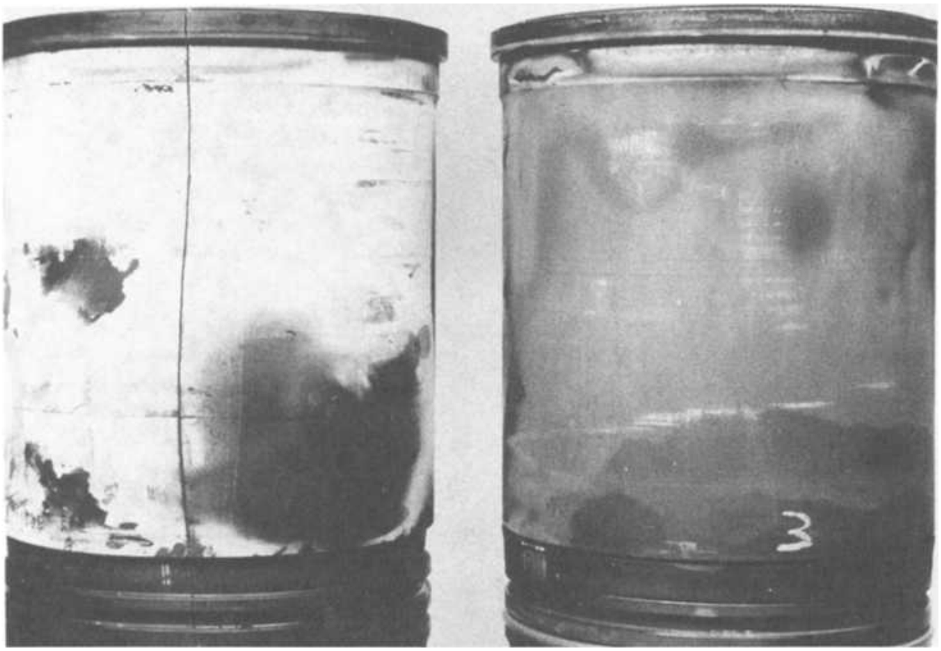


FIG. 15—*Dynamometer scaling test. Liner on left GM-6038 antifreeze alone while the liner on the right was run with GM-6038 combined with the phosphate-molybdate SCA.*

when run by itself allowed appreciable scaling of the liners. However, when the SCA was added to the antifreeze, very little scaling took place (Fig. 15). This shows that the phosphate-molybdate additive can not only prevent scale but make up for the short coming of the antifreeze.

Oil Fouling

It is common to find lubricating oil in the cooling system. We have taken random samples from the field on several occasions and found about 10% of the units with some degree of oil contamination. Oil causes heat transfer problems throughout the cooling system as it breaks down to a semi-solid sludge and coats liners, heads, and heat exchange tubes (Fig. 16). In addition an oil fouled surface is more likely to corrode. This is especially true for the cast iron block where oil fouling is likely to trigger a corrosion problem. Figure 17 shows a coolant filter plugged with iron hydroxide, which was the result of lube oil in the coolant.

FIG. 16—*Coolant side of a cylinder liner fouled with oil sludge.*

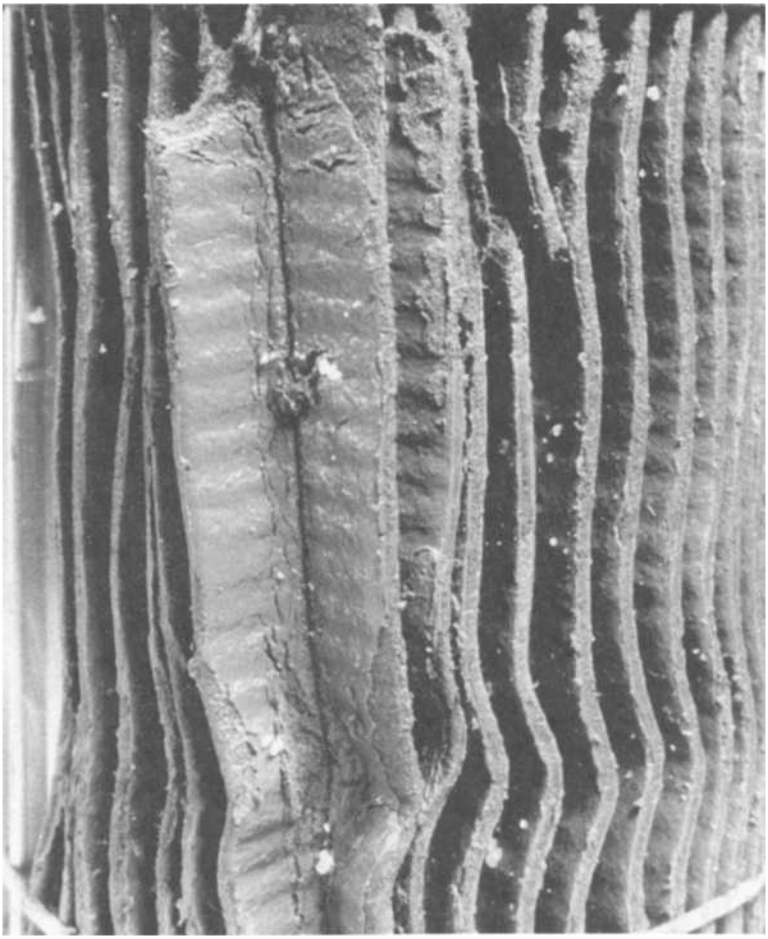


FIG. 17—*Coolant filter plugged with rust as a result of oil fouling of the cooling system.*

A supplemental coolant additive can be formulated to minimize the problems caused when oil seeps into the cooling system. Surfactants can be incorporated into the additive package that lifts oil from the metal surface and emulsifies it in the coolant. Figure 18 shows results from a laboratory test where the phosphate-molybdate SCA with its surfactant package is compared to a conventional SCA. The test is run by placing 5 mL of used-heavily contained lube oil in a 100-mL glass bottle. The bottle is then rotated so that the interior surfaces are coated with a thin film of oil. Next, 100 mL of heated (180°F [82°C]) SCA solution is placed in the bottle, and the solution is shaken vigorously.The solution is poured from the bottle, and the amount of oil film remaining is a measure of the SCA's detergency. As can be seen in Fig. 18, the phosphate-molybdate SCA leaves behind far less oil and can be expected to improve heat transfer and reduce corrosion problems in an oil fouled cooling system.

Low-Temperature Solubility

Phosphate is unusual in that its solubility in coolant can be drastically affected by temperature. It is unique in this regard when compared to the other inorganic coolant additives. Fig-

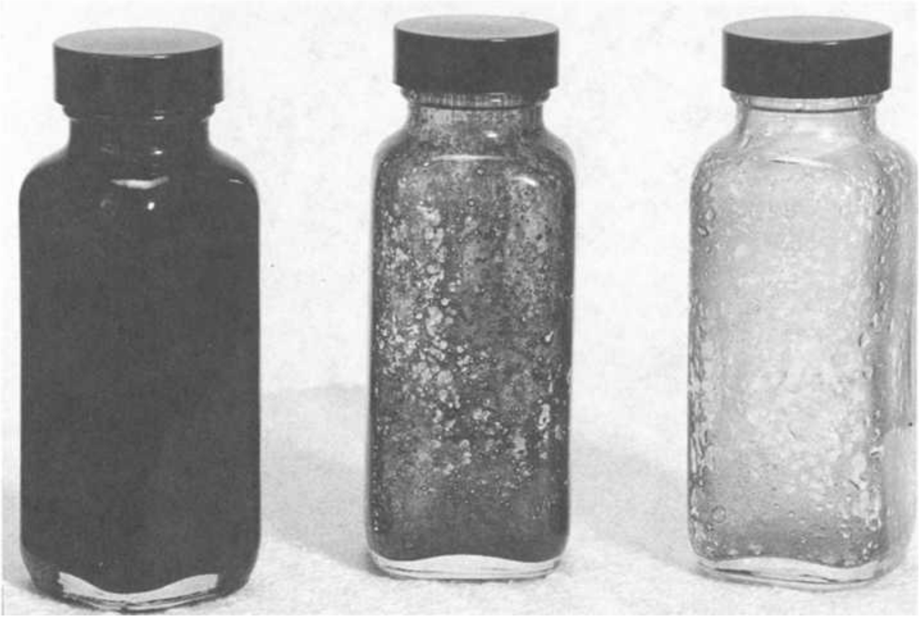


FIG. 18—*Detergency test of SCAs. First bottle shows oil coating sides before testing. Middle bottle is results obtained from a borate-nitrite SCA while bottle to the right was obtained with the phosphate-molybdate SCA.*

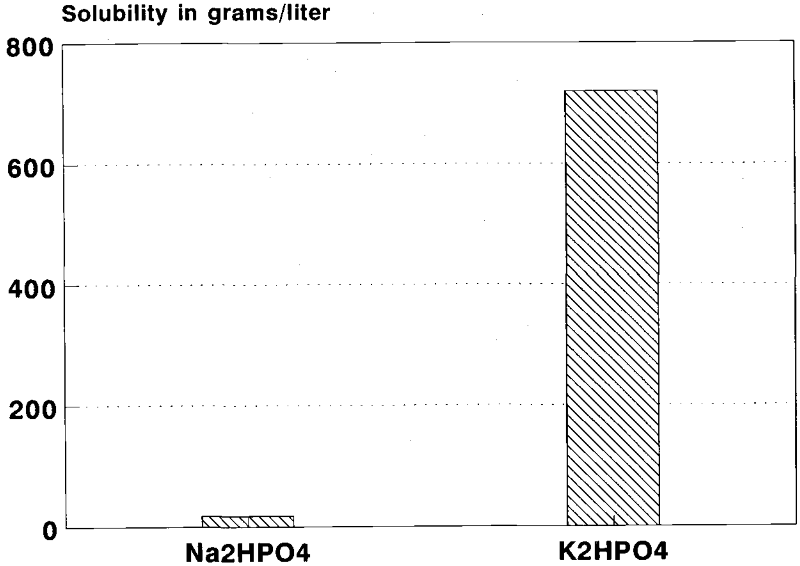


FIG. 19—*Sodium versus potassium phosphate solubility in water at 0°C.*

TABLE 8—*Silicate gelation versus sodium phosphate crystallization.*

Parameters	Silicate Gelation	Sodium Phosphate Crystalization
Antifreeze concentration	Problem above 60%	problem below 50%
High silicate antifreeze	Aggravates the problem greatly	no effect
SCA concentration	becomes a problem above 2x	becomes a problem above 2x
Temperature	> 160°F (71°C)	< 10°F
Nature of solids	once formed will not go back in solution	sodium phosphate crystals melt above 20 to 30°F
Frequency	common 2 to 3%	rare <0.1

ure 19 shows sodium and potassium phosphate solubility as a function of temperature. The solubility of sodium phosphate is very low at reduced temperatures, which can cause problems in cold operating conditions. Sodium phosphate can crystallize, plug the radiator, and cause overheating. It is interesting that as soon as the coolant warms slightly the sodium phosphate crystals melt and there is no further overheating. Table 8 gives the conditions under which phosphate can crystallize in the coolant and contrasts this problem with silicate gelation. The phosphate crystallization problem is easily solved by using the potassium salt in place of the sodium salt because of its far greater low-temperature solubility (Fig. 19).

Summary

A phosphate-molybdate based [*13*] supplemental coolant additive has been developed and patented as an improvement over the borate-nitrite SCAs that have been commonly used in heavy duty diesel engine coolant since the late 1960s. The phosphate buffer gives better solder and all around aluminum corrosion protection. The addition of molybdate gives better liner pitting protection and allows the use of lower amounts of silicate and nitrite in the additive package. This is important as the SCA is often overdosed or builds up to a high level over time.

Lower silicate and nitrite levels in the coolant result in the following:

- Reduced solder bloom and corrosion
- Reduced silicate gelation/better antifreeze compatibility
- Fewer water pump leaks

Finally the phosphate-molybdate additive has been formulated to better tolerate poor quality make-up water, which is often the cause of aluminum corrosion problems.

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[*2*] Vukasovich, M. S. and Sullivan F. J., "Evolution of Molybdate as an Inhibitor in Automotive Engine Coolants," *Materials Performance,* August 1983, pp. 25-33.

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[*7*] Hercamp, R. D. and Hudgens, R. D., "Cavitation Corrosion Bench Test for Engine Coolants," SAE Technical Paper 881269, Sept. 1988.

[*8*] Wiggle, R. R., Hospadaruk, V., and Tibaude, F. M., "Corrosion of Cast Aluminum Alloys under Heat Transfer Conditions," SAE Technical Paper 810038, Feb. 1981.

[*9*] Hercamp, R. D., "Comparison of Fleetguard DCA and DCA 4 for Prevention of Cavitation Corrosion of Cylinder Liners," Cummins Engine Company Technical Report 0789-86009, Dec. 1986.

[*10*] Firestone, N. B. and Mullins, G. A., "DCA 4 Field Test Final Report," Cummins Engine Company Technical Report 0789-87002, 1987.

[*11*] Hudgens, R. D. and Hercamp, R. D., "Filtration of Coolants for Heavy Duty Engines," SAE Technical Paper 881270, Sept. 1988.

[*12*] *Manual on Water, STP 442,* American Society for Testing and Materials, Philadelphia, pp. 204–206.

[*13*] Hercamp, R. D. and Hudgens, R. D., "Diesel Engine Cooling System Composition," U.S. Patent No. 4,717,495, Jan. 1988.

DISCUSSION

Steven Woodward[1] *(written discussion)*—If the 70% high silicate coolant passed tests without supplemental coolant additive, why were they added? Can you comment on why the coolant failed after the addition of supplemental coolant additive?

R. D. Hudgens (author's response)—Heavy duty diesel engines fail because of cylinder liner cavitation corrosion when run using coolant without supplemental coolant additive. Therefore, the water pump seal leakage test in Table 7 was run with a variety of coolant mixtures, most of them containing SCA.

After the addition of borate nitrite supplemental coolant additive to the high silicate antifreeze coolant, the water pump seal leaked presumably because of either high total dissolved solids or high silicate. The phosphate-molybdate SCA contains less silicate and less total dissolved solids than the borate-nitrite SCA, and the water pump seal did not leak using the phosphate-molybdate SCA. Also, the low silicate antifreeze coolant with the borate-nitrite SCA added did not leak. The low silicate antifreeze coolant has lower silicate and lower total dissolved solids than the high silicate antifreeze coolant.

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[1] First Brands Corporation, Danbury, CT 06810.

R. Douglas Hudgens[1] *and R. B. Bustamante*[2]

Toxicity and Disposal of Engine Coolants

REFERENCE: Hudgen, R. D. and Bustamante, R. B., **"Toxicity and Disposal of Engine Coolants,"** *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 149–164.

ABSTRACT: In recent years there has been considerable concern and controversy regarding both the toxicity and disposal of engine coolants. The toxicity of engine coolant relative to human or animal ingestion is largely a function of whether ethylene or propylene glycol is used to provide freeze point depression. The additives used in engine coolants to prevent cooling system deterioration have a measurable, but limited effect on toxicity. The general environmental effects are largely governed by the type of glycol as well as the contaminants that may be present in the coolant.

This paper presents a literature survey on the environmental, disposal, and toxicity issues surrounding engine coolants. In addition, an Acute Lethal Dose (LD_{50}) study is presented comparing the LD_{50} of fully formulated PG antifreeze and supplemental coolant additives. A review of government laws and regulations covering disposal and management of waste coolant is also provided.

KEYWORDS: engine coolants, engine antifreeze, coolant toxicity, disposal, biodegradability, laws and regulations, recycling, environmental concerns

In the late 1960s and early 1970s toxicity and environmental concerns resulted in the elimination of the additives, chromate and arsenite, from engine coolants. Since that time formulations have changed little. However, Federal "Right to Know" laws and our continuing environmental problems have caused renewed concern about the health effects and disposal problems associated with engine coolants.

In dealing with coolant toxicity and disposal issues it is helpful to break down an engine coolant into its component parts:

1. Water (the primary heat removal fluid)—The water content of a coolant will be 40 to 70% depending on the severity of the winter climate. In some warm weather areas freezing temperatures are not encountered and water with a corrosion inhibitor package is used.
2. Freeze Point Depressant, Boil Point Elevation—In most cases ethylene glycol, and recently but to a lesser extent, propylene glycol is used in a range of 30 to 60% by volume to prevent freezing of the water during winter.
3. Additive Package—Containing several different chemicals that are initially added to the glycol to form an antifreeze or concentrate and eventually blended with water to form the coolant. These additives are designed to prevent corrosion, deposit formation, and foaming and are in concentrations of 0.5 to 3% by weight of the final coolant.

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[1] Senior staff chemist, Fleetguard, Inc., Cookeville, TN 38501.

[2] Professor and chairman, Department of Civil Engineering, Tennessee Technological University, Campus Box 5015, Cookeville, TN 38505.

4. Contaminants—Build up as the engine is used and result from the following: thermal or oxidative breakdown of glycol; lube oil and fuel accumulation; metals from cooling system corrosion; and decomposition or oxidation of coolant additives.
5. Supplemental Coolant Additives—Or SCAs are used in heavy duty service to prevent cavitation erosion of cylinder liners and to replenish inhibitor chemicals depleted with service. SCAs are not used or required in passenger cars that have a coolant life of 30 000 to 50 000 miles (48 279 to 80 465 km). Heavy duty service usually demands 200 000 to 300 000 miles (321 860 to 482 790 km). before coolant replacement and hence the need to periodically replenish inhibitors.

This paper is divided into sections dealing with the toxicity, disposal, and general environmental effects of engine coolants. Each section, in turn, is broken down further to discuss in detail the effects of the various coolant components.

Toxicity

General

In 1987 the Annual Report of the American Association of Poison Control Centers' National Data collection System [*1*] stated that there were over 1.1 million poisonings reported by 63 poison control centers. These 63 centers serve about half the U.S. population. About 92% of the reported poisonings occurred in the home and the majority were accidental (89%). Children under six years of age were involved in 62% of the incidences, and ingestion accounted for 77% of the poisoning exposures. This same report noted 2451 poisonings related to glycols with 2372 exposures being accidental, and of those, 765 poisonings were related to children under six years of age. Consequently, our discussion on toxicity focuses mainly on the acute (short-term) oral health effects of coolants on mammals. In general, the greatest concern is the short-term health effects of ingestion by a person or a pet. There can be long-term (chronic) health problems associated with engine coolants, which are primarily related to heavy metals contamination. Chronic health effects will be discussed briefly in the section on disposal.

Although more recent data are available from the American Association of Poison Control Center (1991), 1987 represents a year when only ethylene glycol was available. Propylene glycol (PG) was not used in the manufacture of a PG antifreeze concentrate until 1988. The 1991 data from the Poison Control Center does not vary significantly from the 1987 report, and the conclusion would be the same: ingestion is the greatest concern.

Glycols

Glycols make up 95% by weight of the antifreeze/coolant concentrate, and after blending with water, about 40 to 60% by volume of the coolant used in the vehicle. Conventional antifreeze has for years been formulated with ethylene glycol (EG). EG has provided an efficient and cost effective means of freeze protection for engine coolants. EG is used in a variety of other applications including polyethylene terephthalate for use in polyester films, fibers, and resins.

While EG has served effectively as a freeze point depressant for engine coolants, its one disadvantage is its toxicity to humans and other mammals if ingested. Because of this, there is an increased demand for safer products. Propylene glycol (PG) is a safer alternative for engine coolant antifreeze. This product has been available for years and is used as an ingredient in foods, cosmetics, and medicinal products. During the EG shortage of 1988 through 1989, many antifreeze producers were using PG as an extender for EG in production of conventional antifreeze. However, it was not until the last year or two that there was any significant use by consumers of a PG formulated antifreeze, that is, one without EG.

EG has an acute oral toxicity of 4700 mg/kg (LD$_{50}$) in laboratory rats [*2*]; a rating of 5000 or lower can classify a material as hazardous. (Note the lower the number the higher the toxicity.) Although marginally hazardous by this rating system, EG is a known toxin to humans at relatively low levels (reported as low as 398 mg/kg) [*2*], and consequently is classified by many regulatory authorities as a dangerous material. When ingested, EG is metabolized to glycolic and oxalic acids, which causes an acid base disturbance and results in kidney damage [*3*]. EG has the added complication of a sweet smell and taste.

No material is absolutely safe. However, PG is a much safer material with an LD$_{50}$ in laboratory rats of 28 000 to 30 000 mg/kg [*3,4*]. PG is metabolized to lactic and pyruvic acids, normal body constituents [*3,5,6*].

As previously mentioned, corrosion inhibitors are blended with glycol and sold as formulated antifreeze. These additives are discussed in more detail later. Although there is a significant body of data showing the lower toxicity of PG versus EG, what happens to that advantage once the inhibitors are added?

One means accepted by industrial hygienists for estimating formulation toxicity is a calculation method [*7*]. The LD$_{50}$ value of the individual formulation component is divided into the component's weight fraction. This "reciprocal" value is added to that of all the other components. The sum of this calculation is then divided into 1. The result is an estimate of the LD$_{50}$ of the formulation. The calculation method described above is used in Table 1 to compare LD$_{50}$ values of the standard antifreeze formulation, GM-6038, using either EG or PG.

As can be seen ethylene glycol is the largest single component, and its LD$_{50}$ value largely determines the estimated formulation LD$_{50}$. Note, we have ignored any contribution of the pluronic or dye since they are in extremely low concentrations. Also the water present to solubilize the additives will tend to dilute the toxic effects of the other components and raise the LD$_{50}$ level of the formulation. For this exercise we have chosen to ignore the effect of the small amount of water.

This calculation method would therefore predict that not only is a PG antifreeze less toxic

TABLE 1—*LD$_{50}$ estimate of GM-6038 formulation.*

Ingredient	WT Fraction	LD$_{50}$[a], mg/kg	Reciprocal, $\times 10^{-7}$	
EG	0.9565	4700	2035	...
PG	0.9565	28000	...	342
$NaNO_3$	0.002	3750	5	5
$Na_2B_4O_7 \cdot 5H_2O$	0.01	2660	38	38
$Na_2SiO_3 \cdot 5H_2O$	0.0015	1280	12	12
$Na_3PO_4 \cdot 12H_2O$	0.0045	17000	3	3
NaMBT(50% SOLN)	0.0055	3120	18	18
NaOH	0.002	500	40	40
Pluronic L-61	0.0005	*b*	*b*	*b*
Green dye	0.00005	*b*	*b*	*b*
Water	0.0175	*b*	*b*	*b*
	EG		PG	
Summation of Reciprocal	2150×10^{-7}		457×10^{-7}	
LD$_{50}$ (1/reciprocal)	4650		21 900	

[a] See References *2* and *8*.

[b] Omitted in calculation because of the small amount present.

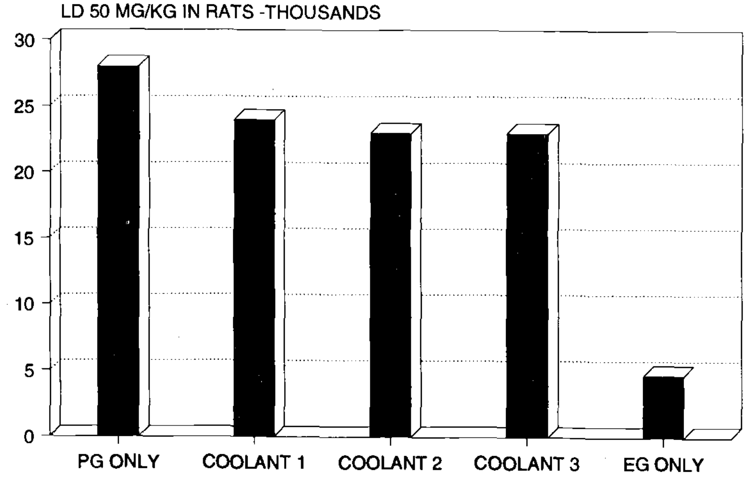

FIG. 1—*Oral toxicity of PB coolants.*

than an EG antifreeze, but that PG antifreeze, like PG, should be classified as essentially nontoxic. To confirm this, several commercial PG antifreezes were actually tested using laboratory rats and the results are presented in Fig. 1. The results compare well with the estimated value for the GM-6038 formula and confirm that PG can be formulated to provide good freeze and corrosion protection while remaining essentially nontoxic.

Please note this calculation method is only a predictive tool to estimate the relative toxicity, and it should be used only for estimating purposes.

Major Additives

The additive package in an antifreeze/coolant and in SCAs (used to replenish inhibitors) will typically consist of from 5 to 15 different chemicals. These additives are broken down into major and minor categories depending on the amount used in an engine coolant formulation (Table 2).

The minor additives should not be of significance to the toxicity of engine coolants because these materials are usually not highly toxic and are used in small quantities.

Table 3 lists the most common corrosion inhibitors and buffers used in engine coolants. Lethal dose information is provided as well as the SAX toxicity rating. Arsenite, which has not been used in engine coolants for 20 years, is shown to give a historical perspective. Common materials, such as aspirin and table salt, are also listed for comparison purposes.

TABLE 2—*Components of antifreezes and SCAs.*

Major (0.05 to 3%)	Minor (<0.05%)
Buffer	defoamer
Corrosion inhibitors	dye
	scale inhibitor
	surfactant
	chelates

TABLE 3—*Common coolant additives, acute oral LD_{50} data.*

Additive	LD_{50} in Rats, mg/kg	Sax Rating	Other Comments
Adipic acid	3600	1	
Benzoate	4070	1	
Borate	2660	2	
Carbonate	4090	2	
Ethylhexanoic Acid	3000[*6*]	1	
Mercaptobenzothiazole	3120	2–3	sensitizer
Molybdate	2810[*13*]	2	
Nitrate	3750	2	oxidizer
Nitrite	85	3	strong oxidizer
Phosphate	17000[*7*]	1	
Sebasic acid	3400	. . .	
Silicates	1280	1	
Benzotriazole	560[*14*]	2	
Tolytriazole	675[*14*]	2	
Triethanolamine	8000	1	
Arsenite	41	3	carcinogen
Aspirin	1500	. . .	
Table salt	3750	. . .	

NOTE: All LD_{50} data taken from Ref *2*.

Sax Acute Ingestion Rating System: (1) low-slight or mild toxicity; (2) moderate, and (3) high-severe toxicity.

Nitrite is clearly the most toxic of the additives still used in engine coolant with an LD_{50} for rats of 85 mg/kg, which is in the range of arsenite. The triazoles are moderately toxic while most of the other components have an LD_{50} value that is the range of table salt and aspirin. It is worthy to note that some significant variations were found in reported LD_{50} data. For example, MBT reported in Ref *2* is 3120 mg/kg. Values as low as 100 and as high as 5000 mg/kg were found in other literature sources.

The toxicity of some coolant additives is effected by their alkalinity. The more alkaline forms of silicate, phosphate, and borate have lower LD_{50} values. Thus, the more alkaline metaborate ($Na_2B_2O_4 \cdot 4H_2O$) has an LD_{50} value of 1700 compared to the less alkaline tetraborate ($Na_2B_4O_7 \cdot 5H_2O$) with a value of 2300 to 3300 mg/kg. This can also be shown for silicates. Sodium silicate with an SiO_2/Na_2O ratio of 1 has an LD_{50} value of 600 mg/kg as compared to 1600 mg/kg for the less alkaline silicate with an SiO_2/Na_2O ratio of 2. The toxicity or more appropriately the skin corrosiveness of metasilicate (pH 13 at 5%) is greatly neutralized when blended into a coolant with a pH in the range of 10. The best example of this is blending phosphoric acid with potassium hydroxide to yield K_2HPO_4 in an antifreeze coolant or liquid SCA. The end product is a mildly alkaline salt which exhibits much less toxicity and corrosiveness than the starting materials. This is shown graphically in Fig. 2.

The discussion to this point has focused on the toxicity of antifreeze and engine coolants, however SCAs are sold as both solid and liquid concentrates. Oral LD_{50}s were determined on two common liquid SCA packages. As can be seen in the Table 4, the calculated values for the liquid concentrate (80% water and 20% additives) were about half of the actual measured values. This probably reflects some positive interaction of the various additives as discussed above, which will tend to lower the overall toxicity of the SCA. When you consider that the recommended dose of these SCAs is 3% by volume, they should have minimal effect at their use dosage on the overall toxicity of the coolant.

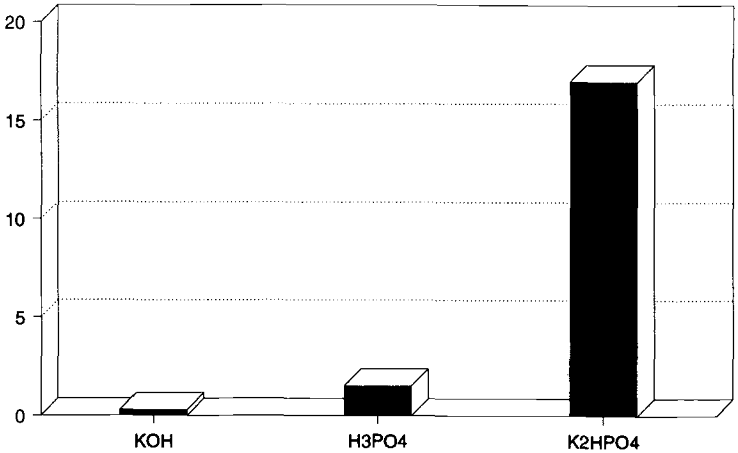

FIG. 2—*Toxicity of reactants versus products (rat Oral LD_{50}, mg/kg hundreds).*

Solid SCAs are usually contained inside a coolant filter which makes access to ingestion unlikely. Consequently, the solid SCAs were not tested.

The chemicals that make a coolant additive package have many common uses. Some of these are listed in Table 5. Adipate, benzoate, carbonate, nitrate, phosphate, and silicate are used in foods. Even nitrite, which has the highest oral toxicity (lowest LD_{50}) of any of the common additives, is used as a food preservative and in medicines. Borate, benzotriazole, carbonate, phosphate, silicate, and triethanolamine are used in soaps and detergents. As with all chemical products, additive chemicals should be handled with care but in formulated engine coolant present no extraordinary health risk.

Contaminants

Over the course of its life, coolant will become contaminated. Table 6 lists some of the contaminants and the concentrations that might be found in a severely degraded product. The maximum level of each contaminant was obtained by reviewing the results of about 12 000 coolant analyses of both passenger cars and heavy duty vehicles, most of which were sent to the Fleetguard "Monitor" coolant analysis program [9].

In most instances, the level of contamination will be far lower than the listed values, but the maximum values listed in Table 6 are useful in dealing with some coolant disposal and toxicology issues. Table 7 presents the actual distribution of copper and lead in 12 000 heavy duty diesel engine coolants. As can be seen in comparing Tables 6 and 7, although lead can be found

TABLE 4—*Calculated values for liquid concentrate.*

Liquid SCA	Borate-Nitrite LD_{50}, mg/kg	Phosphate-Molybdate LD_{50}, mg/kg
Actual	4000	6200
Calculated	1798	2994

TABLE 5—*Other common uses of coolant additives.*

Additive	Use
(1) Adipate	Nylon, food additive, plasticizer, insecticide, adhesive, baking powder
(2) Benzoate	food preservative, antiseptic, medicine, tobacco additive, mildew inhibitor, dye intermediate
(3) Borate	glass, starch, and adhesives, detergents, herbicides, pharmaceuticals, bleach, paint, insecticide, and antiseptic
(4) Carbonate	soaps and detergents, glass manufacture, textile processing, cleaning compounds, food additives, medicine, photography
(5) Ethylhexanoate	plasticizer, paint, and varnish
(6) Mercaptobenzothiazole (MBT)	rubber vulcanization, tire tread manufacturing, fungicide, E.P. additive in greases
(7) Molybdate	medicine, paint pigment, fertilizer, and micronutrient for plants and animals
(8) Nitrate	fertilizer, medicine, black powder and dynamite, antiseptic, pharmaceutical, food preservative, tobacco additive
(9) Nitrite	dye, curing accelerator for rubber, pharmaceuticals, preserving and curing meat, medicine, photographic reagent, bleach
(10) Phosphate	fertilizer, pharmaceuticals, baking powder, coffee creamer, glazes for paper and ceramics, dietary supplement, and animal laxative
(11) Sebasate	fibers, paint, plasticizers, candles, perfumes, Nylon, polyurethanes
(12) Silicates	catalyst, soap and detergents, adhesives, bleach, sizing of textiles, egg preservative
(13) Tolytriazole/benzotriazole	dishwashing detergents, tarnish removers, corrosion inhibitors for dry cleaning equipment
(14) Triethanolamine	soaps detergents, plasticizer, insecticide, rubber cure accelerator

TABLE 6—*Contaminants in engine coolant.*

Contaminant	Maximum Concentration, mg/L	Source
(1) Aluminum	50	corrosion
(2) Copper	100	corrosion
(3) Fuel	100 000	injection system failure
(4) Iron	500	corrosion
(5) Lead	200	corrosion
(6) Oil	100 000	oil cooler failure and sloppy maintenance practices
(7) Organic Acids	5000	glycol oxidation
(8) Sulfate	1000	combustion gas leaking into the coolant
(9) Tin	50	corrosion
(10) Zinc	200	corrosion and hose/gasket additive

TABLE 7—*Copper and lead distribution in H. D. coolants.*

Concentration, mg/L	Copper, %	Lead, %
<5	92.6	81.9
5 to 25	6.2	12.4
26 to 50	0.7	2.7
51 to 100	0.4	1.8
>100	0.1	1.1
Average value	2.5 mg/L	7.0 mg/L

as high as 200 mg/L, the majority of samples analyzed were below 5 mg/L. Consequently, although Table 6 presents maximum contaminant levels, typical values are much lower.

The temperatures in engine cooling systems (93 to 99°C) [200 to 210°F] leads to a slow decomposition (oxidation) of the glycol: either ethylene or propylene glycol. Almost every possible decomposition product that can occur probably does. Many of these compounds are present in minute amounts, however, there are decomposition products that build up to large enough amounts that examination is required [*10*]. Table 8 gives rat oral toxicity data for the major glycol oxidation products [*2,6*]. The values range from 375 mg/kg for oxalic acid to over 3700 mg/kg for lactic acid. Degradation rates and the amount of each individual degradation product can vary widely depending upon the type engine, service, and glycol used. Because of

TABLE 8—*Toxicity of Coolant Contaminants* [2,6].

Contaminant	Rat Oral LD_{50}, mg/kg	Starting Glycol
GLYCOL OXIDATION PRODUCTS		
(1) Glyoxal	1100	EG
(2) Oxalic Acid	375	EG
(3) Glycolic Acid	1950	EG
(4) Glyoxylic Acid	N/A	EG
(5) Formic Acid	1100	EG and PG
(6) Pyruvaldehyde	1170	PG
(7) Pyruvic Acid	N/A	PG
(8) Acetic Acid	3310	PG
(9) Lactic Acid	3730	PG
CORROSION PRODUCTS		
Metal		
aluminum		
chloride	3730	
nitrate	4280	
copper		
chloride	140	
sulfate	300	
iron		
chloride	900	
sulfate	1480	
lead		
acetate	900 LD_{50}	
tin		
chloride	700	
zinc		
acetate	2510	
sulfate	2950	

its toxicity, there is particular concern about the buildup of oxalic acid in engine coolants. Our analysis of used coolants shows that oxalic acid makes up less than 5% of the total amount of organic acids present and therefore should not have a significant impact on used coolant toxicity.

Toxicity information on the various corrosion products is also presented in Table 8. Beyond the numbers provided, aluminum, iron, tin, and zinc are considered to have low acute toxicity [*11*]. Even lead with its associated chronic health problems does not have a significant effect on the acute toxicity of a used engine coolant. From an acute toxicity standpoint, copper provides the most reason for concern as $CuCl_2$ has an LD_{50} of 140 mg/kg.

Table 9 contains estimated LD_{50} values of a GM-6038 type antifreeze (at 50/50 blend with water) with and without the combination of 1000 ppm of copper chloride and 5000 ppm of formic acid. This example assumes the most toxic form of corrosion and glycol oxidation products. This coupled with the fact that the calculation method tends to give conservative (low) LD_{50} values when dealing with engine coolants means that the effect of contaminants on acute toxicity are, if anything, over estimated.

As can be seen in the table, the contaminants only marginally lower the LD_{50} of an EG based coolant. The effect on the PG based coolant is more pronounced; however, the LD_{50} value is still high and provides no reason for concern. One can conclude that the toxicity of a used-contaminated coolant is still primarily a function of whether ethylene glycol or propylene glycol is used to provide freeze-point depression.

Disposal

Laws and Regulations

At the federal level, the management of hazardous waste is regulated through the Resource Conservation and Recovery Act (RCRA) enacted in 1976 and subsequently modified a number of times. RCRA defines hazardous waste as "a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, or infectious characteristics may (1) cause or significantly contribute to, an increase in serious irreversible or incapacitating reversible illness or (2) pose a substantial present or potential hazard to human health or environment when improperly treated, stored, transported or disposed of or otherwise managed." It is important that hazardous waste must first be classified as a solid waste in order for the material to be regulated as a hazardous waste. This does not mean that a solid waste must be solid, but only that it meets the legal definition of solid waste. RCRA does define solid waste as ". . . other discarded material, including solid, liquid, semi-solid, or contained gaseous material . . .". Hazardous waste, therefore, although defined as solid waste, may actually be a liquid or a slurry.

The first question to be asked by a solid waste generator is if the material that is being gen-

TABLE 9—*Effect of contaminants on coolant toxicity.*

Coolant	Ethylene Glycol LD_{50}, mg/kg	Propylene Glycol LD_{50}, mg/kg
GM-6038 at 50%	9 300* mg/kg	43 700
GM-6038 at 50% with 1000 ppm $CuCl_2$ 5000 ppm Formic acid	8 400	29 000

NOTE: Values calculated with reciprocal method as in Table 1 [*7*]. Water present was assumed to have no effect on toxicity.

erated is "hazardous" or not. Management of hazardous waste is a far more delicate and expensive operation than that of a nonhazardous solid waste. The U.S. Environmental Protection Agency has defined hazardous waste as one that (1) exhibits characteristics of ignitability, reactivity, corrosivity, or toxicity (T. C. Rule), (2) is a listed waste (nonspecific source waste, specific source waste, specific commercial chemical), (3) is a mixture containing a listed hazardous waste, or (4) is not excluded by law or regulation. The terminology of characteristic or listed hazardous waste refers to criteria 1 and 2 above when they are used to classify a discarded material. Details of characteristic waste criteria and hazardous waste lists can be found in the Code of Federal Regulations (40 CRF 261).

RCRA regulates all aspects of the management of hazardous waste, from generation to proper disposal. This is what is referred to as "cradle to grave" management. Generators are required to identify the material deemed to be hazardous waste and to manage that waste as licensed treatment, storage, or disposal facilities in full accordance with regulatory requirements. The law provides for civil and criminal penalties to be imposed upon violators. Therefore a generator of a hazardous waste who gives, sells, or pays someone to "dispose" of that waste is responsible to insure that it is properly disposed of in accordance with the law.

Regulation of hazardous waste involves a significant participation by individual states. RCRA provides for the delegation of all or part of the hazardous waste regulatory program to a state provided that such a state has a program that is equal to or more stringent than that prescribed by the EPA. States may have, and sometimes do have, rules and regulations that are more demanding than those published by the EPA. It would be proper for generators and managers of hazardous waste or both to consider the federal regulations as a baseline criteria and to determine if individual states in which they operate have requirements above and beyond those imposed by the EPA.

In determining if a waste antifreeze is hazardous or not, it must be assessed if the material is included in one of the hazardous waste lists published by EPA or by the appropriate state. A second determination must be made to see if the material meets any of the four criteria that would make it a characteristic hazardous waste. Of particular interest would be the presence in the material of heavy metals that might be found as contaminants in the waste. Limits for particular metals, such as lead, are established by the EPA and the individual states (for example, lead, 5 ppm). It is of vital importance that all tests, chemical or otherwise, be performed on waste materials. Tests performed solely on the fresh, unused antifreeze product would not by any means be sufficient. The materials regulated by RCRA are discarded wastes not products.

Should recycle of waste coolant be a goal, it is possible that the material being collected for that purpose would still be regulated under the hazardous waste rules. It would not be wise to assume a material not to be a hazardous waste simply because it is to be subject to recycle or reuse. In all likelihood, part or all management rules indicated for hazardous waste will be active for the management of waste to be recycled, and this might involve operations such as manifesting, storage, and treatment.

Title III, Section 301, of the Clean Air Act Amendment of 1990, also has application to engine coolants. The amendment establishes a list of 172 compounds and 17 compound categories as hazardous air pollutants; this amends Section 112 of Title I of the Clean Air Act (1970).

The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) sometimes referred to as Superfund, defines a hazardous substance to include any hazardous air pollutant listed under Section 112 of the Clean Air Act [*12*]. CERCLA (Section 102) requires the EPA to establish reportable quantities (RQ) for hazardous substances. Unless superseded by regulations establishing a new RQ, the National Response Center must be notified if there is a release of one pound or more of a hazardous pollutant. Therefore all newly identified hazardous air pollutants with no prior RQ should be treated as if they have an RQ of 1 lb (454 g) and any nonpermitted releases in excess of 1 lb (454 g) should be reported immediately to the National Response Center. EG is on the CERCLA list and currently by default has an RQ of 1 lb (454 g). PG is not on the list. Failure to notify may result in fines or imprisonment.

The short review of regulatory issues given in this presentation is an indication of the complexity of the problems associated with the proper management of hazardous waste. Regulations are voluminous, complicated, and confusing. It is sometimes not easy to determine what the true situation is and what to do to properly satisfy regulatory requirements. In some areas, local regulations (city or state) supercede Federal requirements. Good knowledge of the regulations and an extensive technical background on the material generated may optimize the proper management, treatment, and final disposal of the waste material. Later in this paper we discuss those components/contaminants in used coolant which can make it a hazardous waste.

Biodegradability

Glycols—PG and EG are both readily biodegradable. A paper entitled "Biological Treatment of Deicing/Antifreeze Chemicals" [*4*] was presented at the 1991 National Research and Development Conference on the Control of Hazardous materials. The paper concluded that PG and EG are both biodegradable while diethylene glycol (DEG), which is frequently blended into EG antifreeze to reduce costs, biodegrades slower but will ultimately be consumed. The oxygen requirements for biodegradation of these glycols can be readily supplied by conventional aeration equipment that is available in most waste treatment facilities. This is confirmed by data from the glycol biotreatment study that is presented in Table 10. Typical values experienced in publicly owned waste treatment works (POTW) are also shown and confirm that spent glycols can be readily biotreated in existing facilities.

Acclimation of the microbial population to glycols is required to rapidly biodegrade any of the three glycols. Biodegradation of EG, PG, or DEG by unacclimated cultures will occur but

TABLE 10—*Glycol biodegradation test conditions and results. (Acclimated biomass and unbuffered pH).*

Glycol	EG	DEG	PG	Typical Values for Public Waste Treatment Plant
Initial glycol Concentration, mg/L	2000	2100	2400	. . .
Average temperature, °C	19.8	19.3	19.3	. . .
Detention time, h	27	27	24	6 to 12
Initial COD, mg/L	3000	3100	2900	400 to 600
Effluent COD, mg/L	230	2300	140	50 to 100
Initial MLVSS Concentration, mg/L	2260	2700	2860	2000 to 3000
Specific oxygen uptake Rate, mg O_2/h/1000 mg MLVSS	22.5	10.3	16.3	15 to 30
Sludge yield, mg TSS Produced/ mg COD Removed	0.21	0.25	0.33	0.4 to 0.6

NOTES: COD is chemical oxygen demand. MLVSS is mixed liquor volatile suspended solids. TSS is total suspended solids.

at slower reaction rates. As with other chemical and biochemical reactions, the rate of glycol biodegradation decreases as temperature decreases. However, estimated effluent chemical oxygen demand (COD) concentrations for winter conditions (10 and 5°C) indicate that under typical organic loadings, glycols can be biodegraded to meet effluent discharge limitations within reasonable residence times.

The biodegradation of glycols results in a lowering of pH apparently from the production of acids. Data for PG showed less pH depression than for EG or DEG [*4*]. Buffered systems in the range of pH 7 to 8 improved glycol biodegradability considerably. As a result biological treatment systems for glycol containing wastes waters should have provisions for pH adjustment and control.

Major Additives and Contaminants—EG and PG readily biodegrade but what about actual engine coolant that contains several different additives. To answer this question, four different types of antifreeze/coolants were tested for their biodegradability. These coolants were chosen because they contained a range of various additives used as buffers and corrosion inhibitors. Growth medium was added to a 1% solution of the various antifreeze/coolants. The solutions were inoculated with a seed culture from a local POTW that had been acclimated to EG. They were maintained at 20°C with constant shaking, and the onset of strong culture growth was noted as a rapid substantial increase in turbidity. The results of this simple test is presented in Table 11.

A 1% solution of coolant is a much higher concentration than a POTW is ever likely to see, yet the antifreeze coolants were readily biodegradable. These results are not unexpected as the major coolant additives are used in a range of household products that are sewered in large quantities. Further work showed that a 5 to 10% solution of ethylene glycol was lethal to the culture. The commercial antifreezes we evaluated also proved lethal in the same dose range. This suggests that the biodegradability of glycol and commercial antifreeze coolants are similar and that sewering of used coolants can be acceptable means of disposal.

Minimizing Coolant Disposal Problems

The best way to manage a waste is to prevent or limit its generation. Strategies have emerged in the past few years to extend the useful life of a coolant and recycle waste product.

Extending Coolant Life—There are currently three approaches of which the authors are aware where the useful life of a coolant is extended well beyond the 30 000 to 50 000 miles (48 279 to 80 465 km) recommended by most manufacturers.

- Long Life Coolant—Some antifreeze coolant manufacturers are increasing the expected life of their products simply by adding more additives or choosing additives or both that are more stable and therefore deplete at a slower rate.
- Extending Coolant Life (Light Duty)—This is done by filtering the coolant to remove debris and replacing additives that have depleted or been lost through leaks or spills. Sev-

TABLE 11—*Biodegradability of antifreeze coolants.*

Type of Coolant	Days to Acclimation and Growth
Benzoate-nitrite	1 to 2
Sebasate	2 to 3
Phosphate-molybdate	2 to 3
Borate-nitrite	5 to 7

eral companies manufacture portable systems that pull the coolant from the vehicle, filter it, and return the coolant after a booster inhibitor package has been added.

- Extending Coolant Life (Heavy Duty)—For years the acceptable coolant life for many heavy duty vehicles has been 2 years, 240 000 miles (386 232 km) or 6000 h. This has been achieved by using coolant filters on the vehicles as well as adding supplemental coolant additive (SCA) at each oil drain (12 000 to 18 000 miles [19 312 to 28 967 km]). Many fleets, in spite of Original Equipment Manufactures (OEM) recommendations are pushing out their coolant life to 500 000 miles (804 650 km) or until in frame overhaul. This can be achieved with limited risk provided close attention is paid to the amount of SCA added to the cooling system. When too little SCA is added to the system, liner pitting and corrosion will result. Water pump leakage, cooling system deposits, and over heating are caused when too much additive builds up in the coolant. Another caution is that excessive coolant loss, which is the rule rather than the exception in many heavy duty truck fleets, can make the management of SCA levels very difficult.

Recycling—A coolant will finally get to the point where filtration and further SCA addition will not render it fit for further use. The level of dissolved solids and soluble contaminants will build to the point that they cause poor heat transfer, water pump leakage, and corrosion. Recycling, where the old additives and contaminants are removed, is required at this point; otherwise the coolant should be properly disposed. Distillation and deionization are the only processes that currently meet some Heavy Duty OEM requirements for a truly recycled product. Note, other light and heavy duty OEMs still have not approved the use of recycled coolant. Companies are now available, especially in the Western United States, which pick up, process, and return engine coolant. In addition, there are several different portable systems on the market that make it possible for a fleet operation or mining site to recycle their own coolant. ASTM is currently developing a specification for recycled antifreeze/coolant.

Environmental Concerns and Alternatives

Worldwide nearly 400 million gal (1514 million litres) of antifreeze are sold every year. It is estimated that 25 to 50% of this volume ends up improperly in the environment. Dumping by consumers is a major cause of this pollution. This can only be corrected by increased consumer awareness through education.

Another major source is leakage, spills, and overflows in the heavy duty industry. Experience with heavy duty vehicles shows that it is common to lose 10% of the coolant volume every 12 000 to 18 000 miles (19 312 to 28 967 km). This equates to a gallon/month (4 L/month) for the typical on-highway truck, or a leakage rate of one drop per min. A coolant leak that small is likely to go unnoticed but still results in a significant loss. For example, many heavy duty fleets never change coolant but purchase enough antifreeze every year to replace the coolant in each of their vehicles.

In some heavy duty operations, overflows account for far more coolant loss than leaks at the water pump, hose clamps, or radiator core. If a heavy duty radiator without a overflow tank is topped off, it can lose a quart or more of coolant when the engine heats up (expanding the coolant) to operating temperature.

Small spills and leaks (less than a gallon) of coolant, while undesirable, present little impact to the environment. Glycols, the main ingredient other than water, may present a toxic danger to wildlife, but will fully biodegrade. Additives and contaminants are present in small quantities and consequently do not represent a significant hazard. Cleanup, where possible, is always recommended to prevent animal poisonings.

Larger spills or on-purpose dumping are of more concern. Although glycols will readily biodegrade even at concentrations of 50 000 mg/L, high concentrations of contaminants, such as copper, could negatively affect soil biological activity. Lead, another corrosion product, can contaminate soil, leach into water tables, move up the food chain, and have serious effects on higher life forms. While glycols will biodegrade in soil or water, they place an oxygen demand on lakes, rivers, and streams. Depleted oxygen levels can suffocate aquatic life. For all the above reasons, generators of spent coolant, both private and commercial, should not dump the waste product.

We have discussed at some length the problems that can occur when engine coolant gets into the environment. However, what are the issues when a business or an individual wishes to responsibly dispose of waste coolant? First, spent coolant should be considered a hazardous waste unless proven otherwise. Lead content is the primary reason for the hazardous designation, but some states are also concerned with the EG content as well. In addition, POTWs limit the oil and grease content of a waste in the range of 100 to 300 mg/L. Experience with heavy duty vehicles shows that about 10% have some oil contamination of the cooling system. Therefore, oil levels of waste coolant also need to be considered before it is discharged to a sewage system. In some areas the POTW will simply charge a fee if the oil and grease exceeds their limit. Table 12 summarizes the disposal concerns of waste engine coolant.

For the individual who occasionally must dispose of a few gallons of waste coolant, the RCRA/EPA guidelines do not apply. The guideline 40 CFR 261.4 simply states that household waste will not be considered hazardous even though technically it may be. However for everyone else, the corner service station to the largest fleet or mine, RCRA does apply. Table 13 breaks down the RCRA requirements based on the amount of waste that is produced each month.

If coolant wastes are collected and properly treated, the resulting environmental concerns can be minimal. Bulk collection, transport, and disposal in accordance with laws and regulations is the recommended method of waste coolant management.

Recycling is always desirable but not always practical. Several competent and effective "antifreeze" recycling operations have begun in recent years, but they are primarily focused on serving commercial generators, which account for only 10 to 20% of spent coolant. Some communities have started recycling centers for hazardous wastes, but collection, segregation, and transport to recyclers is difficult, inconvenient, and costly.

Generators should select a recycler cautiously. The primary liability rests with the generator to insure proper disposal including residual metals and additives.

What action should be taken to dispose of spent coolant? Large-scale commercial generators can recycle or biotreat the waste. Note, ASTM has not yet approved specifications for recycled antifreeze, but going back to the "pure" glycol and then reinhibiting should yield as good a product as that originally put in the vehicle. Commercial generators should check with their local waste treatment authority; permitting may be required, which could involve some type of pretreatment. This may be as simple as checking the pH or checking the lead content of the

TABLE 12—*What makes coolant a hazardous waste.*

Area of Concern	Comment
Lead	limit 5PPM
Other heavy metals	varies
Oil and grease	limit 100 to 300 mg/L of concern
Ethylene glycol	in some states

TABLE 13—*RCRA requirements by size of waste generator.*

Size	Waste Produced, kg/month	Volume of Waste Content, (L/month) (approx.)	Requirements
Large	>1000	1000	Collect, Manage and Report
Medium	100 to 1000	100 to 1000	" "
Small	<100	<100	Must Manage No Reporting

waste coolant. Also treatment plants may ask generators to slowly feed spent glycol so as to avoid shocking the microorganism population. Under no circumstances should any amount of spent antifreeze be dumped on the ground or into a body of water.

Consumers, whose cooling systems are typically 2 to 5 gal (7.6 to 18.9 L), should follow similar guidelines. If recycling is not available, speak with your local officials about setting up a program. If local regulations allow, pour spent coolant down your drain as opposed to dumping it in the back yard. Municipal treatment facilities will easily handle small quantities of spent coolant. Caution, do not pour large quantities (above 2 gal [7.6 L]) of spent coolant into a septic system. Too much coolant too quickly can shock the "bugs" and necessitate reseeding the system.

As a final note, good housekeeping is always recommended. Clean up leaks and spills, and properly dispose of used coolant.

Summary

The acute oral toxicity of spent antifreeze is largely determined by the glycol used. Additives and contaminants will have a minimal effect on coolant toxicity.

Spent coolant should not be dumped on the ground or into bodies of water but properly disposed of by biological treatment or recycling. No spill is insignificant, but small quantities are not a major threat to the environment. Regardless of size, spills or leaks can pose an acute oral toxicity danger to wildlife and pets. Consequently all spills and leaks should be cleaned up.

Heavy metals, such as lead, present a chronic health concern, and along with ethylene glycol may be one of the primary reasons why a used coolant falls under RCRA guidelines. Improper dumping can result in heavy metal contamination of soil and water and present a real danger to the food chain.

Spent coolant can be safely biologically degraded in waste treatment plants. Testing can confirm that a waste is not in the hazardous classification. Commercial generators should check with waste treatment officials for permitting requirements, and the rules and regulations governing disposal in their communities. Homeowners and other small quantity generators should also check their POTW and governing bodies before discharging.

Commercial generators can recycle spent coolant. However, the ASTM has not finalized specifications for recycled antifreeze. Until specifications are available, generators/users would be wise to only use antifreeze/coolant products that fully meet the performance requirements of "fresh" antifreeze. Recycling for the average consumer is not readily available. We would encourage interested parties to work with their local government to set up recycling programs.

Disposal problems can be minimized by extending coolant life. Extended life products and maintenance methods are under development by many of the antifreeze producers. Consumers, both private and commercial, should support the development and use of such products.

For instance, filtration and SCA addition have long been used to extent the life of heavy duty engine coolants. Now this concept is beginning to be applied to extend the life of passenger car coolants.

The authors urge heat exchanger manufacturer's to continue the trend toward air-side soldering. This will minimize the lead (from the solder) in contact with the coolant, which will in turn reduce the lead levels in engine coolants. Alternative types of solder, which are available, should be evaluated in an attempt to eliminate a source of lead contamination and the related serious health concerns.

Heavy duty OEM's should consider installing overflow systems on their vehicles to simplify maintenance, limit overfilling of the radiator, significantly reduce coolant loss, and thus benefit the environment.

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DISCUSSION

James A. Lima[1] *(written discussion)*—Doug, given your data, it seems to me that filtration to remove most of the lead, followed by POTW treatment should be a viable means of disposal. Do you agree?

R. D. Hudgens and R. B. Bustamante (written discussion)—In my experience, the lead in the coolant is largely soluble. I attribute this to the glycol oxidation products that act as a lead chelate and hold the metal in solution. If filtration is effective at lead removal, then it will have to be very fine filtration, below a micron.

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[1] Houghton Chemical Corporation, Allston, MA.

Paul R. Hemmes,[1] Thomas H. Kreiser,[1] Sarah Valle,[1] and Richard D. Hercamp[1]

Test Strips for Rapid On-Site Analysis of Engine Coolants

REFERENCE: Hemmes, P. R., Kreiser, T. H., Valle, S., and Hercamp, R. D., **"Test Strips for Rapid On-Site Analysis of Engine Coolants,"** *Engine Coolant Testing: Third Volume, ASTM STP 1192,* Roy E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 165–179.

ABSTRACT: This paper reviews the use of test strips for measuring the composition of engine coolants. The tests described include test strips for freezepoint, cylinder lining cavitation corrosion protection, reserve alkalinity, pH, chloride, and mercaptobenzothiazole.

Freezepoint strips work with reasonable accuracy with both ethylene glycol and propylene glycol based coolants. They will also work with mixtures of the two. The strips are shown to work with coolants containing phosphates, borates, or benzoates. Data show that good results can be obtained with new users so that training is minimized.

Strips for liner cavitation protection are described. Good results were obtained with visually read strips for nitrite in the range of 200 to 4000 ppm and for molybdate in the range of 75 to 1500 ppm. A hand-held reflectance meter to read these strips is described. Precision and accuracy data are given. The strips are not sensitive to glycol concentration.

Data are presented for the accuracy of test strips for reserve alkalinity and pH. Test strips for mercaptobenzothiazole are described. A description is also provided of a prototype test for chloride levels in used coolants where the makeup water may have contained salts. In all cases, test strips were found to be accurate, easy-to-use, inexpensive devices useful for routine field monitoring of coolants.

KEYWORDS: test strips, freezepoint, reserve alkalinity, cylinder lining cavitation protection, pH of coolant, mercaptobenzothiazole, chloride

Test strips for monitoring the field condition of engine coolants consist of small chemically treated pads attached to a plastic handle. When immersed in coolant, the pads develop color. The strip is removed from the sample after a specified time. After another specified time (ranging from 15 s to 1 min), the pad color is compared to a color chart, which has been calibrated to read the level of the particular constituent in the coolant.

The history of test strips began with simple laboratory test papers such as litmus paper for checking the acidity of aqueous solutions. However, the use of test strips for semi-quantitative measurements was first developed in the area of medical diagnostics. In the middle 1950s, test strips were introduced for monitoring glucose and protein levels in urine. These tests were widely used for screening patients to detect the presence of diabetes and urinary tract problems [*1*]. In the mid-1960s, blood glucose strips were introduced to allow patients to control diabetes. Today, tens of millions of people, worldwide, use blood glucose strips to help control diabetes. Urine test strips, some with as many as ten analyses on a single strip, are widely used in doctor's offices and hospitals to screen for possible health problems.

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[1] Vice-president of Operations, senior scientist, assistant research scientist, and consultant, respectively, Environmental Test Systems, Inc., P.O. Box 4659, Elkhart, IN 46514.

The first use of test strips for testing engine coolants was by the military *[2]* and they were adapted for coolant maintenance in heavy-duty vehicles.

Test strips have several unique advantages over other methods of field analysis of engine coolants. These include:

1. Testing using strips is more convenient than laboratory testing because the results are obtained within minutes at the site where the vehicle is located. The vehicle is still in the maintenance area so that appropriate maintenance can be accomplished in a single visit.
2. The cost for each test performed by test strips is less than the cost for most laboratory tests.
3. For fleet maintenance, the used strip can be stapled to the vehicle maintenance record to provide a positive record that the testing has been performed.
4. The initial cost for freezepoint testing is much lower than for a refractometer, and breakage is not a problem.
5. Cross contamination from vehicle to vehicle caused by poor cleanup procedures is eliminated because each strip is used only once.

Poor coolant maintenance is widespread and leads to major cooling system failures *[3]*. In spite of this, field analysis of coolants has almost exclusively been restricted to determination of the freezing point of an ethylene glycol (EG) based coolant by means of a hydrometer. In recent years, however, many changes have occurred that make this approach unacceptable. Some of these changes are:

1. Commercial use of propylene glycol (PG) based coolants raises the possibility of finding vehicles with EG, PG, or mixtures in any given vehicle. Without knowledge of the type of coolant in a given vehicle, measuring the freezepoint protection is greatly complicated.
2. With extended use of coolants due to supply shortages and problems of disposal of used coolants, there is a greater chance of coolant problems developing. This is especially true of corrosion and cavitation protection additives, which deplete with time.
3. Extended warranties of vehicle manufacturers make the manufacturer liable for repairs required because of poor coolant maintenance.
4. Changes in the mid 1980s in the inhibitor chemistries used in heavy-duty vehicle coolants, such as the addition of molybdate to nitrite for liner corrosion protection in the mid-1980s.

This paper discusses test strips for analysis of the following coolant properties:

1. Freezepoint,
2. Cylinder lining cavitation protection,
3. Reserve alkalinity (RA),
4. pH,
5. Chloride, and
6. Mercaptobenzothiazole (MBT).

Test Strip Overview

Before discussing the individual tests, it is useful to consider some general features of test strips and the factors that influence visual readings. Strips are read by means of optical detection of color changes, which occur in response to exposure to the sample containing a particular component. To describe color, we must consider three things: the detector, the light source, and the sample.

For visually read strips, the detector is the eye. The human eye responds differently to light of various wavelengths. In general, the eye is most sensitive to light at about 570 nm wavelength and rapidly decreases as wavelength either increases or decreases from this maximum. The response of the eye is, however, quite individual. It is probably true that no two people see colors exactly the same way. Nevertheless, we are so adapted to color that these differences cause far fewer problems than might be expected. The only real exceptions come with the condition of color blindness. In many cases, even mild color blindness does not prevent the user from using test strips. This is due to the fact that a color comparison is actually done against the color chart. Color-blind people can often match two colors that to them may appear as gray shades.

The light source is of more concern. It is common for one observer to find that two colors that match under one light source do not match under another. This is called *metamerism.* The three most common types of light sources are sunlight, incandescent lighting, and fluorescent lighting. In theory, colors appear somewhat different under each source. Usually, however, these effects are small enough that they cause few problems. We use special inks for printing our color charts, which minimizes metamerism. In general, we use fluorescent lighting as the standard light source for coolant strips. It is important to remember the possible presence of metamerism if testing of one sample is done under several light sources.

Finally, the physical properties of the sample affect the visual appearance. For example, at certain viewing angles, a wet strip may appear to have a glossy appearance. This is due to specular reflectance from the surface. In general, a rough surface provides diffuse reflectance, which depends less on the viewing angle. Again, these problems are generally of little importance, especially for experienced users.

During development of a test strip, we use special instrumentation that measures color in terms of three color coordinates. This gives us a means to describe color and color changes quantitatively. Many of the various factors that influence the color of the strip can be controlled by this instrument.

Some people have difficulty in judging color matches especially when the levels of material being tested lie between the levels shown on the color chart. This subjectivity of visual readings of strip tests for nitrites and molybdates can be avoided by the use of a hand-held reflectance meter for these strips, which was recently introduced and will be discussed in the appropriate section of this paper.

Freezepoint Strips

The use of hydrometers for measuring the freezepoint of coolants has been widespread due to their relatively low cost compared to refractometers. The fact that the refractometer is more accurate than the hydrometer [*4*] has led to the adoption of the refractometer for larger fleets where the initial cost is less of a factor. The refractometer is strongly recommended over the hydrometer for heavy-duty fleet work. As PG-based coolants become more prevalent, the hydrometer becomes inappropriate due to the large differences between the densities of EG and PG. It requires prior knowledge of the composition of the coolant to use hydrometers at all. When PG or EG or mixtures of the two can be found in the vehicles being tested, only refractometers with both a EG and PG scale can be used and then with diminished accuracy [*5*].

Test strips have been in commercial use for measuring freezepoints of engine coolants since 1976. The chemistry of this test is detailed in the Appendix. The strip has been patented [*6*].

In addition to the general advantages test strips have over other methods, the freezepoint test can be used without prior knowledge of the coolant composition. That is, the test strip is equally effective with EG or PG or mixtures of the two. Table 1 shows experimental refractometer readings on either the EG scale or the PG scale. The column labeled calculated freezepoint is a listing of the freezepoint estimated from the known concentrations. The data for pure PG samples show a tendency for overestimating the freezepoint protection at low levels of PG and underestimating it at high concentrations. In mixtures containing significant levels of EG, the test strips are accurate. In very high glycol solutions, there is a small tendency for underestimation of protection. Planned modifications of the color chart will improve the performance at these levels.

Table 2 shows the effect of additives on freezepoint depression as measured by strips, refractometers, and by ASTM Test Method for the Freezing Point of Aqueous Engine Coolant Solution (D1177). This study was done to investigate the effect of various salt additives, which are expected to lower the freezepoint. One of the salts chosen was sodium benzoate. This was chosen because the benzoate ion is expected to have an abnormal effect on the refractive index of solutions due to its electronic structure. This was a possible problem for the refractometer readings. In fact, both the refractometer and the strips read these solutions accurately.

TABLE 1—*Refractometer and strip readings on EG and PG mixtures.*

Volume Percent		Total Glycol	Refractometer, °F		Calculated Freezepoint[a]	Strip, Visual Results
EG	PG		EG Scale	PG Scale		
0	10	10	24	26	26	+10
0	20	20	13	19	19	+5
0	30	30	−3	10.5	10.5	−5
0	40	40	−24	−6	−6	−20
0	50	50	−42	−27	−27	−30
0	60	60	−68	−65	−65	−45
10	0	10	25	27	25	+15
10	10	20	13	19	16	+5
10	20	30	−2	11	6.7	−5
10	30	40	−17	0	−4.3	−20
10	40	50	−41	−25	−28.2	−30
10	50	60	−65	−52	−54.2	−45
20	0	20	14	20	14	+5
20	10	30	0	12	4	−5
20	20	40	−18	−1	−9.5	−20
20	30	50	−42	−26	−32.4	−30
20	40	60	−63	−59	−60.3	−45
30	0	30	2	13	2	0
30	10	40	−16	1	−11.8	−20
30	20	50	−36	−18	−28.8	−30
30	30	60	−60	−53	−56.5	−45
40	0	40	−14	2	−14	−10
40	10	50	−36	−18	−32.4	−30
40	20	60	−70	−75	−71.7	−60
50	0	50	−35	−18	−35	−30
50	10	60	−57	−49	−55.7	−45
60	0	60	−59	−52	−59	−45

[a] The proportion of EG or PG in the mixture determined the calculated freezepoint from the EG or PG scales on the refractometer.

TABLE 2—*Freezepoints in 50% glycol (EG or PG).*

Glycol	Solute	ASTM Method D 1177-88	Refractometer	Strip
EG	None	−36.7	−35	−30
EG	2% Sodium benzoate	−42.9	−44	−45
EG	1% NaH_2PO_4	−39.8	−39	−45
EG	2% Na_2HPO_4	−41.8	−42	−45
EG	1% Sodium borate	−38.7	−38	−30
EG	2% Sodium borate	−39.4	−41	−45
EG	1% Na_2HPO_4/1% Sodium borate	−38.6	−41	−45
EG	1% Na_2HPO_4/0.14M Formate	−35.4	−38	−30
PG	None	−28.1	−30	−30
PG	2% Sodium borate	−33.4	−37	−40

Table 3 contains the results of a study designed to test the ability of new operators to use both refractometers and test strips. Two different refractometers were compared using an experienced operator. Then an inexperienced operator used one of the refractometers. Finally, an experienced lab person read strips along with an inexperienced strip reader selected from the office staff. There were some surprisingly large variations between refractometers as shown, for example, by the results of samples 23306 and 23310. Experience level was not significant in reading the same refractometer. Experience level also was not a significant factor in reading strips.

TABLE 3—*Results of study to test new operators.*

Sample Number	Refractometer Readings, EG Scale, °F[a]			Strip Readings, °F[b]	
	#1-Lab	#2-Lab	#2-Office	Lab	Office
23292	−42	−46	−48	−45	−45
23293	−15	−24	−24	−30	−30
23294	−23	−28	−29	−20	−30
23295	−37	−47	−48	−60	−60
23296	−34	−33	−33	−30	−45
23297	10	7	6	0	−5
23298	−54	−54	−54	−45	−70
23301	−37	−38	−38	−30	−45
23302	−37	−37	−37	−30	−30
23303	−68	−60	−59	−70	−70
23304	−54	−51	−51	−60	−45
23305	13	7	7	0	5
23306	−19	−30	−30	−30	−20
23307	−6	−13	−12	−20	−20
23308	17	15	14	10	15
23309	18	15	13	10	15
23310	−23	−31	−31	−30	−30
23311	−1	−5	−6	−5	−10

[a] Two refractometers were compared by one experienced lab operator. One refractometer was used by an inexperienced office worker.

[b] Strips were read by both a lab and office person. $t°C = (t°F - 32)/1.8$.

The strips are designed to be read at room temperature (65 to 85°F [18 to 29°C]). Reading hot solutions causes errors because the indicator's degree of ionization is temperature-dependent. The recommended procedure is to withdraw a small sample into a cup. This should quickly cool to the proper range. A strip can then be dipped and read.

In summary, the use of test strips is a fast, easy, accurate method for monitoring the freeze protection of cooling systems. The strips work well in EG, PG, and mixtures of the two.

Cylinder Liner Cavitation Protection

The two coolant additives used in most of the world to protect cast iron cylinder liners from cavitation corrosion are nitrite and molybdate salts. Although chromate was the predominant additive in the 1950s and 1960s, it has been replaced because of its toxicity. Nitrites were almost exclusively used to replace chromates until the mid 1980s when molybdate also began to be used in supplemental coolant additives (SCAs). The so-called mixed system test kit is shown in Fig. 1. It is designed to measure both nitrite and molybdate in coolants [7]. It has enjoyed extensive commercial use since 1988. The chemistry of both strips is discussed in Appendix 1. The test procedure consists of drawing a sample of coolant, adding an equal volume of acidic solution, and then dipping two strips, one after the other. The color chart for this test is a two-dimensional array (Fig. 2). After dipping in the acidified sample, the molybdate strip (called strip A) is read on the vertical brownish orange blocks. The nitrite strip (strip B) is read on the horizontal, pink blocks. A vertical line from the position where the nitrite strip best matches the color block will intersect a horizontal line from where the molybdate strip best matches the color blocks. The point of intersection of the two lines will lie in a zone corresponding to a specified treatment procedure for the coolant.

Although the visually read test strips have been well-received for the past several years, some people are not comfortable with color matching. For this reason, we have developed a small, portable, reflectance meter to read the test strips (Fig. 3). In operation, the test strips are developed in much the same way as in the visual test. The molybdate strip is first inserted into the

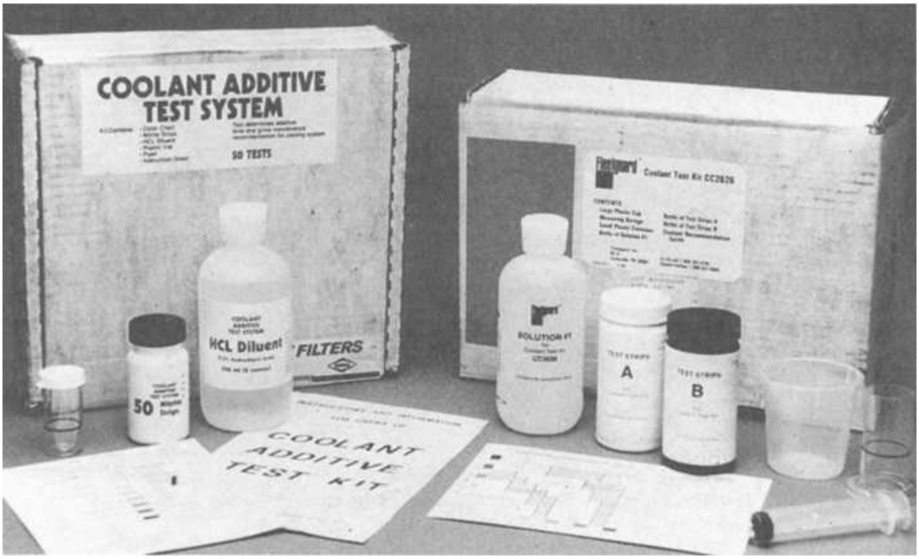
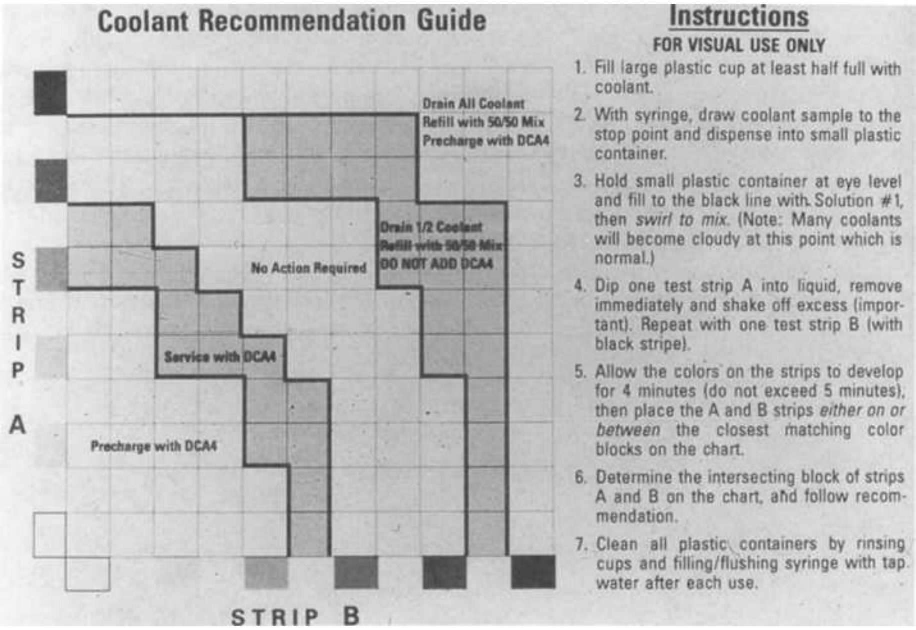


FIG. 1—*"Mixed system" test kit.*



Coolant Recommendation Guide

Drain All Coolant
Refill with 50/50 Mix
Precharge with DCA4

Drain 1/2 Coolant
Refill with 50/50 Mix
DO NOT ADD DCA4

No Action Required

Service with DCA4

Precharge with DCA4

STRIP A

STRIP B

Instructions

FOR VISUAL USE ONLY

1. Fill large plastic cup at least half full with coolant.
2. With syringe, draw coolant sample to the stop point and dispense into small plastic container.
3. Hold small plastic container at eye level and fill to the black line with Solution #1, then *swirl to mix.* (Note: Many coolants will become cloudy at this point which is normal.)
4. Dip one test strip A into liquid, remove immediately and shake off excess (important). Repeat with one test strip B (with black stripe).
5. Allow the colors on the strips to develop for 4 minutes (do not exceed 5 minutes), then place the A and B strips *either on or between* the closest matching color blocks on the chart.
6. Determine the intersecting block of strips A and B on the chart, and follow recommendation.
7. Clean all plastic containers by rinsing cups and filling/flushing syringe with tap water after each use.

FIG. 2—*Color chart for the mixed system test kit.*

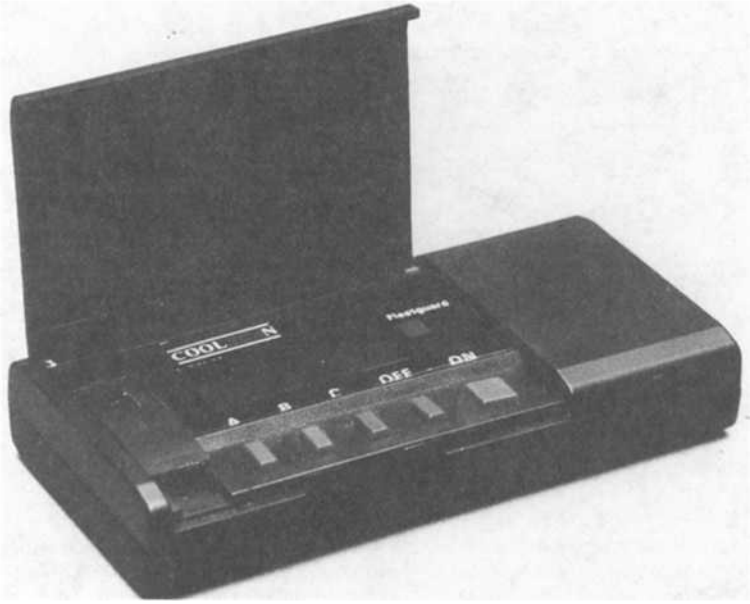


FIG. 3—*Hand-held reflectance meter for nitrite and molybdate strips.*

meter. A light-emitting diode of fixed wavelength momentarily focuses a bright spot of light on the reacted pad. Some of this light is reflected from the pad to a detector. This detector converts the light intensity into an electrical signal, which is processed by the microprocessor in the meter. The nitrite strip is read in the same manner. The microprocessor uses the calculated levels of nitrite and molybdate to calculate a recommended treatment code for the operator. The operator does not have to read strips or compute treatment codes. The actual concentrations can be obtained from the instrument using a special procedure. This allows for troubleshooting of the system and also provides a means for generating accurate and precise data on the coolant composition, if this is required.

One important difference between the strips for nitrite and molybdate as read on the meter is the different instrument responses to concentration. The reflected light intensity is a linear function of molybdate concentration and a nonlinear function of nitrite concentration. This

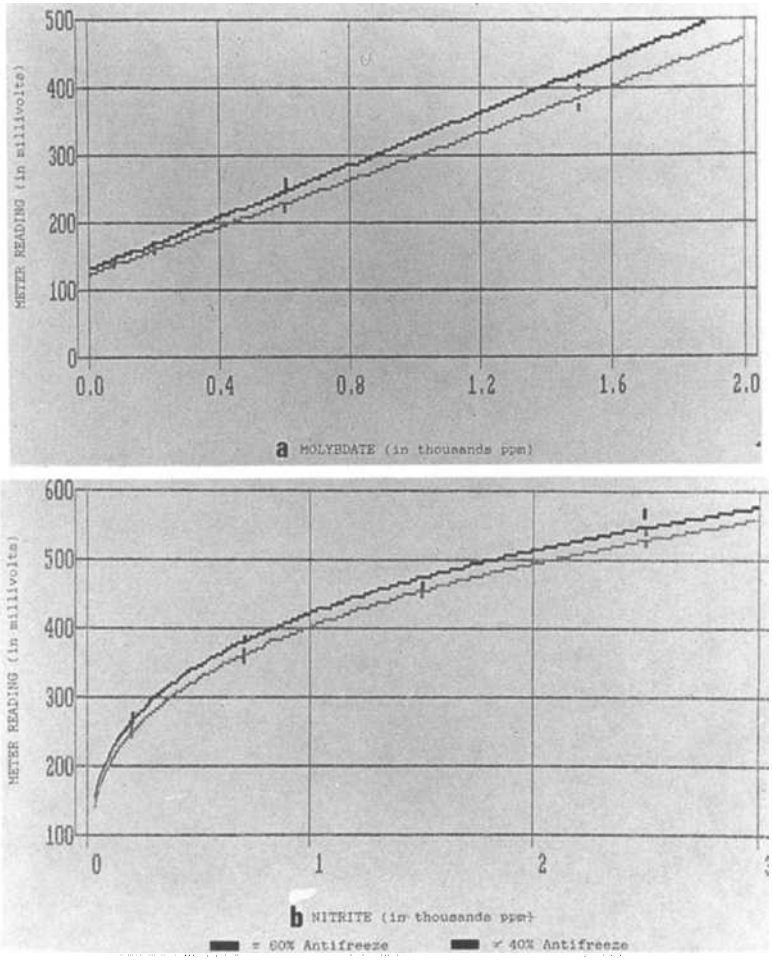


FIG. 4—(a) *Instrument response to molybdate concentrations in coolants. The* y-axis *represents instrument units that are proportional to reflected light intensity. The response at both 40% and 60% glycol is shown.* (b) *Instrument response to nitrite concentrations in coolants at both 40% and 60% glycol. Upper line is 40% antifreeze and lower line is 60% antifreeze.*

TABLE 4—*Ion chromatography and strip results.*

Sample Number	Ion Chromatography, ppm	Strip Results, ppm
1	42	7
2	190	60
3	230	95
4	710	700
5	1190	990
6	1000	860
7	1060	990
8	1850	1790
9	1040	1000
10	1050	1170
11	1320	1480
12	2890	2370
13	1740	1990
14	2920	3290
15[a]	1500	2790

[a] Sample 15 contained a great deal of suspended carbon. When this sample was applied to the strip, the strip was darkened by the carbon and gave a high result as a consequence.

difference is shown in Fig. 4*a* and *b*. This in no way affects the operation of the system in the hands of the user. We have deliberately designed the system so that low samples (200 ppm or less) would read even lower than actual. This ensures that the recommended treatment for such critically low samples calls for supplemental additives. The design philosophy behind this system has consistently been to give the maintenance person doing the test the proper treatment recommendations under all circumstances. The system does this effectively. The low bias is shown in the section on accuracy.

The accuracy and precision of the meter-read test strips were checked with field samples. Nitrite was determined in a number of field samples using ion chromatography [*8*] and compared with the meter-read test strip results. The results are given in Table 4.

Table 5 contains results of the molybdate strip test compared with an inductively coupled plasma (ICP) reference method. To investigate the reproducibility of the test strip results, ten replicates were run on a single meter at four levels of molybdate and five nitrite levels. Table 6 gives the results of this study in terms of the true concentration, the average of the ten replicates, the standard deviation of the replicates, and the percent coefficient of variation (%CV). The latter is 100 times the standard deviation divided by the average.

The influence of the glycol level was investigated. Figure 4*a* and *b* also shows the meter response to molybdate and nitrite concentrations at 40% and 60% EG. In general, the system is remarkably free from interferences.

We are developing an improvement of the system. We have been able to develop a molybdate and nitrite test strip that does not need the acid dilution step. Both visual and instrument versions of these strips are under development with a planned introduction near the end of 1991.

Reserve Alkalinity Test Strip

A dip-and-read reserve alkalinity (RA) test has been used by the military for nearly 20 years [*9*]. In 1984, a two-pad multiple strip consisting of a freezepoint test and an RA test was intro-

TABLE 5—*Molybdate strip results compared with ICP reference method.*

Sample Number	Lab Value (ICP)	Strip Value
1	1567	1427
2	979	878
3	1447	1137
4	594	557
5	404	487
6	408	481
7	600	916
8	964	824
9	237	305
10	563	519
11	132	198
12	483	473
13	117	145
14	20	23
15	1069	1076
16	3	0

duced commercially under the name Radi-Aider® (Radi-Aider produced and sold by Environmental Test Systems, Inc., Elkhart, IN 46514. The chemistry and mechanism of the RA strip are described in the Appendix. In an evaluation of the RA test, a major manufacturer of coolants obtained the test results shown in Table 7. The strip values are compared with those measured using ASTM Test Method for Reserve Alkalinity of Engine Coolants and Antirusts (D 1121).

These results indicate that the RA test gives good results compared with ASTM Test Method D 1121.

As noted in ASTM Test Method D 1121-88, care is required in the interpretation of any RA measurement. When the chemical nature of the coolant additives changes, the RA changes. European coolants using organic acid salts always appear to have a low RA, even when fresh. When the composition of the coolant is well-defined, as, for example, in military service or large fleets, a precipitous drop in RA can serve to indicate a problem with the coolant. RA is a measure of buffer capacity. Thus, a low RA value can exist along with a proper pH. However,

TABLE 6—*Ten repliates run on a single meter at 4 levels of molybdate and nitrite.*

Parameters	Level 1	Level 2	Level 3		Level 4
		Molybdate			
True concentration, ppm	75	200	600		1500
Average, ppm	74.3	201	631		1460
Standard deviation, ppm	8.9	11.2	46.3		78.3
% CV	12	5.6	7.3		5.4
		Nitrite			
True concentration, ppm	200	700	1500	2500	4000
Average, ppm	178	698	1439	2479	4481
Standard deviation, ppm	22	68	191	247	203
% CV	12.5	9.8	13.3	10	5

TABLE 7—*Results of evaluation of reserve alkalinity test.*

% Ethylene Glycol	RA (ASTM Method D 1121-88)	RA (Strip)
	New Antifreeze Solutions	
33	5.1	6
50	7.0	8
80	11.2	10+
	Used Antifreeze Solutions	
33	9	10
50	7.1	8
47	6.9	6+
47	10.5	10+
42	5.7	6−
37	4.9	6−
42	5.8	6
41	5.2	6
34	3.7	6−

the low RA value implies that the useful life of the coolant is short because the basic materials added to the coolant are nearly exhausted.

Test Strips for Coolant pH

We have developed a test strip for coolant pH that gives visual pH readings that correlate with those measured by ASTM Test Method for pH of Engine Antifreezes, Antirusts, and Coolants (D 1287). The chemistry is simply the use of selected acid-base indicators incorporated into a paper matrix. The pH of a coolant may or may not be a significant indicator of condition. If the pH is below 7, indicating an acid condition, the coolant should be replaced at once. On the other hand, a pH of 8 may not be worse than a more alkaline coolant due to the type of additives used. The performance of these test strips is shown in Table 8.

TABLE 8—*Results of a test strip for coolant pH.*

% Ethylene Glycol	pH (ASTM Method D 1287-85)	pH (Strip)
	New Antifreeze Solutions	
33	10.2	9+
50	10.5	9
80	10.8	9+
*50	7.0	7
*50	6.0	6
	Used Antifreeze Solutions	
33	7.8	8.5
50	7.3	8
47	7.9	8
47	8.2	8.5
42	8.7	9−
37	9.0	9
42	9.7	9
41	8.3	9
34	8.5	8.5

The pH strip does not respond properly in pure glycol. This may account for the low reading in 80% solutions. The test is more accurate in used samples. This may be related to the high RA of such solutions. The two samples of new glycol (marked with an asterisk in Table 8) were acidified in the lab to the pH values determined by pH meter.

Test Strip for Chloride in Coolants

Chloride is a possible serious contaminant of coolant systems. When present in high levels, it causes corrosion of iron (Fe) and aluminum (Al) parts. There is no industry-wide agreement on what constitutes too high a level of chloride, but opinion ranges from 100 to 200 ppm as chloride. We have developed a prototype of a test strip for chloride in coolants as part of a program to produce a screening test for reconditioning coolants. Clearly, a heavily contaminated coolant is not worth reconditioning. The chloride test we developed is designed to detect a threshold level of chloride. That is, if the level of chloride is 175 ppm or more, the strip turns blue. Below this level, it remains colorless. The chemistry is given in the Appendix. In addition, we have designed the test to eliminate interferences by mercaptobenzothiazole (MBT) up to about 700 ppm of MBT. ASTM testing requires a special procedure for the laboratory determination of chloride in the presence of MBT, Test Method for Trace Chloride Ion in Engine Coolants (D 3634).

In addition, we plan to use our existing test strip for MBT in conjunction with this chloride test so that fresh coolants with high MBT levels are not confused with heavily salt-contaminated, used coolants. The chloride test strips are being patented. They have been evaluated by a major coolant manufacturer (Table 9). The samples were prepared by dissolving known amounts (if it was known, it had to have been weighed) of salt into a glycol–water mixture. A yes means that the strip was blue, positive for chloride. A no means that the strip was negative for chloride.

Test Strip for MBT

MBT has been used as an additive in coolants to provide some protection for copper (Cu) components in the cooling system. The level of MBT in a coolant decreases rather quickly due to adsorption onto the metal parts and chemical degradation. Because of this rapid decay, MBT has been replaced with longer lasting additives such as tolyltriazole (TTZ). Nevertheless, MBT is still found in a number of antifreeze formulations (particularly for light-duty use) and

TABLE 9—*Results of evaluation by coolant manufacturer.*

	Samples								
Readers	A	B	C	D	E	F	G	H	I
Cl, ppm[a]	150	160	170	180	190	200	220	250[b]	300
1	No	No	Yes	Yes	Yes	Yes	Yes	No	Yes
2	No	No	Yes	No	Yes	Yes	Yes	Yes	Yes
3	na[c]	na	na	na	na	na	Yes	Yes	Yes

[a] The above results indicate that the chloride test strips serve as an adequate screen for high levels of chloride in coolants. A Yes means that the strip was blue, positive for chloride. A No means that the strip was negative for chloride.

[b] Although one reader found a 250-ppm sample to be negative, this abnormal finding could not be confirmed by an additional reader.

[c] The symbol na means that a third reading was not made on this sample.

in some supplemental additives. A strip test for MBT was developed and sold some years ago but was withdrawn from the market as the use of MBT declined. It is being reintroduced only in conjunction with the chloride test for the reasons stated in that section. The chemistry of this test strip is given in the Appendix.

Summary

Test strips are easy-to-use, accurate, versatile, and cost-effective devices for the rapid testing of engine coolants. They have been used successfully for more than 10 years to measure freezepoint and are expected to gain increased use as PG use increases. The use of strips for monitoring the levels of cylinder liner cavitation protecting agents is growing due to the immediate treatment recommendations they provide. Newer tests for testing the suitability of coolants for reconditioning are being developed. The use of test strips in monitoring coolant systems, both heavy- and light-duty uses, is expected to grow.

APPENDIX

The chemistries used in various test strips are as follows:

Freezepoint

The freezepoint test is based on the fact that certain acid–base indicators change color when placed in a mixed solvent containing water and an organic liquid. This effect occurs even if the solution contains material that in water would buffer the solution to constant pH. The reaction can be written:

$$HIn + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O} + In^-$$

In this reaction, HIn is the acid form of the indicator and In^- is the ionic form.

For the indicator used in the freezepoint test, HIn is yellow, whereas In^- is blue. The mixture gives shades of yellow greens.

The effect may arise from several causes. Because the quantity of the deprotonated species, *In*, increases with increasing organic solvent content, the presence of the organic liquid must stabilize this form. This must be a type of specific interaction because electrostatics predict that the ionic forms will be less stable in water–organic mixtures. This specific effect does not differ much among EG, PG, or simple alcohols such as methanol. The lack of strong dependence on the nature of the organic substance is the reason this chemistry works to indicate the freezepoint of aqueous mixtures of either EG or PG.

Reserve Alkalinity

This test consists of a strip treated with a buffer compound and an acid–base indicator. In the presence of alkaline materials, some of the buffer acids are converted to the corresponding salt. This changes the ratio of buffer acid to salt and thereby changes the equilibrium pH. The indicator provides a visual response to this pH change.

Cavitation Corrosion Protection Strips

The two types of strips now in use involve tests for nitrite and molybdate. The nitrite test strips use the following chemistry:

$$\text{nitrite} + \text{sulfonamide} \rightarrow \text{diazo compound}$$

$$\text{diazo compound} + \text{aromatic amine} \rightarrow \text{azo compound}$$

A number of sulfonamides can be used, including sulfanilamide. The formation of the diazo compound occurs only in acidic solution. The coupling of this material to an aromatic amine in acid solution produces a highly colored azo compound. This reaction is specific for nitrite.

The molybdate test is based on the formation of a complex between molybdate and a complexing agent. This complex is then reduced chemically to an intensely colored compound. This test is highly specific for molybdate.

Test Strip for Chloride

This test consists of a pad treated with silver (Ag) salts and a proprietary indicator material. When chloride is added, it reacts with Ag first. Once the Ag is consumed, any excess chloride reacts with the indicator to give a blue color. Because MBT reacts with Ag, it is an interfering substance. We use a material in the pad that preferentially reacts with MBT. Then the MBT is not free to react with Ag. This is effective with modest levels of MBT, up to about 700 ppm. Higher levels still interfere because the material we use to minimize interference is not 100% effective. At high levels of MBT, the small fraction of MBT that reacts with Ag is enough to develop some color.

MBT Strip

For the above reason, we supplement the chloride test strip with one specific for MBT. This provides a warning that high levels of MBT are present and that the chloride test may be giving a false reading but also is useful in checking that reconditioning has taken place, because many treatments contain some MBT. This test is based on the fact that MBT can be made to develop a mixed complex in the presence of certain metal ions and amino acids. The orange color of the complex of the metal, MBT, and amino acid is quite specific. The test measures levels of MBT up to about 1200 ppm.

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DISCUSSION

Joseph A. Lima[1] *(written discussion)*—A very informative paper was presented in *Chemtech* recently that describes the complex technology used to produce test strips. My concern is that many men are color-blind and would have difficulty comparing colors and making the interpretations necessary to read these strips. I believe it to be important to mention because indiscriminate use of the strips by people who are not aware of such limitations could present an obvious problem. I would be interested in hearing your comments about this particular problem and also would like to know the cost of the color comparison device that you mention, which I gather is meant to circumvent this color-blindness problem.

Paul R. Hemmes (author's response)—Color-blind persons have been found to be quite capable of using strips except in a few extreme cases or with a particular color change on a strip. What is actually being done when a strip is used is to compare the strip with a color chart. Thus, one is making a color comparison. Color-blindness is less of a problem when matching two colors held side by side.

In the medical diagnostic field, millions of diabetics worldwide use test strips to measure blood glucose levels. Many continue to use visual reading with satisfactory results. The use of a meter is not dictated by the problem of color blindness. Some people with perfect vision are uncomfortable making judgments of the match between the strip and the color chart. This is particularly true when the measured level is between two color blocks. Such people prefer the objective meter readout to their own color match.

The only meter for engine coolant test strips is available from Fleetguard, Inc. They should be contacted for retail prices.

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[1] Houghton Chemical Corporation, Allston, MA.

Walter Zamechek[1] *and Dale A. McKenzie*[2]

Application of Inductively Coupled Plasma (ICP) Emission Spectroscopy and Laser Ablation-ICP for Problem Solving in Coolant Systems

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REFERENCE: Zamechek, W. and McKenzie, D. A., "**Application of Inductively Coupled Plasma (ICP) Emission Spectroscopy and Laser Ablation-ICP for Problem Solving in Coolant Systems,**" *Engine Coolant Testing: Third Volume, ASTM STP 1192,* Roy E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 180–189.

ABSTRACT: Since the introduction of commercial instrumentation in 1975, inductively coupled plasma (ICP) emission spectroscopy has become the technique of choice for the determination of metals for many environmental, clinical, geological, and industrial applications. This is due to the method's relative freedom from interferences, speed, and flexibility. Described are some main characteristics of ICP spectroscopy, typical sample preparation approaches, and results for the analysis of coolants and deposits from different parts of cooling systems. Laser ablation-ICP (LA-ICP) was used to map the spacial distribution of metals across the surface of water pump seals. Design of the ablation system and standardization method are described. These results are compared to the analysis of the same samples by scanning electron microscopy/energy dispersive X-ray (SEM/EDX), electron spectroscopy for chemical analysis (ESCA), and scanning auger microprobe/energy dispersive x-ray (SAM/EDX).

KEYWORDS: inductively coupled plasma (ICP) spectroscopy, coolants, radiator deposits, laser ablation-ICP

Since the introduction of commercial instrumentation in 1975, inductively coupled plasma (ICP) emission spectroscopy has become the method of choice for the determination of metals in a wide variety of materials with applications covering most industries. The Central Scientific Laboratory (CSL) of Union Carbide Chemicals and Plastics Company, Inc., has been using ICP spectroscopy since 1976 as a tool for the routine analysis and problem solving related to cooling systems. Described are some of the methods that have been developed for the bulk analysis of coolants and deposits from many parts of the systems.

As a part of a problem-solving effort, laser ablation-ICP (LA-ICP) was used for spacial mapping of elements on the surface of water pump seal faces. This method proved to be useful and provided information used to complement data from other surface analysis methods.

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[1] Group leader, Union Carbide Chemicals and Plastics Company, Inc., Central Scientific Laboratory, 777 Old Saw Mill River Rd., Tarrytown, NY 10591.

[2] Manager, OEM & Technology Services, Corporate Fellow, First Brands Corp., Still River Corporate Park, 55 Federal Rd., Danbury, CT 06810.

Method

Detailed descriptions of emission spectroscopy and ICP emission spectroscopy, its main attributes, analytical considerations and spectrometer designs, have been published elsewhere [*1*,*2*]. However, a few major aspects of the method are worth mentioning here.

Emission spectroscopy is a method based on the detection and quantification of energy, emitted as photons, by the outer electrons in excited atoms and ions. Emissions from the excited species occur at the same time, thus, emission spectroscopy is inherently a simultaneous analytical method. In ICP emission spectroscopy, an argon (Ar) gas plasma is used as an excitation source. The high temperatures and electron densities of the plasma allow for the determination of all metals and some nonmetals, such as phosphorus (P), sulfur (S), and carbon (C). The polychromatic emissions from the source are dispersed with a grating and detected with photomultipliers. Spectrometers are available as sequential, simultaneous, or combination instruments.

Quantification is achieved by comparison with standards. In aqueous solutions, quantitative detection limits (ten times the standard deviation of the background), assuming no interferences are present, are in the range of 0.02 to 0.1 μg/mL, with a linear dynamic range of four to five orders of magnitude.

Spectral overlap is the major source of interferences in emission spectroscopy. It is caused by the inability of the spectrometers to resolve completely the large number of emission lines present in typical spectra. The extent of interferences depends on instrument resolution, line selection, and the elemental composition of the sample. Typical spectrometer software packages allow for empirical corrections by comparison with standards. This approach is satisfactory in most cases, however, the accuracy and detection limits for the interfered element are degraded. In cases where the interferences are severe or high accuracy is desired, a secondary emission line for the element of interest must be used. In some cases, a chemical separation must be performed before analysis.

Samples are generally introduced into the ICP source as a fine liquid spray. Solid materials, where bulk composition is of interest, must be dissolved before analysis. In special cases, samples have been introduced as slurries, powders, or gases [*3*]. In LA-ICP, a laser is used to ablate/vaporize small amounts of sample, which are then swept as a gas into an ICP source and, except for desolvation, undergo the same excitation processes as aqueous samples. Detailed descriptions of LA-ICP and analysis of selected materials have been published elsewhere [*3*,*4*].

In our laboratory, LA-ICP capability has been developed for the determination of trace (ppm) metal contaminants in refractory ceramics and electronic materials. This is necessary because conventional sample dissolution methods of these hard, refractory materials are prone to contamination from the grinding and the robust decomposition conditions. In addition, it is often necessary to analyze special "features" or determine elemental distributions on the surface of these materials, and this is not possible with bulk dissolution methods.

Experiment

All solution analyses were performed using a Jarrell-Ash Model 1100 polychromater also equipped with a 0.5-m Ebert monochromater, both operated at standard conditions (Table 1). Table 1 lists the laser operating conditions. All spectral interference corrections and data reduction were performed with in-house software, which has been described previously [*5*], however, it has undergone several revisions; details are available on request.

Developing LA-ICP required solutions to three problem areas: design of the sample cell,

TABLE 1—*Operating system.*

Operating System	Parameters
Polychromater	Jarrell-Ash Model 1100
grating	2400 Grooves/mm
entrance slit	25 μm
viewing height	16 mm above coil
Monochromater	Jarrell-Ash 0.5-m Ebert
grating	1180 Grooves/mm
entrance slit	25 μm
exit slit	25 μm
viewing height	16 mm above coil
Forward power	1000 W
Reflected power	<10 W
Torch sample uptake tube	Polyethylene tipped with sapphire
nebulizer	Jarrell-Ash Cross-flow
sample gas flow	1 L/min
coolant gas	18 L/min
Laser	Control Laser Model 512Q
wavelength	1064 nm
maximum (cw) power	50 W
Q switched mode	10–20-Hz rate

alignment of the target area with the laser, and calibration. The sample introduction system for conventional and LA-ICP analysis is shown in Fig. 1. The gas inlet provides tangential flow of Ar. The three-way valve allows for conventional introduction of solutions or gas from the sample cell. For target alignment, the sample cell can be moved vertically and the sample spoon can be moved horizontally or rotated.

A target locator was designed for the alignment of the spot to be sampled (target) with the laser. Two small telescopes, one with a pinhole and one with a slit image, were attached to the main laser tube at such angles that the images are coincident when the entire assembly is at the proper focal distance from the target. The laser focal spot is at the center of the point where the slit and pinhole images overlap. Alignment by eye with a resolution of approximately 0.1 mm is possible.

In conventional ICP, calibration is achieved by comparing the sample solution emission intensity to that of the standard solution. The same is true for LA-ICP if homogeneous solid standards are available, as in the case of glasses and alloys. Such standards are not available for ceramic materials. Semiquantitative analysis can be achieved by comparing ceramic samples with standard glasses or alloys. Alternatively, approximate emission intensity per microgram of an element can be calculated from solution analysis and compared to LA-ICP. In many cases, calibration is not vital because a simple empirical comparison of a "good" and "bad" sample or feature can also provide valuable information.

Results and Discussion of Solution Analysis

Analysis of Coolants

The sensitivity of the ICP technique allows direct determination of coolant additives and solubilized metallic corrosion products. The spectrometer is calibrated with aqueous standards, then the sample is diluted 50-fold and analyzed. Typical results are shown in Table 2.

Laboratory testing of experimental engine coolant formulations is performed in a controlled, closed-loop system, with specimens (usually aluminum or brass) of interest suspended

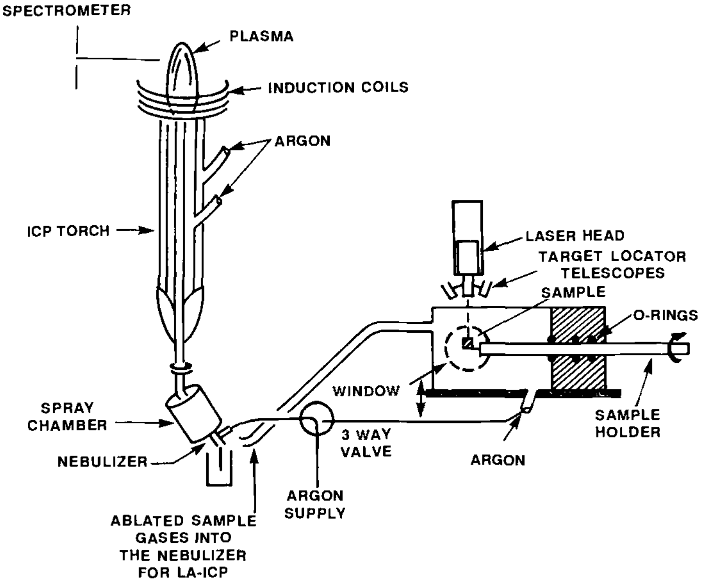

FIG. 1—*Conventional and LA-ICP sample introduction system.*

in the coolant. Performance evaluation is based on elemental analysis of used coolants and deposits. A mass balance is also obtained, and the surface elemental composition of specimens is determined by successive rinsing with nitric acid and potassium hydroxide. Typical results for the analysis of used coolants reflect changes in elemental concentrations as a function of time in use; these are shown in Table 3. The changes in the concentrations of silicon (Si), aluminum (Al), and calcium (Ca) in this coolant, as a function of testing time, are readily apparent. Water is the likely source of Ca. The concentrations of sodium (Na) and boron (B) remained constant. Typical results for the basic and acidic washing of a specimen are shown in Table 4. The analysis of deposits is described in the next section.

TABLE 2—*Typical coolant concentrate analysis.*

Element	μg/mL
Al	<3.00
B	708
Ba	<1.20
Ca	<0.60
Cu	<3.00
Fe	<3.00
Mg	<0.60
Mo	<3.00
Na	5990
P	1940
Pb	<6.00
Si	622
Sn	<12.0
Zn	<0.60
K	<6.00

TABLE 3—*Analysis of an experimental coolant formulation, soluble fraction. Concentration changes as a function of time in use.*

	Elements				
Sample	Si, μg/mL	Al, μg/mL	Ca, μg/mL	B, mg/mL	Na, mg/mL
Initial	132	<3	26.4	1.14	3.06
100 h	105	<3	12.9	1.13	3.03
200	66	<3	3.0	1.13	3.01
300	49	3.9	2.4	1.13	3.00
400	14	14.3	0.7	1.14	3.01
500	12	8.6	1.6	1.14	3.01
600	13	39	<0.6	1.13	3.01
700	12	31	1.3	1.12	2.99
800	12	30	1.3	1.11	3.00
900	11	20	2.4	1.17	3.15

In special cases, where better detection limits are needed, more concentrated coolant solutions can be analyzed. We have analyzed coolant solutions with ethylene glycol concentrations ranging from 10% to 100%. For these cases, the standards must be prepared in matching ethylene glycol concentrations. Detection limits on the order of 0.05 to 2 μg/mL were obtained. An example is the determination of lead (Pb), which is a toxic element, in used and treated coolants.

Analysis of Solids

Solid deposits recovered from different parts of cooling systems have been analyzed. The analysis of these materials is generally related to a problem-solving effort.

Many used coolants contain insoluble materials. These are separated from the coolant by centrifuging. The supernate is decanted, and the unwashed solids are dissolved in a loosely capped 15-mL polystyrene centrifuge tube. A mixture of 3:1:0.1 hydrochloric:nitric:hydrofluoric acids is used at approximately 90°C; digestion at higher temperatures may volatilize Si and B. In general, these solids have been found to contain one or more metals

TABLE 4—*Acid and base rinses of treated specimens.*

Element	KOH Rinse, μg/mL	HNO_3 Rinse, μg/mL
Al	85.4	1260
B	71.3	110
Ca	1.40	702
Cd	<0.20	2.23
Cu	90.4	975
Fe	18.8	63.7
Mg	<0.10	19.2
Mn	0.79	19.1
Na	229	170
Pb	124	138
Si	81.1	10.9
Sn	26.8	31.2
Zn	72.6	312
K	...	1.41

TABLE 5—*Unwashed insolubles in a used coolant—typical analysis.*

Element	μg/mL
Al	40
B	12
Ca	36
Fe	52
Cu	6.7
Na	120
P	79
Si	82
Zn	11.2
K	62

related to water quality, corrosion problems, solder components, or silicate dropout. Typical data are shown in Table 5.

Deposits from radiators, thermostats, water pump components, and filters have been analyzed. For bulk compositional analysis, these samples are generally solubilized by attack with mineral acids. Organic residue, if present, is eliminated by dry ashing at 450°C, or by digestion with nitric-perchloric acids.

Occasionally, only a small amount of sample is available for analysis; however, good sensitivity is possible. For example, dissolution of a 10-mg sample into 2 mL, the approximate minimum solution volume needed for a simultaneous spectrometer, results in detection limits in the range of 10 to 50 μg/g. Very small quantities of deposits have been removed by ultrasonic agitation or wiping with filter paper and subsequent leaching.

Data for the analyses of deposits from three different radiators are shown in Table 6. These results exhibit wide concentration ranges and elemental compositions typical of deposits. The concentration differences for such metals as Al, copper (Cu), tin (Sn), Pb, and zinc (Z) are important in ascertaining causes of system failures.

TABLE 6—*Radiator deposit analyses.*

Compound	Sample 1, %	Sample 2, %	Sample 3, %
Al_2O_3	44.3	14.9	15.6
B_2O_3	2.0	0.4	1.5
CaO	4.4	7.5	2.8
CuO	0.5	5.2	11.3
CdO	<0.004	<0.0004	0.036
Fe_2O_3	2.8	1.3	2.5
K_2O	0.5	<0.1	0.4
MgO	1.15	0.04	0.60
MnO_2	0.05	0.02	0.06
Na_2O	5.4	1.9	2.5
P_2O_5	0.4	<0.2	2.6
PbO	2.5	2.3	11.8
SiO_2	25.7	10.6	11.8
SnO_2	0.9	0.3	23.9
ZnO	0.7	1.3	6.6
% LOI 450°C	44	74	21

Results reported as oxide. Results corrected for loss on ignition (LOI) at 450°C.

TABLE 7—*Analysis of deposits on water pump seal springs.*

Element	Sample A, Total mg	Sample B, Total mg
Al	1.15	0.068
B	0.20	0.010
Ca	0.006	0.001
Cu	0.29	0.064
Fe	3.03	0.116
Mo	<0.001	0.092
Na	1.54	0.16
P	0.57	<0.01
Pb	0.15	0.16
Si	2.6	0.33
Sn	0.024	0.023
Zn	7.67	14.9
K	0.12	0.023

Data in Table 7 are for the analysis of deposits on springs of two failed water pump seals (Fig. 2). The deposit was removed by leaching the spring with 10% hydrochloric-hydrofluoric solutions. In each case, approximately 15 mg of material was leached, however, the elemental composition is different. The presence of Zn in the cooling system has been shown to be undesirable [6]. The different concentrations of molybdenum (Mo) and P are indicative of exposure to different coolant formulations.

LA-ICP

The amount of material that is ablated depends on the laser power, operating conditions, and sample characteristics. In general, conditions are adjusted to achieve a smooth ablation rate for the duration of lasing. For metals and alloys, approximately 1 to 10 μg of sample are ablated, whereas 200 to 300 μg are ablated from new alumina ceramics used in water pump seals. Typical ablation craters are shown in Fig. 3. Results for the bulk analysis of the alumina by conventional ICP and semi-quantitative LA-ICP are shown in Table 8.

During an investigation of premature water pump failures [6], alumina faces from good and failed seals were examined. As can be seen in Fig. 4, these faces have three distinct zones; the

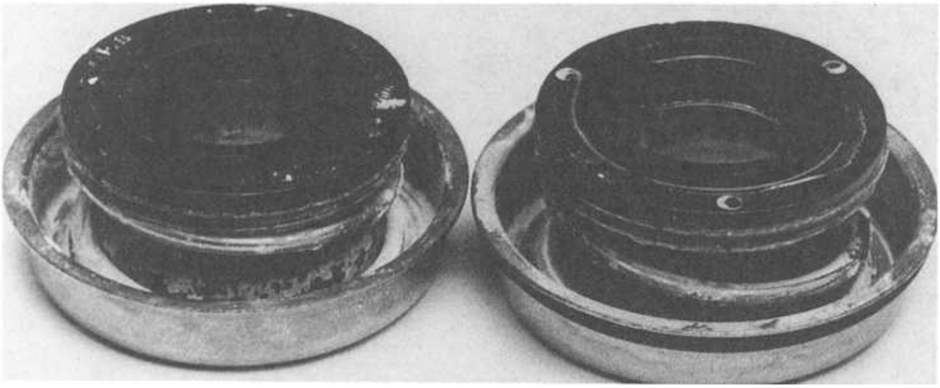

FIG. 2—*Deposits on exposed pump parts.*

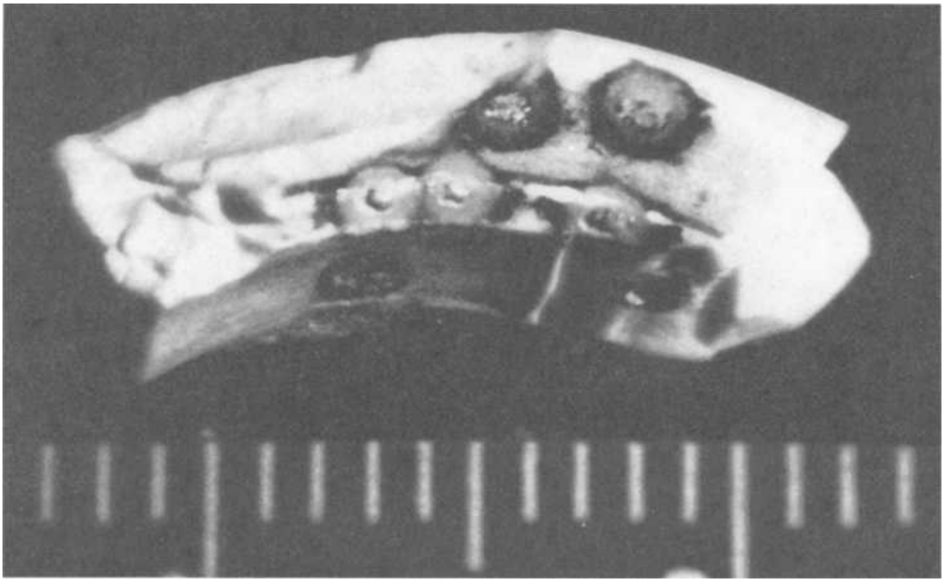

FIG. 3—*Typical ablation craters on alumina ceramic.*

coolant side, the sealing zone, and the air side. The bronze in the sealing zone is deposited from the phenolic-bronze stator face of the seal. Several surface analysis techniques were used to map the distribution of metals across the width of used ceramic seal faces; these included scanning electron microscopy/energy dispersive X-ray (SEM/EDX), electron spectroscopy for chemical analysis (ESCA), scanning auger microprobe/energy dispersive X-ray (SAM/EDX), and LA-ICP.

Data obtained from LA-ICP revealed that every failed ceramic face contained large concentrations of Zn and P in the sealing zone. It was ascertained that this relationship was not observed with other methods because of different sampling depths and location of the Zn/P layer.

TABLE 8—*Comparison of ICP and LA-ICP analysis of ceramic seal face material.*

Element Oxide	ICP, %	LA-ICP, %
Al_2O_3	85.8	Major
BaO	0.57	1.1
CaO	1.27	0.9
Cr_2O_3	0.13	0.03
CuO	0.017	0.017
Fe_2O_3	0.23	0.20
MgO	2.14	3.2
Na_2O	0.14	1.3*
SiO_2	7.8	Major
TiO_2	0.12	0.16
ZnO	0.01	0.01

* Contamination of real enrichment of sodium on the surface.

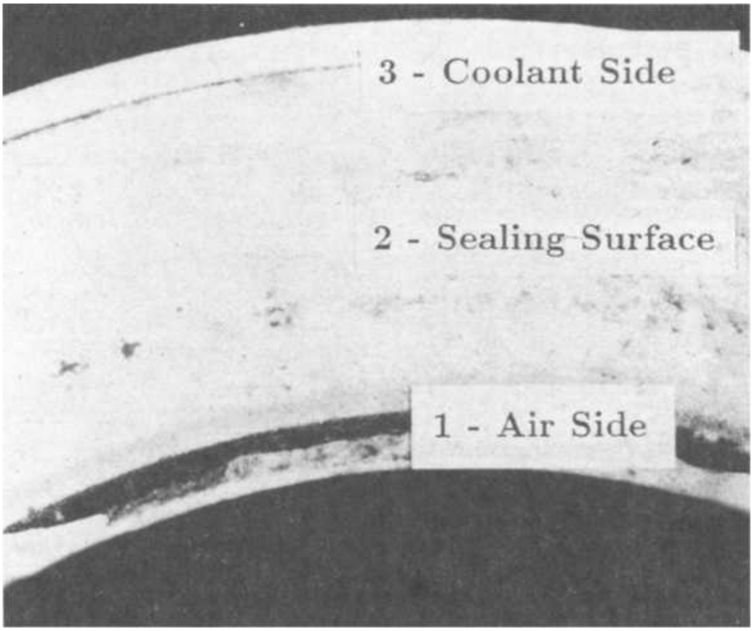

FIG. 4—*Ceramic seal surfaces. Areas analyzed by LA-ICP.*

Lasing of bronze deposits on alumina is akin to ablating metals. Small amounts of material were ablated with a sampling depth of 100 to 500 nm, the apparent depth of the Zn/P layer on these samples. Due to extreme surface sensitivity, 1 to 5 nm, ESCA detected approximately the same concentrations of coolant and bronze components on all faces. Although some Zn was detected by SEM/EDX, its concentration appeared to be minor. It was determined that the Zn signal was "diluted" by contributions from the ceramic base, which was sampled due to the 1000 to 5000-nm SEM/EDX sampling depth. From these data, the film thickness is estimated to be about 100 to 500 nm. The LA-ICP results were instrumental in determining the cause of premature water pump seal failures. These data are summarized in Table 9.

TABLE 9—*LA-ICP analysis of "good" and "failed" ceramic seals, sealing zone.*

	Relative Concentration			
Samples	P	Cu	Sn	Zn
"Good"				
Seal 1	8	68	11	13
Seal 2	2	78	13	7
Seal 3	3	66	25	7
Seal 4	9	66	19	7
Seal 5	8	73	12	8
"Failed"				
Seal 1	21	5	7	66
Seal 2	55	3	12	30
Seal 3	9	13	13	65

Other uses of LA-ICP in our laboratory have included the analysis of silicon carbide pump seals and radiator hoses. The expected coolant components and some Zn were detected on the carbide faces. However, no correlation with performance could be established. New radiator hoses were found to be a potential source of Zn contamination.

Conclusions

With appropriate decomposition methods, ICP emission spectroscopy is a tool for the rapid determination of metals in engine coolants and other components of cooling systems. The method is especially useful with a limited sample size or as a part of a problem-solving effort.

The use of laser ablation for sample introduction into an ICP source allows for quick empirical or semiquantitative analysis of refractory ceramics and metallic films. This was especially important here because the 100 to 500-nm sampling depth of LA-ICP is not readily available with other surface analysis methods.

Acknowledgments

The authors would like to thank Dr. J. N. Pike for his assistance in setting up the laser ablation system.

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DISCUSSION

W. D. Berg[1] *(written discussion)*—From your ICP results, how do you go about determining the oxide form of each element, as your data indicated? More specifically, can ICP provide you with CuO and CuO_2 level from a simple analysis of copper?

Walter Zamechek (author's response)—ICP results reported as oxides, were simply calculated as oxides and do not suggest that the elements are present as such. Perhaps Table 6 should have a statement that reads "reported as oxides." Only elemental concentrations can be determined by ICP. The results for the deposits were reported as oxides in order to facilitate mass balance calculations. If compound identification is required, X-ray diffraction or classical chemical methods can be utilized.

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[1] Mobay Corp., Mobay Rd., Bldg. 14, Pittsburgh, PA 15205.

Peter M. Woyciesjes[1]

The Chemistry of Oxalic Acid Cleaning of Engine Cooling Systems

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REFERENCE: Woyciesjes, P. M., **"The Chemistry of Oxalic Acid Cleaning of Engine Cooling Systems,"** *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 190–204.

ABSTRACT: Engine coolant candidates undergo a progression of tests to evaluate various physical properties and performance characteristics. Key to this test progression is the evaluation of the coolant in vehicles. It serves as the final check point, tieing together the results of the other various tests. In the fleet test, the corrosion protection and performance characteristics of an engine coolant are evaluated under actual use conditions.

The methodology used in testing a coolant in a passenger car or a light duty truck is critical. ASTM Practice for Testing In Car and Light Truck Service (D 2847) serves as an industry accepted standard for evaluating coolants in vehicles. This standard provides a full discussion of testing protocol.

Sections 9.3 and 9.4 of ASTM D 2847 outline the cooling system cleaning and conditioning procedures. These sections stipulate the use of oxalic acid as a chemical cleaner followed by a borate buffer conditioning fluid. The purpose of these two steps are (1) oxalic acid cleaning removes inhibitors, rust and other deposition from the cooling system, and (2) borate conditioning fluid removes excess oxalate to leave a conditioned surface in the cooling system which is neither detrimental nor beneficial to the performance of the coolant to be evaluated.

The ASTM Committee D-15 on Engine Coolants is reconsidering the use of oxalic acid cleaner in the automotive cooling system. Concerns have been raised regarding potential carryover effects oxalic acid could have on the performance of a coolant.

This paper reviews the chemistry of the oxalic acid cleaner as well as discusses the effects that oxalic acid cleaning has on the cooling system surfaces and its potential carryover effects to the test coolant. An understanding of the chemistry of oxalic acid is crucial in judging its efficacy as a cleaner to bring cooling system surfaces of a test vehicle to a reproducible base condition before performance testing.

KEYWORDS: oxalic acid, vehicle testing, oxalate, iron oxalate, borate conditioner, antifreeze testing

Today's engine coolants are formulated to meet a variety of requirements. Although its primary function is to transfer heat from the engine to the radiator for dissipation, there are other important corrosion inhibition and freeze point properties that the coolant must exhibit to be fully functional. The ASTM Specification for Ethylene Glycol Base Engine Coolant for Automotive and Light Duty Service (D 3306) outlines certain minimum physical, chemical, and performance requirements that all ethylene glycol base engine coolants must meet.

The physical and chemical requirements have been developed around the use of ethylene glycol as the coolant base. All major commercial ethylene glycol base coolants meet these standards.

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[1] Group leader, Coolant R&D, First Brands Automotive R&D Laboratory, 55 Federal Rd., Danbury, CT 06810.

In terms of performance requirements, ASTM D 3306 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. ASTM D 3306 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 performance. A well designed development program structured initially around the tests outlined in ASTM D 3306 provides the coolant scientist with minimum performance requirements to evaluate a test coolant against and 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. Given the time, effort, and cost that must be expended to run a fleet test, it is imperative that the fleet test be well designed, maintained, and controlled.

ASTM Practice for Testing Engine Coolants in Car and Light Truck Service (D 2847), provides a procedure for evaluating the corrosion protection and performance of an engine coolant in passenger cars and light trucks. As part of the pre-test preparation procedure, both the engine and cooling system are checked to ensure integrity. Before initiating the coolant test, it is desirable to remove inhibitors and resulting deposits and establish a reproducible, conditioned surface on the cooling system components. The current cleaning (Section 9.3) and conditioning procedure (Section 9.4) recommends the use of oxalic acid ($H_2C_2O_4$) followed by a low pH borate conditioner (Annexes A.3). This paper discusses some concerns that should be addressed when cleaning with oxalic acid.

Background

The ability to run a well controlled, statistically significant fleet test is, in part, dependent upon being able to control the variables (the vehicle and cooling system history, operating conditions, test procedures, and so forth) introduced into the test.

A brief summary of the cleaning and conditioning steps as outlined in ASTM D 2847 is as follows: First, drain the cooling system of its coolant and flush the system with water. The system should then be drained of any remaining water and refilled with water. Oxalic acid is added to the system, and the engine started. The engine is run for 1 h after the thermostat has opened to allow the hot oxalic acid solution to circulate throughout the cooling system. The system is drained and water flushed to remove residual oxalic acid and reaction products. The system is drained and a 50% solution of the low pH borate conditioning coolant is installed. The conditioning fluid remains in the system for one week or 1125 km (700 miles).

The oxalic acid reacts with the metal surfaces it comes into contact with during the cleaning procedure, removing residual rust and deposits. The water flushing removes most of the oxalic acid and its reaction products. Some of the oxalic acid, however, will react with the ferrous metals to form an insoluble species, which is not always removed completely in the subsequent conditioning and flushing steps. As a result, it will be shown that at high concentrations the oxalate species can have a negative effect on the performance of the test coolant which follows.

Chemistry of Oxalic Acid

Oxalic acid is one of the oldest known acids and for many years has been used extensively as a precipitating and chelating agent. The oxalate ion, $C_2O_4^{-2}$, functions as a bidentate ligand with the formation of the five-membered chelate ring. Simple or complex oxalate compounds, or both, are known for most of the metals on the periodic table [1]. Except for the alkali metals, most simple oxalates are insoluble in water. However, all oxalates dissolve in acids and most dissolve in excess oxalate to form complexes. For instance, the solubility of lead oxalate, PbC_2O_4, increases linearly with excess oxalate ion concentration [2], which is indicated by the formation of $Pb(C_2O_4)_2^{-2}$.

During the cleaning step, the oxalic acid will react with the surfaces with which it comes in contact, removing inhibitors and deposits. Oxalate has been shown to form a variety of complexes with the metals typically found in an automobile's cooling system (for example, aluminum, iron, copper, and lead (Table 1).

Cooling System Chemistry

Most engines today employ a cast iron block, and either a cast iron or aluminum cylinder head. Depending on the history of the engine, the condition of the cooling system surfaces can be quite different from one vehicle to another. The reactions that occur on each surface will, in part, be dependent on its history. This paper discusses the chemistry of the cast iron surfaces that can result from the oxalic acid cleaning and borate conditioning steps.

It has been shown that during normal use the metals in the cooling system can be corroded by direct chemical attack or by electrochemical processes, either galvanic when dissimilar metals are electrically coupled, or local-cell action between anodes and cathodes on the surface of a single metal [3].

Local cell action on an iron surface in a neutral or alkaline environment is represented by the following equations

$$2Fe^0 \rightarrow 2Fe^{+2} + 4e^- \qquad (1)$$
$$4e^- + 2H_2O + O_2 \rightarrow 4(OH)^- \qquad (2)$$
$$2Fe^{+2} + 4(OH)^- \rightarrow 2Fe(OH)_2 \qquad (3)$$
$$2Fe(OH)_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow 2Fe(OH)_3 \qquad (4)$$

Equations 1 through 4 provide a path by which iron dissolves at the local anode, and electrons, e^-, flow within the metal to a cathodic area of the same metal surface. Oxygen and water accept

TABLE 1—*A listing of several common metal oxalate complexes that could be formed as the result of oxalic acid cleaning an automobile's cooling system* [10].

Oxalate Compound	Color	Solubility in[a]	
		Cold Water	Hot Water
$Al_2(C_2O_4)_3 \cdot 4H_2O$	white	insoluble	insoluble
CaC_2O_4	colorless	0.00067	0.0014
$CaC_2O_4 \cdot H_2O$	colorless	insoluble	insoluble
$CuC_2O_4 \cdot \tfrac{1}{2}H_2O$	bluish white	0.00253	...
$FeC_2O_4 \cdot 2H_2O$	pale yellow	0.022	0.026
$Fe(C_2O_4)_3 \cdot 5H_2O$	yellow	vs	vs
PbC_2O_4	white	0.00016	...
$ZnC_2O_4 \cdot 2H_2O$	white	0.00079	...

[a] vs = very soluble. All oxalate complexes dissolve in acids, and most of them in excess oxalate to form complexes [1].

the electrons to produce hydroxyl ions, OH^-. The hydroxyl ions react with the dissolved iron to produce insoluble ferrous hydroxide, $Fe(OH)_2$, which can be further oxidized to ferric hydroxide, $Fe(OH)_3$.

The hydrolysis of ferric solutions with sodium hydroxide solutions develops with the formation of dimer iron complexes, $[(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{+4}$, followed by a series of polynuclear complexes. When these complexes are sufficiently large in size, coagulation takes place and an amorphous gel-like precipitate of ferric hydroxide is formed.

There are a number of iron oxides that are important to iron chemistry (Table 2). The iron oxides formed in a cooling system depends on the local environment. Certain differences appear to exist between iron oxides formed in water and glycol solutions.

The iron oxides formed in a car with 100% water as the coolant shows Fe_3O_4, gamma-Fe_2O_3, and gamma-$Fe_2O_3 \cdot H_2O$ on the surfaces. These three oxides and alpha-$Fe_2O_3 \cdot H_2O$ are found also in solution. The oxides formed, appear to be larger and more crystalline in nature when compared to those formed in a car containing a 50% ethylene glycol solution [*4*].

In the earlier study [*4*], the surface oxide formed in a car containing ethylene glycol coolant solution consists of gamma-Fe_2O_3 and Fe_3O_4 with Fe_3O_4 and gamma-Fe_2O_3 in solution. In a latter study [*5*], the iron oxides formed in cars with neglected ethylene glycol antifreezes were found to be predominately Fe_2O_3 with small amounts of FeO. In both glycol studies, the oxide particles formed are smaller than those in cars run with 100% water, and are often accompanied by amorphous material. The oxalic acid will be added to this environment.

Titration of an Automobile's Cooling System

In order to develop a better understanding of the effect the oxalic acid cleaner has on the cooling system a titration of a vehicle's cooling system that had been oxalic acid cleaned was carried out using measured caustic additions. A Chevrolet Impala with a cast iron engine was conditioned using the following procedure: (1) drain the cooling system and water flush, (2) pre-rust for 2 h with a dilute acetic acid solution, (3) water flush, (4) oxalic acid clean for 1 h,

TABLE 2—*Listing of some common forms of iron oxide* [4,10].

Iron Compound	Crystal Structure	Color	Comments
FeO	cubic	blue, black	frequency of occurrence not clear
FeO(OH)	. . .	brown	when heated to 200°C forms alpha-Fe_2O_3
$Fe(OH)_2$	hexagonal	pale green	oxidizes and darkens quickly in air
$Fe(OH)_3$	. . .	reddish-brown	not stable, converts to hydrous oxide
gamma-$Fe_2O_3 \cdot H_2O$	orthorhombic	light brown to yellow	abundant constituent of ordinary rust
alpha-$Fe_2O_3 \cdot H_2O$	orthorhombic	yellow	generally found associated with gamma-$Fe_2O_3 \cdot H_2O$, but in minor quantities
$Fe_2O_3 \cdot xH_2O$	amorphous	red-brown	hydrated Fe_2O_3
gamma-Fe_2O_3	cubic	often reddish	diffraction lines similar to those of magnetic iron oxide
alpha-Fe_2O_3	rhombohedral	reddish brown	frequently produced at elevated temperatures
Fe_3O_4	cubic	black	magnetic iron oxide

(5) water flush, and (6) drain the system and fill with distilled water and allow the system to come to equilibrium, approximately 16 h. At this point, the titration of the car's cooling system was initiated.

The car was started each morning at approximately 8:15 am and allowed to warm up for 30 min. 1 mL of a 50% by weight sodium hydroxide solution (NaOH, 50%) was added directly to the cooling system every 45 min until approximately 4:00 pm. The car was then turned off and allowed to sit overnight. Before each addition, a sample was taken from the system for analysis. Over the course of 4 days the pH, RA, and oxalate levels were monitored. The titration profile of the oxalic acid cleaned vehicle is shown in Fig. 1.

The initial pH of the water in the system is slightly acidic. It is clear from the titration profile that the cooling system is behaving in a manner characteristic of a buffered system between pH 7.0 and 8.0. The addition of base has very little effect on the pH of the system in the pH region <8.0. However, at a pH >8.0, only a small amount of additional base is required to significantly increase the pH of the solution.

In addition to the titration curve, a profile of pH versus oxalate level was plotted (Fig. 2). The two profiles can almost be superimposed, suggesting that the pH and oxalate levels are closely related. Furthermore, this chemistry occurs at a pH >8.0. This can easily be seen from a plot of oxalate level versus NaOH addition (Fig. 3). The soluble oxalate level starts out at zero and increases linearly with the addition the NaOH. The increase closely corresponds to a 2:1 molar ratio of NaOH to oxalate. Only at higher levels of NaOH, at a pH $>$ 8.0, is there any appreciable deviation of the experimental line away from the theoretical 2:1 molar ratio line.

This 2:1 molar ratio is consistent with the bidentate coordination chemistry of oxalate discussed earlier. These results support the idea that the oxalic acid reacts with the iron surfaces to form an insoluble ferrous oxalate ($FeC_2O_4 \cdot 2H_2O$) film. This species then behaves as a pseudo buffer between a pH range of 7.0 and 8.0. The addition of a high pH fluid, engine coolant, or as in this case NaOH, will react with the residual ferrous oxalate in a 2:1 molar ratio to free oxalate from the surface and results in the consumption of base and lowering of

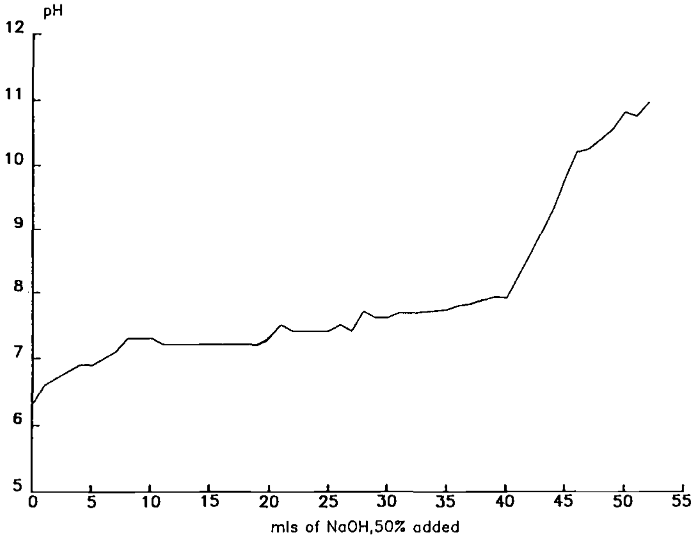

FIG. 1—*Titration of the cooling system of a Chevrolet Impala that has been oxalic acid cleaned.*

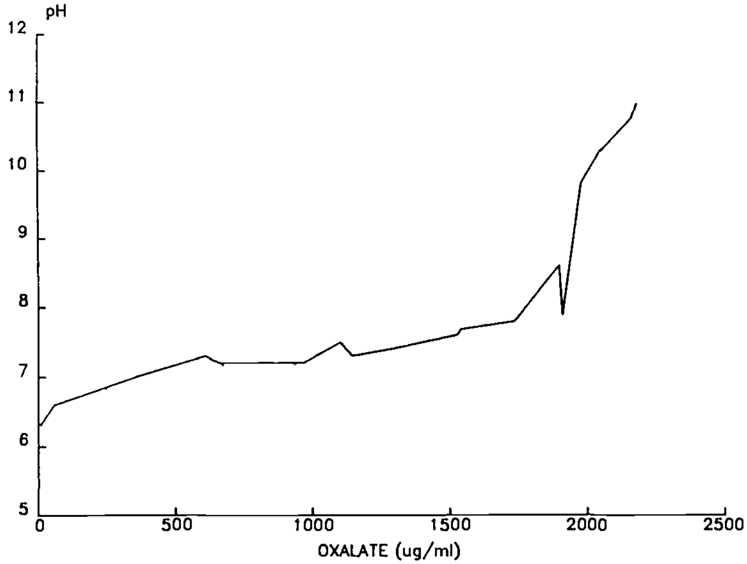

FIG. 2—*Results from the titration of a Chevrolet Impala: oxalate level as a function of pH.*

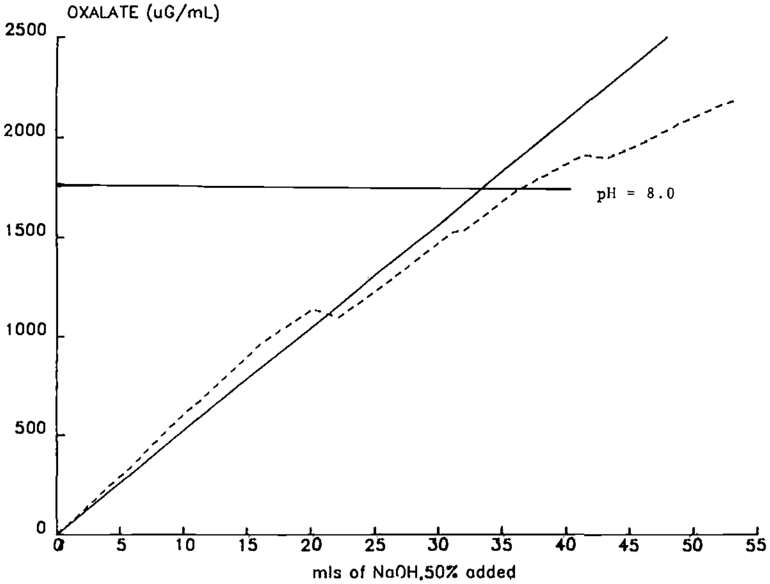

FIG. 3—*Plot of milliliters titrant (NaOH, 50% by wt) versus the appearance of oxalate in solution. (—) theoretical line, 2:1 NaOH to oxalate mole ratio; (- - -) experimental line, NaOH to oxalate.*

the pH and RA of the solution. The magnitude of the pH and RA drop will be dependent on the amount of ferrous oxalate present in the system.

The Formation of Iron Oxalate

To develop a better understanding of the chemistry involved with the oxalic acid cleaning step, it is necessary to characterize the actual species formed on the iron surface. Of particular interest are the oxalate complexes that might form in a cast iron system treated with oxalic acid. Two common forms of iron oxalate have been reported in the literature: ferrous oxalate ($FeC_2O_4 \cdot 2H_2O$) and ferric oxalate ($Fe_2(C_2O_4)_3 \cdot 5H_2O$). They can be formed directly by reaction of oxalate solutions with iron oxide.

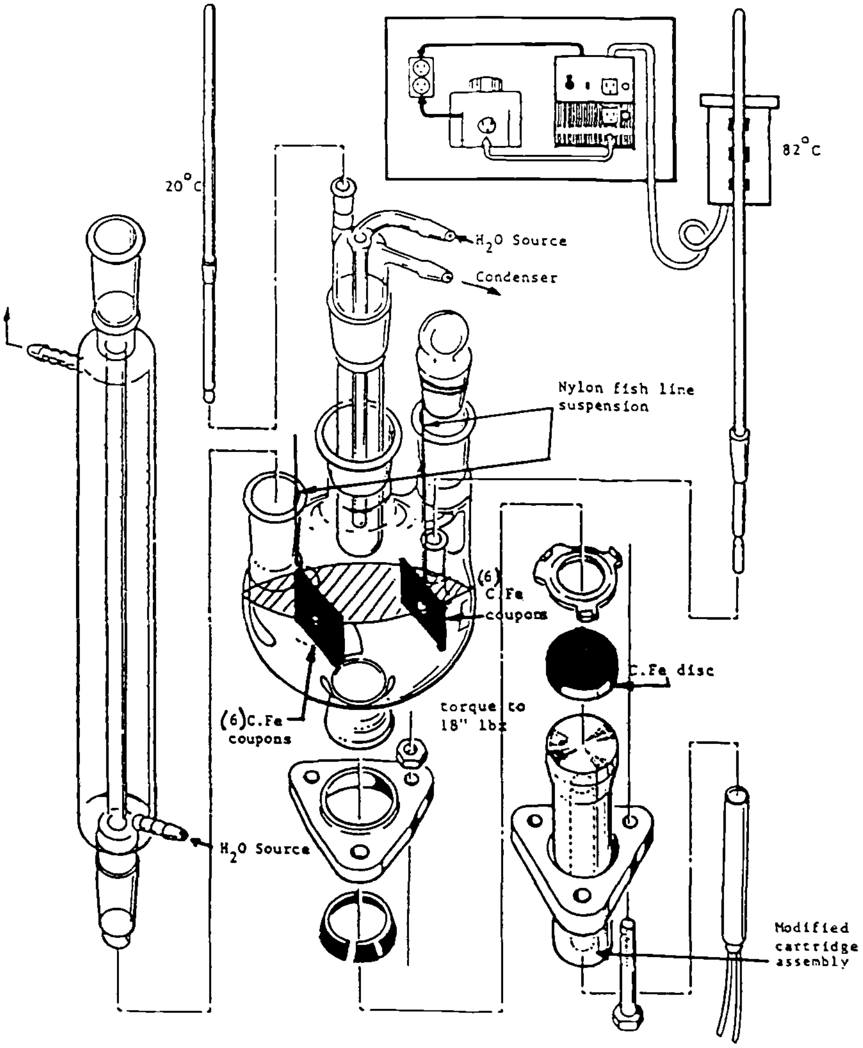

FIG. 4—*Heat flux test assembly.*

In automobiles oxalic acid will react with the cast iron and steel surfaces of the cooling system as well as with any iron oxide deposits that might have accumulated in the system. It was shown in earlier studies [*4*] that cleaning a cast iron automobile engine with oxalic acid can result in the formation of ferrous oxalate on the walls of the cooling system.

Work was undertaken in the laboratory to confirm this result and to determine the effect of the conditioning with low pH borate solution on this film. A test [*6*] utilizing a series of heat rejecting and accepting gray cast iron specimens was undertaken (Fig. 4). The test was run as follows: the metal specimens were oxalic acid cleaned for 2 h at 82°C (Fig. 5), conditioned with borate at 82°C for 24 h and exposed to a fresh fill of a standard 50% engine coolant solution at 82°C for 1 week. Samples taken before the oxalic wash and after each subsequent step were examined by optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), auger electron spectroscopy (AES), and energy dispersive X-ray analysis (EDX) [*7*]. Emphasis was placed on characterizing the heat rejecting surfaces.

The most notable result from the X-ray diffraction work is that a heavy layer of ferrous oxalate ($FeC_2O_4 \cdot 2H_2O$) forms on both the heat rejecting and heat accepting cast iron surfaces washed with oxalic acid. Cross-sectional SEM micrographs show the ferrous oxalate on the heat rejecting specimen is often in excess of 10 μm thick. The surface appears patchy with thin spots in areas (Fig. 6).

These results are in agreement with work done by Laudere et al. [*8*]. They investigated the reaction of a 5% aqueous solution of oxalic acid with products of iron corrosion. Synthetic Fe_3O_4 and gamma FeO(OH) were treated with oxalic acid, and the course of dissolution was followed by X-ray diffraction. Crystals of oxalic acid and $Fe_2(C_2O_4)_3 \cdot 5H_2O$ were isolated from the liquid phase and solid gamma-FeO(OH) from the reaction of gamma FeO(OH) with oxalic acid (Eq 5).

$$FeO(OH)(s) + H_2C_2O_4 \rightarrow Fe_2(C_2O_4)_3 + H_2C_2O_4 + FeO(OH)(s) \qquad (5)$$

The reaction of Fe_3O_4 with oxalic acid yielded Fe_3O_4 and $FeC_2O_4 \cdot 2H_2O$ in the solid phase. Crystals of oxalic acid, $Fe_2(C_2O_4)_3 \cdot 5H_2O$ and $FeC_2O_4 \cdot 2H_2O$, were isolated from the liquid phase (Eq 6).

$$Fe_3O_4(s) + H_2C_2O_4 \rightarrow Fe_3O_4(s) + FeC_2O_4 \cdot 2H_2O(s) + H_2C_2O_4 + Fe_2(C_2O_4)_3 \cdot 5H_2O \qquad (6)$$

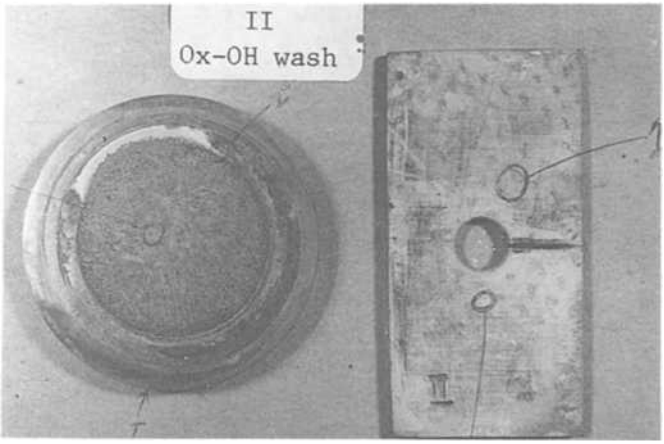

FIG. 5—*The heat-rejecting iron disk and heat-accepting iron coupon after cleaning with oxalic acid.*

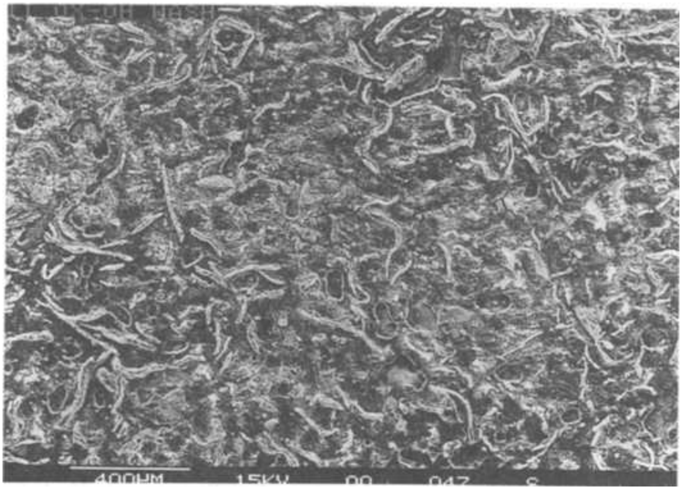

FIG. 6—*SEM micrograph (× 50) of the oxalic acid cleaned surface of the heat-rejecting cast iron disk.*

Oxalic acid reacts with the iron surfaces to form the slightly soluble ferrous oxalate dihydrate and the soluble $Fe_2(C_2O_4)_3 \cdot 5H_2O$. In practice, as a result of the cleaning procedure $FeC_2O_4 \cdot 2H_2O$ will be left behind as a film on the walls of the cooling system while the soluble $Fe_2(C_2O_4)_3 \cdot 5H_2O$ species is washed out of the system by the subsequent water flushing steps.

Following the borate conditioning step, the surface topography is more patchy, indicating partial removal of the iron oxalate (Fig. 7). XRD shows that the iron oxalate deposits remaining behind on the heat rejecting and accepting specimen appear to have been converted to calcium oxalate, $CaC_2O_4 \cdot H_2O$. Auger analysis of the heat-rejecting surface reveals iron, oxygen, and calcium together with lesser amounts of sodium, boron, and carbon. This is consis-

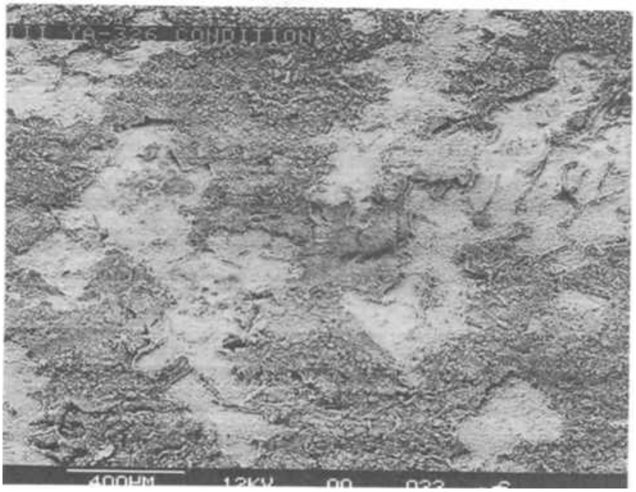

FIG. 7—*SEM micrograph (× 50) of the heat-rejecting cast iron disk surface following the 24-h treatment in the borate conditioner.*

tent with the formation of calcium oxalate with some deposits of sodium borate, $Na_2B_4O_7$. Iron oxides are also present. It is apparent from this work that the borate conditioning step does not remove all of the oxalate from the metal surfaces.

XRD shows that after one week exposure to a 50% solution of fully formulated coolant, oxalate species are no longer present on the heat rejecting or accepting metal surfaces. The only major component shown by XRD on the heat-rejecting surface was gamma-Fe_2O_3. The heat-accepting surface has a relatively thin layer of material present. It cannot be identified by XRD because of its noncrystalline nature. The heat-rejecting surface also contains some noncrystalline material, which is masked by the dominant gamma-Fe_2O_3 X-ray pattern. AES and EDX spectra suggest that the underlying bulk consists mostly of Fe_2O_3 with a thin upper film containing silicon, magnesium, oxygen, calcium, carbon, and phosphorous. This suggests an upper film made up of silicate and phosphate, which are the inhibitors present in the coolant.

These results are consistent with the findings reported above, which describe the formation of gamma-Fe_2O_3 in ethylene glycol coolant solution. The absence of Fe_3O_4 could be a result of differences in the length of exposure to the coolant or the starting condition of the surfaces, or both. In both examples, the presence of an amorphous or noncrystalline material was detected.

Fleet Test Results

A reasonable question to ask at this point is: "Will there be any carry over effect from the oxalic acid cleaning on the performance testing of the coolant which follows?" In a fleet test [*9*] of 33 Ford Econoline 150 vans with 300 CID (4.9-L) six cylinder cast iron engines, which were oxalic acid cleaned and conditioned according to D 2847, there were pronounced differences in the performance of the test antifreezes depending on the starting mileage of the test vehicles. The fluids' performances were seriously impaired when tested in high mileage vehicles. As can be seen in the 24 140-km (15 000-mile) specimen weight loss for fluids A&B (Table 3), the weight losses were greater in the vehicles having the higher starting mileage. The same trend holds for the other three coolants tested, with emphasis on aluminum, cast iron, and solder weight losses.

TABLE 3—*24 140-km (15 000-miles) Ford Econoline fleet test results. The average (of 2) metal specimen weight loss data (mg/specimen) for Fluids A and B.*

Initial Mileage	Oxalate[a] Level, ppm	Modine Solder	Copper	ASTM Solder	Brass	Steel	Cast Iron	Cast Al
			EXPERIMENTAL FLUID A					
2 433	230	41	32	17	24	6	1	10
62 835	. . .	125	19	283	10	10	24	22
79 585	865	261	13	482	16	54	95	37
82 890	. . .	208	12	465	12	95	44	32
99 189	972	160	4	358	7	83	36	36
			EXPERIMENTAL FLUID B					
2 982	110	67	34	22	25	5	8	6
3 167	287	31	23	18	22	11	1	7
72 850	606	160	16	361	14	16	62	24
101 744	801	186	16	464	22	74	62	28
135 003	950	96	16	306	15	46	27	27

[a] Oxalate levels were measured at 16 093 text km (10 000 test miles).

Analysis of the 16 093-km (10 000-miles) solution data showed significant correlations between the RA(Linde)[2] drop, starting odometer mileage and soluble oxalate level in the antifreeze solution. The correlation between starting mileage and oxalate is fairly good for each fluid, R^2 = 0.9965, 0.9662, 0.9252, 0.4180, and 0.4263 for fluids A–E, respectively. This supports the theory that the higher the starting mileage the higher the oxalate level. In Table 3, the metal specimen weight loss has not been negatively affected for the lower mileage vehicles (<4000 miles) with low oxalate levels. However, the specimen weight loss data obtained in the higher mileage vehicles has been negatively biased by the oxalic acid cleaning step. The composite correlation for fluids A–E of starting mileage versus oxalate level appears to hold, R^2 = 0.6400, although there is more scatter in the data. This is due, in part, to differences in the test coolants and the prior history of the cooling system. Figure 8 gives a composite plot of the fleet test results for five different test fluids, A–E.

It is proposed that oxalate enters the system as a result of the oxalic acid cleaning step. An insoluble layer of ferrous oxalate is formed in the cooling system, which is not washed out in the subsequent flushing steps, and is not always completely cleaned out with the low pH borate conditioning solution. This residue of ferrous oxalate appears to be the reason for the larger than usual drop in RA and pH and may be responsible for the large drop in some of the coolant's inhibitors. Regression analyses of the starting miles versus RA(Linde) drop (Fig. 9) and oxalate versus RA(Linde) drop (Fig. 10) show that there is a stronger correlation between the oxalate level and RA(Linde) drop than the starting miles versus the RA drop; R^2 = 0.4985 versus 0.2816, respectively. The magnitude of the RA drop appears to be related to oxalate

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[2] Reserve Alkalinity (Linde) is equivalent to RA(ASTM) for a 33% by volume solution. It is a way of expressing the RA for fixed EG-water solution. It provides a way of comparing RAs directly. The RA of any fluid can be converted to RA(Linde) using the following equation: RA(Linde) = RA(ASTM) * 330/ % by volume ethylene glycol in the sample. It is defined as the number of millilitres of 0.1 N HCl required to titrate 100 mL of a 33% by volume solution of antifreeze to a pH of 5.5.

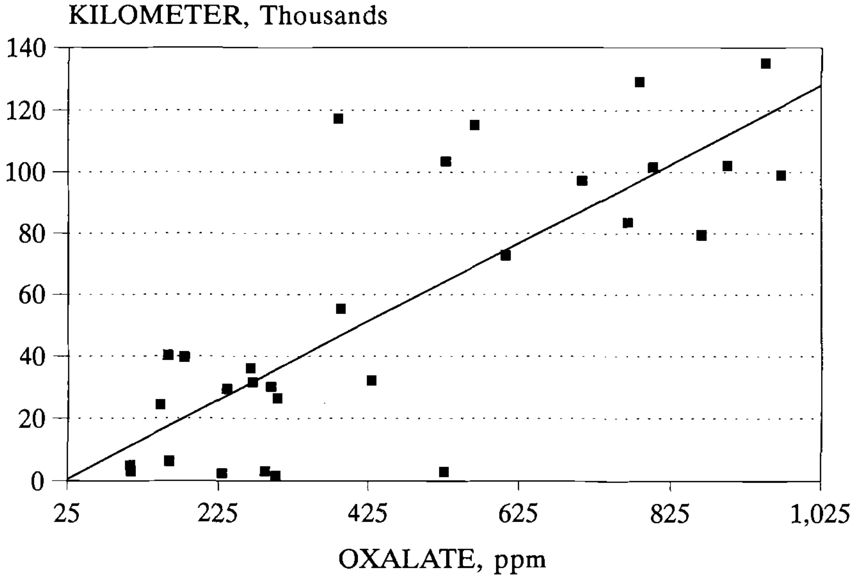

FIG. 8—*Oxalate level as a function of starting mileage for Ford Econoline fleet test, at 16 092 test km (10 000 test miles).*

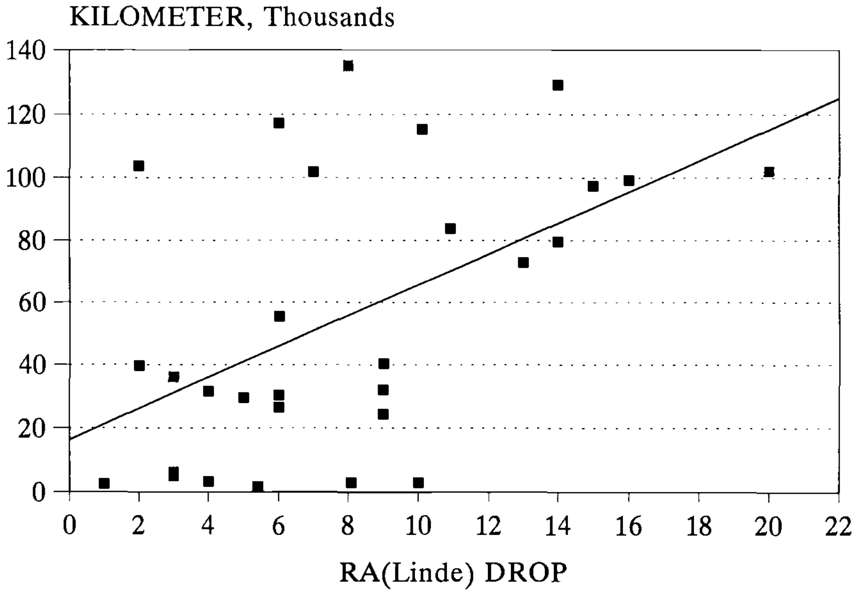

FIG. 9—*RA(Linde) drop as a function of mileage for Ford Econoline fleet test, at 16 092 test km (10 000 test miles).*

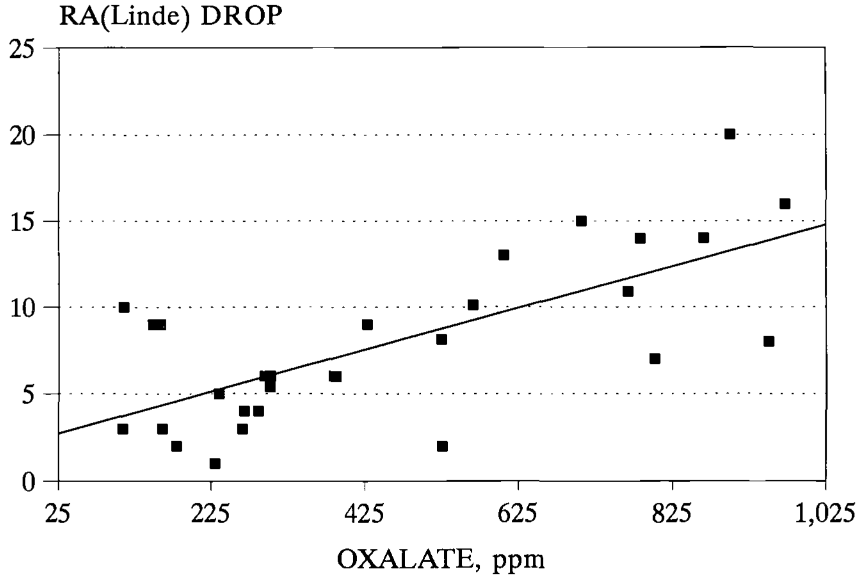

FIG. 10—*Oxalate level as a function of RA(Linde) drop for Ford Econoline fleet test, at 16 092 test km (10 000 test miles).*

concentration (Fig. 10). However, it is apparent from the magnitude of R^2 that there are other variables that contribute to the RA drop, such as ethylene glycol degradation and corrosion processes.

Alternative Conditioning Procedure

From the data presented here it is apparent that oxalic acid cleaning of a vehicle's cooling system can leave behind an insoluble film of ferrous oxalate that is not adequately removed in subsequent flushing and conditioning steps. Although oxalic acid is an effective cleaner, the residual ferrous oxalate can bias the subsequent test. It is necessary to find a way to remove this film with a conditioning step.

As noted above, the current borate conditioning step is not always effective in removing the oxalate film. The car titration showed the iron oxalate film buffers in the same range as the conditioner, and that only at higher pH, >8.0, is the oxalate cleaved from the surface. It is theorized that a higher pH version of the borate conditioner should remove the residual oxalate more efficiently.

Table 4 shows the oxalate levels for a fleet of 1989 Grand Am's equipped with 2.3-L Quad-4 engines. The engine consists of a cast iron block and aluminum head. All the test vehicles had accumulated approximately 48 280 km (30 000 miles) on a previous antifreeze/coolant test. The vehicles were cleaned and conditioned following D 2847 procedures, except that a pH 10.0 borate solution was used in the conditioning step in place of the low pH borate conditioner specified in the standard. In all cases the oxalate levels in the test vehicles were low, and the vehicles did not experience a large initial drop in pH or RA. It appears that the higher pH conditioner was effective in removing the oxalate from the cooling system surfaces. As can be seen in Table 5, the metal specimen weight loss data for these vehicle have not been affected by the oxalate cleaning. The values are similar in magnitude to the low mileage vehicles listed in Table 3.

At the end of the second 48 280 km (30 000 miles) test, six of the vehicles were cleaned and

TABLE 4—*Oxalate levels form the Grand Am fleet test as a function of test mileage.*

	Fleet Test 1			Fleet Test 2		
Test Vehicle	Initial, km	Oxalate Level, ppm At x Test km		Initial, km	Oxalate Level, ppm At x Test Miles	
846	53 440	31	24 140	. . .	. . .	. . .
		36	48 280	. . .	. . .	. . .
856	51 452	15	24 140	100 993	19	8 047
		15	48 280			
858	51 909	14	24 140	102 660	86	8 047
		. . .	48 280			
860	51 727	. . .	24 140	101 406	134	8 047
		43	48 280			
862	51 752	32	24 140			
		. . .	48 280			
864	51 850	15	24 140	110 320	64	8 047
		16	48 280			
868	51 787	. . .	24 140	109 320	54	8 044
		18	48 280			
870	52 709	15	24 140	111 631	134	8 047
		19	48 280			

TABLE 5—*24 140-km (15 000 miles) Grand Am fleet test results. The average (of 2) metal specimen weight loss data (mg/specimen) for Vehicles 846, 856, 858, 860, 862.*

Test Vehicle	Initial Mileage	Oxalate, Level, ppm	Modine Solder	Copper	ASTM Solder	Brass	Steel	Cast Iron	Cast Al
846	53 440	31	27	14	3	7	1	1	21
856	51 452	15	10	19	15	16	2	2	30
858	51 909	14	8	4	5	6	2	1	11
860	51 727	43[a]	3	7	3	9	1	−1	18
862	51 752	32	21	4	4	5	1	0	17
864	51 850	15	23	5	3	7	1	1	27
868	51 787	18[a]	17	5	1	7	1	−3	26
870	52 709	15	19	4	6	5	2	−1	10

[a] Oxalate level, ppm, at 48 280 km.

conditioned for use in a 8047 km (5000 miles) test. In these six vehicles the oxalate levels remained relatively low as compared to the oxalate levels reported in Table 3; however, they are higher than in the previous test. A rise in oxalate has been seen in other tests at the First Brands Corporation's Laboratory. It appears that repeated oxalic acid cleaning can increase the oxalate levels. It is postulated that the oxalic acid is effectively increasing the surface area and the amount of residual ferrous oxalate in the cooling system with each cleaning.

Discussion and Conclusions

It has been demonstrated that oxalic acid will react with the metal surfaces with which it comes in contact in the automobile's cooling system. The reaction of oxalic acid with the iron surfaces present in the cooling system results in the formation of ferric and ferrous oxalates. The ferric oxalate and some of the ferrous oxalate is removed from the system with the water flush following the oxalic acid cleaning step.

A residual ferrous oxalate film will remain on the iron surfaces. The amount of iron oxalate depends on the condition of the cooling system before the cleaning step and the number of times it has been oxalic acid cleaned. A cooling system with a larger surface area will have larger deposits of ferrous oxalate. The borate conditioning step removes ferrous oxalate from the surface of the cooling system. However, in some cases residual ferrous oxalate will remain. It has been shown that this oxalate can have a detrimental effect on the pH, RA, and inhibitor levels of the coolant solution added to the vehicle following the conditioning step. This effect can be minimized by using a high pH borate conditioning fluid and, when necessary, repeating the conditioning step with the high pH conditioner.

The option selected depends on the purpose of the fleet test. In all cases, the better the vehicle histories are matched in a fleet, the better probability that final test results will be statistically significant. In new vehicles, the oxalic acid effect appears to be minimal. A single conditioning step with the high pH conditioner should be sufficient. The older the vehicle, the higher the mileage, and the number of times the vehicle has been oxalic acid cleaned will determine the need for repeating the conditioning step.

As a matter of course, the radiator and water pump should be changed following the conditioning step to minimize the effects that the cleaning and conditioning steps will have on the cooling system.

A vehicle showing extensive signs of corrosion of the cast iron or cast aluminum cylinder heads and blocks are not suitable for coolant testing. Heavy corrosion deposits will not be removed by oxalic acid cleaning, or other commercially available in-situ cleaners.

Acknowledgment

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Randall J. Stafford[1]

Investigation of Deposits on Water Pump Seal Faces

REFERENCE: Stafford, R. J., "**Investigation of Deposits on Water Pump Seal Faces,**" *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 205–214.

ABSTRACT: Mechanical water pump face seals from heavy duty diesel on-highway engines which were reported to leak were analyzed and were compared to nonleaking seals. The siliconized graphite seal face pairs did not exhibit any significant wear of the faces. Coolant leakage was traced to deposit film build-up, which resulted in separation of the seal faces.

Analysis of the films by wavelength dispersive spectroscopy revealed elements from the coolant and coolant additives (Si, C, O, S, P, K, Na, B, Mo), corrosion metals from the engine (Fe, Cu, Cr) and hard water elements and contaminants (Ca, Mg, Zn, Al, Mn, Cl). Calcium from hard water and iron from corrosion are believed to accelerate the deposit formation.

KEYWORDS: water pump seal, mechanical face seal, face deposit

The water pump has historically been a weak link in the cooling system of engines with a majority of the water pump leakage attributed to the mechanical face seal within the water pump. Trends in face seal leakage have been documented for the automotive industry [*1*]; but no comparable documentation has been published for the heavy duty diesel industry. Even though water pump and seal leakage have been a major development area for many years, this lack of documentation for heavy duty diesels has not allowed a complete assessment of failure modes.

Standard warranty for heavy duty diesel is 100 000 miles (161 000 km) in the U.S. with extended warranty coverage up to 500 000 miles (804 500 km). Automotive warranty is typically 10 000 to 15 000 miles (16 100 to 24 100 km) with extended warranty coverage to 50 000 miles (80 450 km). The greater warranty expectations for heavy duty diesel has driven the engine manufacturers to increase durability, reliability, and reduce warranty expense through improvements in seal design and materials.

The design parameters for automotive seal components [*2*] have been used as guidelines for the design development of diesel water pump seals. Furthermore, one of the primary failure modes, abrasion and wear of the face in automotive applications [*3*], has been greatly reduced through face material development. The current heavy duty diesel seal construction incorporates the design enhancement of unitized seals, and the materials advancements of siliconized graphite primary and mating rings.

The reduction of seal wear by use of a hard abrasion resistant siliconized graphite face pair significantly reduced seal failures and shifted attention from leakage due to face wear to seal leakage being attributed to deposit formation on the faces. These deposits have been reported in the automotive industry [*4,5,6*]. Many interrelated factors can contribute to the deposit formation such as coolant type and composition, engine duty cycle, make-up water, face

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[1] Senior Engineer, Ceramic Engineering & Tribology, Cummins Engine Co., Inc., Columbus, IN.

design and composition, and coolant temperature. Deposits have been reported in the heavy duty diesel industry for alumina/carbon face pairs[2] [*5,7*].

Heavy duty diesel coolant is usually a low silicate formulation automotive coolant with the major component, ethylene glycol, and minor components, such as sodium salts of nitrate, borate, metasilicate, orthophosphate, merceptobenzothiazole and tolytriazole [*8*]. The greater engine life expectancy for heavy duty diesels and higher engine load factor require use of supplemental cooling additives (SCAs) to provide adequate corrosion protection, liner pitting protection, coolant pH control, and hot surface scale inhibition. The SCAs have major components that are sodium or potassium salts of borate, nitrate, nitrite, metasilicate, phosphate, molybdate, adipate, mercaptobenzothiazole and tolytriazole [*9*].

The intent of this paper is to document analysis of deposits on the siliconized graphite face materials in current use for many heavy duty diesels in the U.S. The older seal designs and secondary market replacement seals represented by two piece construction seals and seals with alumina/carbon face pairs were not evaluated.

Seal Examination

The seals examined in this investigation were limited to a unitized construction having a nitrile rubber bellows secondary seal and siliconized graphite primary and mating rings.

The seals were removed from water pumps of heavy duty diesel 10 and 14 L displacement engines (Cummins L10 and NT). The water pumps were returned directly by Cummins field service representatives or returned after collection at a rebuilding facility (Diesel Recon). Water pumps removed from service due to coolant leakage were examined. The indication of leakage was visible leakage of coolant or dried deposits of coolant on the water pump body. The pumps were leak tested (5 psig air pressure in the weephole with water around seal) to limit the seals for examination to those with face leaks or unidentifiable leaks. A schematic of the water pump assembly is shown in Fig. 1.

Of the ninety water pumps returned, the majority (70%) of these were attributed to face leakage due to deposits, debris, or indeterminate causes. The remaining 30% of the water pumps were removed from service due to leakage through faces cracked in manufacturing or assembly, torn bellows, misassembly in pump, and excessive rotor run-out, or mechanical failures of bearings, pulley, shaft, casting and mounting.

The lag time between water pump leakage and removal of the seal for examination was approximately 3 to 6 months. Because there was no control over the removal and handling of the pump prior to analysis, the seals were examined in the "as-received" condition and all analysis was performed without any cleaning procedures. Limited information such as mileage was provided on some of the pumps by Cummins service representatives. The mileage at pump removal ranged from 28 000 to 199 000 miles (45 000 to 320 000 km).

In addition to the leaking water pumps, five nonleaking water pumps were obtained. These pumps provided baseline information on the face appearance and seal condition of an operating water pump. The nonleaking pumps were subjected to the same teardown and leak testing procedures as the leaking pumps. The information received with the pumps indicated that these pumps were removed from service for analysis after 146 000 to 243 000 miles (235 000 to 391 000 km).

Experimental

The seal faces of each seal were visually inspected under a Zeiss reflected light stereomicroscope at 20X magnification. A random selection of seals, including nonleaking seals, was

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[2] Rathert, B., Cummins Diesel Australia, personal communication.

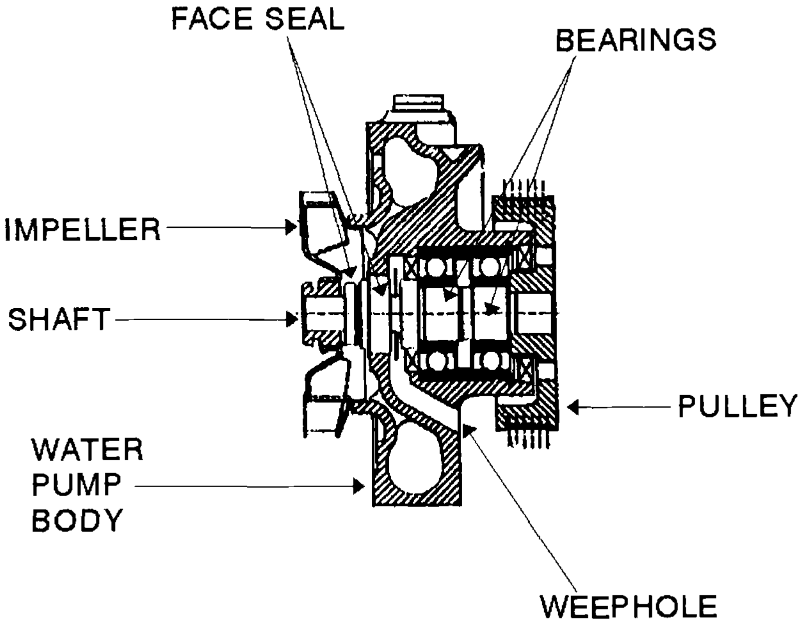

FIG. 1—*Schematic drawing of water pump assembly.*

examined further in an Amray Model 1645 scanning electron microscope (SEM) and the observed deposits were analyzed for elemental composition by wavelength dispersive spectroscopy (WDS) using a Microspec Model WDX-3PC spectrometer with a Model WDX-2A detector. The deposits on these seal faces were also characterized by Fourier transform infrared spectroscopy (FTIR) using a Nicolet Instrument Model 450 FTIR, with 4 cm^{-1} resolution, to determine the molecular bonding characteristics of the deposits on the surfaces. Deposits were analyzed using a microscope attachment to the FTIR in the reflectance mode.

Results

Visual examination of the seal faces from leaking water pumps showed a range of conditions from full face deposits to no discernable deposit. Examination of the seal faces from nonleaking water pumps revealed the same range of surface conditions (full face deposit to no deposit). There was no evidence of any significant wear on any of the seal faces, with only a few localized scratches in the graphite surface of the siliconized graphite material.

Examination of the seal faces in the SEM showed no evidence of wear. A reference photograph of a new seal face is shown in Fig. 2. The surface microstructure consists of a silicon carbide matrix with islands of graphite and random irregular pores.

Faces from nonleaking seals are shown in Figs. 3 and 4 and represent the range in face appearance observed for nonleaking seals. The thick full face deposit in Fig. 3 was the sealing surface during operation. Where the thick deposit is broken away from the surface, an additional underlying thin film deposit was observed. There was no deposit on the wear face of the seal in Fig. 4, but crystalline dried coolant deposits were scattered across the face.

Faces from leaking seals are shown in Figs. 5 through 9 and represent the typical face appearances observed for leaking seals. Comparison of the seal in Fig. 5 to the new seal in Fig. 2 shows that the graphite islands and surface porosity are covered by a full face deposit. Additional raised deposits, from gel dehydration, cover part of the outer 50% of the surface. Figure 6 shows

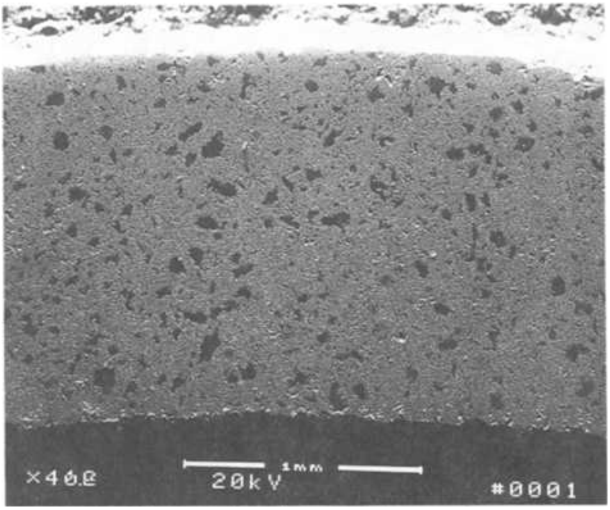

FIG. 2—*New seal face of siliconized graphite, primary ring.*

a deposit band covering the inner 35% of the seal face. The deposit does not fully cover the surface graphite within the deposit band. Figure 7 shows sporadic deposits on the face with an underlying deposit band covering the inner 50% of the face. Figure 8 shows a single local deposit on the seal face. Figure 9 shows a seal face with no apparent deposit and wear scratches in the graphite phase.

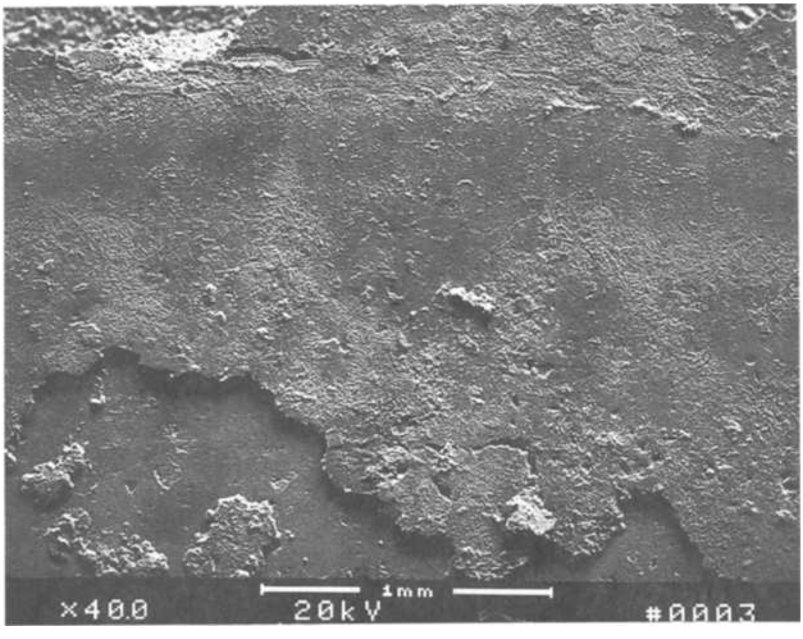

FIG. 3—*Nonleaking seal face with thick deposit film, primary ring.*

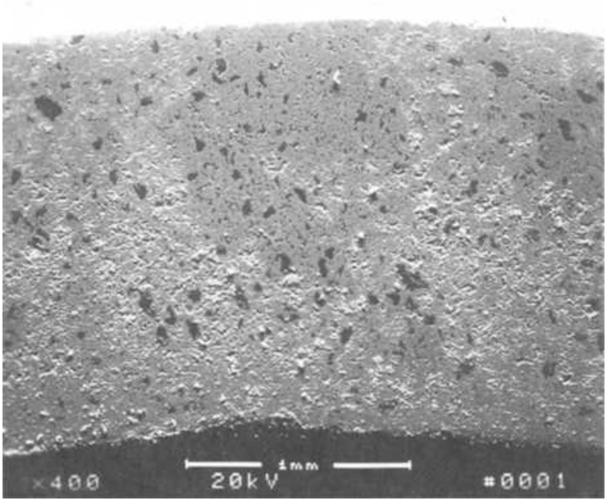

FIG. 4—*Nonleaking seal face with dried coolant crystals on surface, primary ring.*

The results of the WDS analysis are summarized in Table 1. The elements present in the coolant are all present in the seal face deposit including corrosion metals from the cooling system. For the leaking seals, calcium and magnesium are also present in the adherent deposit. The presence of sodium and magnesium on the new seal face may be due to handling during seal assembly.

FTIR analysis showed that silicate, phosphate and methyl group bonds were present in the deposits on all seal faces with carbonyl, amine and hydroxyl group bonds detected on individual faces. No clear differences in chemical bonding in the deposits on the leaking and nonleaking seal faces could be determined.

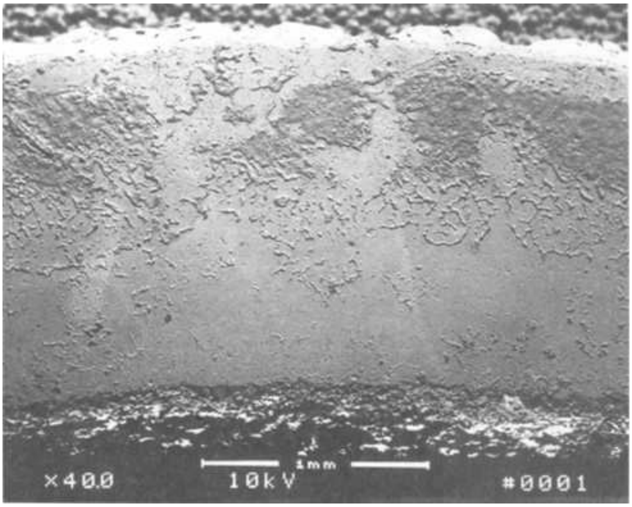

FIG. 5—*Leaking seal face with discrete thick film deposits and underlying smeared film over full face width, primary ring.*

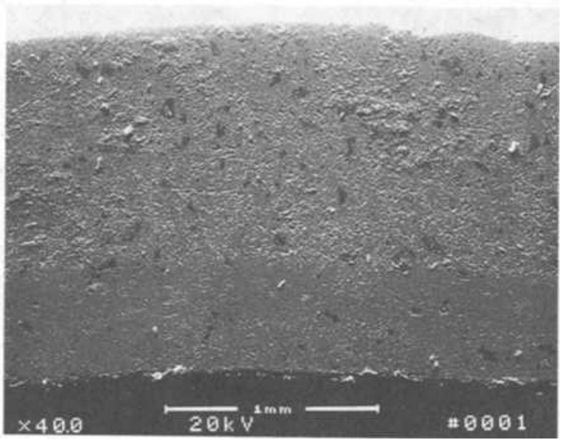

FIG. 6—*Leaking seal face with discrete random deposits and smeared film over inner 35% of face width, primary ring.*

Discussion

The deposits analyzed on the leaking seal faces were classified as filming failures, with the film causing separation of the faces and allowing coolant leakage.

Elemental analysis shows the presence of calcium, iron and phosphorus on the seal faces in Figs. 6 through 8. The presence of these three elements was in agreement with Kiryu's work on deposit formation [*4*], where calcium, iron, and phosphorus in solution and nucleate boiling between the faces are required for adherent deposit formation. Absence of calcium or iron from the system produced nonadherent precipitates.

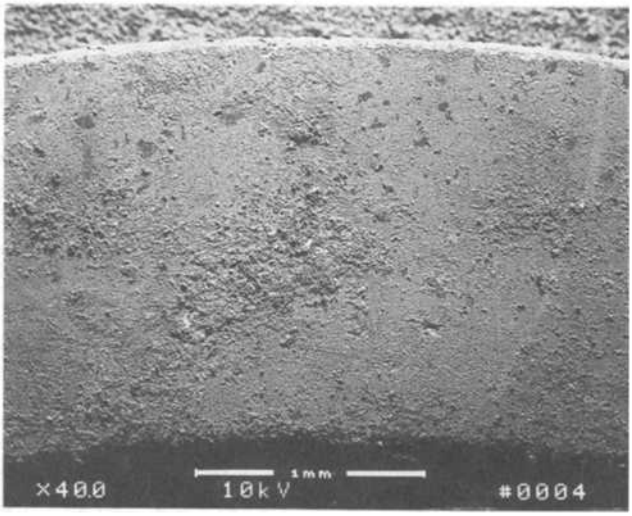

FIG. 7—*Leaking seal face with discrete random deposits and smeared film over inner 50% of face width, primary ring.*

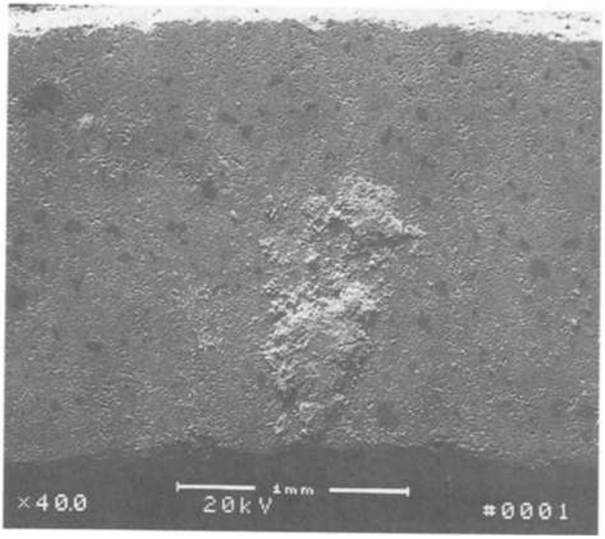

FIG. 8—*Leaking seal face with large discrete local deposit, primary ring.*

While the seal deposits in Figs. 6 through 8 agree with Kiryu's work, the seal deposits shown in Fig. 5 are not in agreement and do not contain iron required for deposit formation. However, boron and molybdenum are present indicating that some of the borate and molybdate coolant additives were part of the deposit. Hercamp and Hudgens [*10*] have shown that silicate gel formation is enhanced by the presence of borate or calcium, or both, and Kiryu [*5*] has shown that deposit height is greatly increased by the presence of borate. The relative peak heights for silicon, oxygen and carbon in the WDS spectrum showed significant increases in oxygen and carbon compared to the new seal face analysis. We examined the rubber compo-

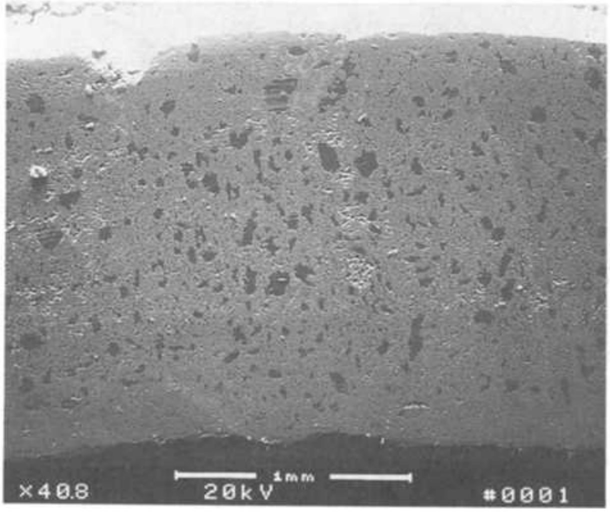

FIG. 9—*Leaking seal face with no visible deposit, wear scratches in graphite phase, primary ring.*

TABLE 1—*Deposit elemental composition from WDS.*

Figure References	Condition	Element																	
		Si[c]	C[c]	Fe	P	K	S	Na	Zn	Cu	Ca	Mg	Al	Mn	O	B	Mo	Cl	Cr
2	New	X	X	X				X				X			X				
3	Non Leak	X	X		X	X	X	X							X				
4	Non Leak	X	X	X	X	X	X[a]	X			X[b]				X				
5	Leak	X	X			X	X	X			X	X			X	X	X	X	
6	Leak	X	X	X	X	X	X	X			X	X			X				X
7	Leak	X	X	X	X	X	X	X			X	X	X		X				
8	Leak	X	X	X	X	X	X	X	X	X	X	X	X	X	X				
9	Leak	X	X	X	X	X	X	X		X	X	X			X				

[a] No presence of sulphur in scan of area without dried coolant crystals.
[b] Peak height reduction of 55% in scan of area without dried coolant crystals.
[c] Seal face material constituents.

nents of the seal and the graphite in the seal face and they showed no evidence of damage or degradation, so therefore it is not believed that the increase in carbon peak height can be attributed to either of these sources. Formation and deposition of a silicate and glycol colloidal gel is suggested by the silicate and glycol chemistry observed in the FTIR spectrum and this gel is believed to be the source of the increased oxygen and carbon in the WDS spectrum.

The elemental analysis for the seal face in Fig. 4 shows the presence of calcium, iron and phosphorus, however, no deposits are present. This seal did not leak and although the necessary coolant chemical constituents are present for deposit formation (calcium, iron, and phosphorus), the operational characteristics (nucleate boiling in the seal face coolant film) may not have occurred.

Comparison of the seal face in Fig. 4 with the seal face in Fig. 9 shows no deposits adhering to the seal surface in either case and elemental analysis for both seals reveals similar compositions of the surfaces. The similarity in appearance and elemental analysis for these two seals, one nonleaking and one leaking, confirms that seal leakage is a complex issue.

The other nonleaking seal (Fig. 3) did not show the presence of calcium, iron, or phosphorus (elements believed necessary to form adherent deposits). The smooth surface of the film indicated that it acted as the sealing surface during operation. Comparison of the relative peak heights for silicon, oxygen and carbon in the WDS spectrum again show significant increases in oxygen and carbon compared to the new face analysis. Once again, we examined the rubber components of the seal and the graphite in the seal face and neither showed evidence of damage or degradation; therefore, the increase in carbon peak height could not be attributed to either of these sources. The FTIR spectrum of the deposit was indicative of silicate and glycol chemistry, thus the deposit was most likely a silicate and glycol colloidal gel, which would account for the increase in the oxygen and carbon concentration in the WDS spectrum. While calcium and boron are not present, silicate gel formation is possible, especially if the coolant silicate additions were greater than the silicate solubility. The heavy film of, presumably, silicate and glycol gel on the seal face still does not provide an explanation for the seal not leaking or suggest the mechanism for deposit formation and retention on the face. Further work using water pump test rigs is necessary to investigate this phenomena.

Water pump test rig work on operating conditions, coolant composition and hard water effects is in progress to investigate the deposit formation and retention mechanisms in a diesel engine water pump face seal.

Conclusions

Deposits present on leaking seal faces have formed by adherence of calcium-iron-phosphate complexes precipitated during nucleate boiling episodes induced by engine operational conditions. These deposits are sufficient to cause face separation and leakage of coolant.

Deposits on nonleaking seal faces have formed by a mechanism related to silicate gelation and are not presently understood.

The similar appearance of one leaking and one nonleaking seal face pair with the same elemental analysis illustrates that seal leakage is a complex phenomena involving coolant chemistry, face materials and engine duty cycle.

Acknowledgments

The author would like to thank Cummins Engine Co., Inc. for permission to publish this paper, and T. M. Yonushonis, C. J. Hurt, J. B. Cofrin, J. S. Kolhouse, G. A. Totten, T. Robinson, and W. Moenning for their technical or laboratory assistance, or both.

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DISCUSSION

W. Mercer[1] *(written discussion)*—Thirty percent of the observed pump failures were attributed solely to quality control problems in assembly of the pumps. Could you comment on the possibility that the remainder of the failures were also caused by less obvious quality control problems?

R. J. Stafford (author's response)—The 30% of the seal leaks referenced represent all quality problems involved in manufacture of the faces, the seal assembly and the water pump as well as including all leaks caused by bellows or rubber gasketing failures and leaks due to mechanical alignment and runout. The less obvious quality problems, such as face material and rubber component quality were included in this group of failures.

Since the focus of the paper was on deposits observed on the seal face, all of the above identifiable causes of leakage were grouped together to present a total picture of the water pump analysis. The remaining 70% of the leaking seals were subjected to additional analysis for deposits and are represented by the data presented.

Peter Woyciesjes[1] *(written discussion)*—You stated that you do not see silicate deposits on the seal surfaces and that a low silicate coolant was used with a phosphate/molybdate/nitrite package. How can you substantiate that pumps are failing as a result of silicate gels?

R. J. Stafford (author's response)—Silicate gelation is not frequently seen in the heavy duty diesel cooling system given the present state of technology with specifications for low silicate formulation coolants. However, deposits are observed on some seal faces, which can be attributed to silicate gel formation on the seal surface.

Hercamp and Hudgens [*1*] showed that the silicate concentration in coolant of heavy duty diesel trucks ranges between 200 and 600 ppm. The initial fill of low silicate coolant with the recommended dosage of supplemental coolant additives (SCAs) provides 1450 to 2050 ppm of silicate in the cooling system [*2,3*]. The excess silicate beyond the 200 to 600 ppm in solution forms protective layers on internal surfaces of the engine and cooling system components. Addition of SCAs before depletion of the protective layers, use of precharging SCA dosages instead of maintenance SCA dosages, or development of coolant conditions that reduce the silicate solubility will result in silicate sols and gels being deposited on the surfaces within the cooling system.

The seal faces shown in Figs. 3 and 5 of the paper have deposits attributed to silicate gel formation. In the analysis of these seal faces, detection of silicate on the seal surface by wavelength dispersive spectroscopy (WDS) was not possible because of the masking effect of the silicon carbide in the seal ring. However, strong silicate molecular bonding was detected by Fourier transform infrared (FTIR) spectroscopy for the deposits on the seal surface and after removal from the surface.

Deposition of silicate on the seal surface as a full face film can create a sealing surface (Fig. 3) and allow the seal to operate without leakage. In contrast, a similar visual seal face appearance (Fig. 5) with similar WDS and FTIR spectra was shown for a seal that had leaked.

As was stated in the paper, we do not presently understand the silicate gelation mechanism for these heavy duty diesel engine seals and believe that the coolant chemistry, surface interactions, face materials, and engine operating conditions all play roles in how a silicate gel is generated and deposited on the seal face.

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[1] First Brands Corporation, Danbury, CT 06804.

Kenji Kiryu,[1] *Osamu Hirata,*[1] *Akira Yoshino,*[1] *Ken Okada,*[1] *and Hiroshi Hirabayashi*[1]

The Relationship Between Sealing Performance of Mechanical Seals and Composition of Coolants for Automotive Engines

REFERENCE: Kiryu, K., Hirata, O., Yoshino, A., Okada, K., and Hirabayashi, H., "**The Relationship Between Sealing Performance of Mechanical Seals and Composition of Coolants for Automotive Engines,**" *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 215–233.

ABSTRACT: Because the mechanical face seals in automotive water pumps play an important role in maintaining the good performance of engines, they must exhibit reliable sealing performance and long operating life. Generally, the sealing performance of mechanical seals is closely related to the properties of the liquid to be sealed. Automotive engine coolants are generally formulated with a variety of inhibitors to prevent corrosion and erosion of cooling system parts. A few of these inhibitors have a detrimental effect on the performance of water pump seals.

In this paper, representative types of deposit formation on sealing surfaces are reported. These seals were taken from pumps that failed due to seal leakage believed to be caused by a combination of coolant formulations, contaminations into coolant, and changes in engine operation conditions. The failure mechanisms and possible countermeasures involving the sealing materials, surface quality, and seal structure are discussed.

KEYWORDS: mechanical seal, long life coolant, inhibitors, deposit, wetting, contact angle

End face mechanical seals are generally used for sealing devices in water pumps of automotive engines [*1*]. Because they play an important role in achieving the optimum operation of engines, their reliable long lives are required. A variety of failure modes have been experienced in actual service use, such as thermal cracking of the seal ring, excessive wear of the sealing surfaces caused by abrasive particles, squeaking, and so forth. By applying the appropriate countermeasure for each type of failure mode, the probability of these seal failures has been decreasing [*2,3*]. However, another type of failure has also been observed and is caused by the formation of deposits on seal faces, which results in severe leakage. A solution to this worldwide problem is required [*4–10*].

This urgent problem is attributed to a combination of three factors:

1. Qualitative and quantitative changes in long life coolant (LLC) formulations,
2. An increase in severity of engine operation conditions, and
3. Contaminations into LLC from various parts in the cooling system.

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[1] Dr. Eng., assistant manager of R & D #3 Section; chief engineer of R & D #7 Section; manager of design #2 Section; Dr. Eng., senior manager of R & D #1 Department; and Dr. Eng., executive vice president; respectively, Eagle Industry Co., Ltd., 1500 Katayanagi, Sakado-shi, Saitama-ken, 350-02, Japan.

This paper deals with the investigation of deposit formation caused by three different formulations of LLC together with their mechanisms and appropriate countermeasures.

Mechanical Seals for Water Pumps

Figure 1 shows the structure and construction materials of the representative mechanical seal used in field service. The stationary seal ring is loaded by a coil spring. The mating ring is used on the rotating shaft side. Generally, the seal ring materials are softer (for example, a variety of carbon materials), and the mating ring materials are much harder (for example, alumina and silicon carbide). All of the metallic parts (parts 5, 6, 7, and 8 in Fig. 1) are composed of stainless steel, which is corrosion resistant to the LLC containing additives. In actual field service, the failure of most mechanical seals is due to leakage across the sealing surfaces (parts 2 and 3 in Fig. 1).

The mode and probability of occurrence of seal failures are strongly affected by the internal design of the pump and the layout of the exterior cooling system. In particular, heat and mass transfer of cooling water including additive are considered to have predominant influences on the seal failure. In view of these experiences, reproducible tests were carried out under laboratory conditions, so that test results using LLC with different inhibitor formulations could be compared.

Properties of LLC

For automotive engine coolants, suppression of corrosion and scale deposition on metallic parts and degradation of rubber parts is required [*4*]. To satisfy these requirements, a variety of organic and inorganic inhibitors are prescribed [*11,12*]. Table 1 shows a list of the typical chemical properties of the three LLC used in the present investigation. The main features of these three LLC are:

1. *LLC-A:* This type of LLC is characterized by inorganic inhibitor at a high concentration of silicate to prevent mainly corrosion of aluminum (Al) parts. For prevention of silicate gelation, the pH of the LLC is maintained at a high level, approximately 10.
2. *LLC-B:* This type of LLC is characterized by triethanolamine, an organic corrosion inhibitor for ferrous and Al parts. An inorganic phosphoric salt is also added at a high concentration to prevent corrosion of ferrous parts.
3. *LLC-C:* In this formulation, inorganic inhibitors to prevent corrosion of ferrous and Al parts (for example, phosphoric and nitric salts) are substituted for the triethanolamine found in the LLC-B formulation. In addition, mercaptobenzothiazole (MBT) is added

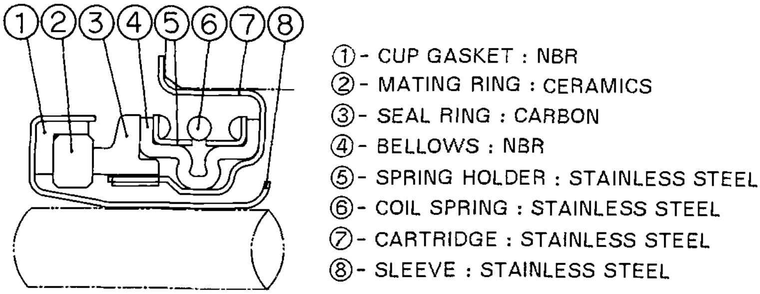


FIG. 1—*Mechanical seal for automotive water pump.*

TABLE 1—*Chemical analysis of LLC.*

	Parameters	LLC-A	LLC-B	LLC-C
	pH	10.1	8.1	8.3
Organic	mercaptan benzo triazole	0.28	0.49	0.73
	benzoic acid	ND	3.72	3.90
	triethanolamine	ND	4.10	ND
Inorganic	phosphate (PO_4^{-3})	1.01	1.14	0.84
	nitrate (NO_3^-)	ND	ND	0.45
	silicate (SiO_3^{-2})	0.15	ND	ND
Ion	K^+	0.52	0.03	1.06
	Na^+	0.17	0.80	0.62

at relatively high concentration as organic corrosion inhibitor for copper (Cu) and brass parts.

Mechanism of Deposit Formation

In this section, deposit formation phenomena are described in relation to the three representative LLC formulations. The process of the seal failure due to deposition and leakage is believed to progress as follows:

1. Deposit formation on seal ring or mating ring surfaces,
2. Growth of deposits,
3. Increase in gap between sealing surfaces, and
4. Occurrence of excessive leakage.

Deposition of Silicate

Typically, two different types of deposit profiles were found on the surfaces of failed seals taken from actual vehicles that used the LLC-A type coolant. These deposits, which resulted in leakage across the seals, are shown in Fig. 2. The type 1 deposit is usually observed when a combination of graphitic C as the seal ring material and alumina as the mating ring one is used. In this case, a black deposit is formed on the surface of the alumina and severe wear of the C ring occurs. On the other hand, type 2 deposit formation takes place only when the seal ring material is amorphous C. This failure is characterized by the formation of a white deposit on the seal ring side and little deposit formation on the mating ring side. Figure 3 shows scanning electron microscopy (SEM) images of type 1 and type 2 deposits together with element mapping by means of electron probe X-ray micro analysis (EPMA). In the case of type 1 deposits, the elements on the mating ring surface are found to be mainly silicon (Si), oxygen (O), and C. Based on the chemical analysis of LLC-A shown in Table 1 and the profile curves showing severe wear of the seal ring, it is considered that the deposit on the mating ring surface is composed of silicate from the LLC-A and wear particles of C from the seal ring. In the type 2 deposits, only Si and O are detected on the seal ring surface and it is believed that the deposit is composed mainly of silicate from the LLC-A.

It was reported by Hercamp and Hudgens [5] that silicate gelation can result in deposit formation and subsequent seal leakage. In connection with this problem, the authors carried out heating tests of LLC-A type formulations in a container with or without a lid in a furnace at temperatures of 120°C and 150°C for 1 h. Figure 4 shows changes of LLC-A after the heating

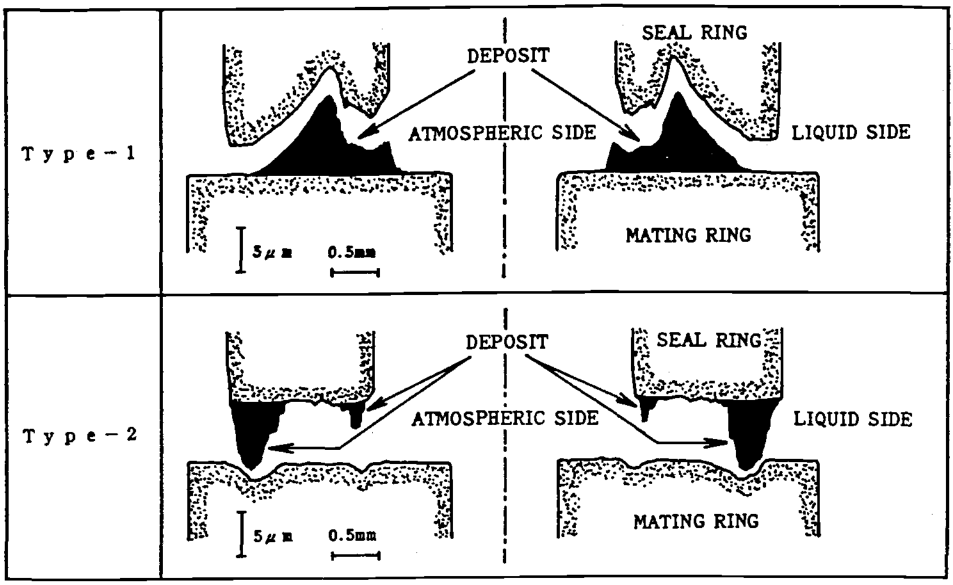


FIG. 2—*Two types of silicate deposits in field service.*

test. Under the closed condition with the lid, clusters of colloidal particles are found in the liquid phase. Comparing the change at 150°C with that at 120°C, it is noted that the number of clusters increased remarkably. The EPMA analysis (energy dispersive X-ray [EDX] spectrometry) of the clusters and the filtrate taken from the LLC-A heated at 150°C by means of filtration was carried out as shown in Fig. 5. The detective intensity of Si in the clusters is much stronger than that in the filtrate, so it is believed that the clusters are composed of silicate gel. In contrast to this, under the opened condition without a lid, the liquid phase transforms into gel, showing increased viscosity.

Sakka and Kamiya investigated the characteristics of silicate for preparation of functional materials by the sol-gel method [*13*]. According to them, in hydrolysis and condensation reaction, silicate causes gel formation as coagulation of clusters at higher water content. On the other hand, at lower water content, it forms network gel. The result of the present heating tests shown in Fig. 4 are verified also by their investigation. Under the opened condition without a lid at 150°C, the LLC-A coolant completely dries up and forms a solid composed of the additives in LLC-A, mainly sodium phosphate and silicate.

To estimate the temperature rise on rubbing surfaces due to frictional heat, finite element method (FEM) analysis is attempted as shown in Fig. 6. The calculated result using the input data simulating practical operating conditions of mechanical seals indicates the elevated temperature on rubbing surfaces from 140°C to 150°C, near to the temperature range of silicate coagulation. Moreover, the following fact should be taken into consideration due to the vapor pressure of 50% solution of ethylene glycol: On the inner side of rubbing surfaces near to atmosphere, the liquid temperature exceeds the boiling point, whereas on the exterior side near to pressurized liquid, hardly any boiling occurs. This means that the vapor–liquid interface is necessarily formed between the inner and outer peripheries of rubbing surfaces. Consequently, it is easily suggested that the gelation of silicate in LLC-A occurs between sealing surfaces.

Besides these tests carried out under static condition, a number of running tests were carried

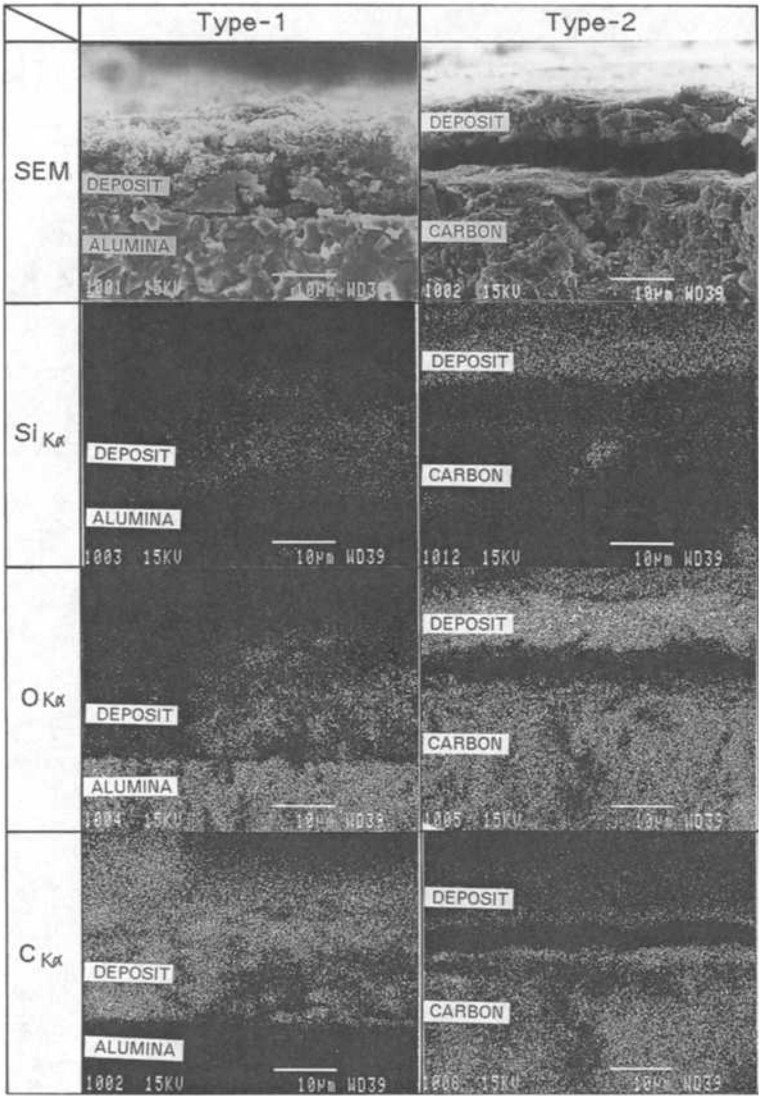


FIG. 3—*SEM images and X-ray mapping of silicate deposits.*

out at various liquid temperatures to relate with the dynamic phenomena in actual sealing of LLC-A. The observed results of deposit height are shown in Fig. 7. Here, remarkable temperature dependency is confirmed, that is, the deposit height shows a rapid increase with raising temperature. This fact is considered to verify that the supposition derived from the static test results emphasizing the significant role of condensation reaction of silicate by dehydration is also applicable to the dynamic tests.

From the above discussion, the cause of recent increase in the number of the leakage failures due to the silicate deposition on sealing surfaces can be explained as follows: The increase in

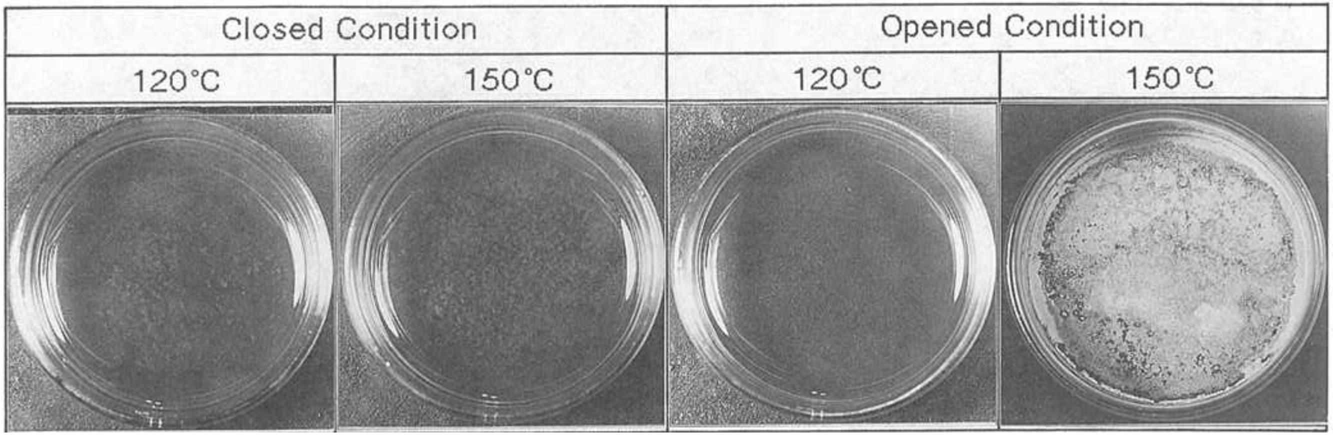


FIG. 4—*Static heating test result of LLC-A.*

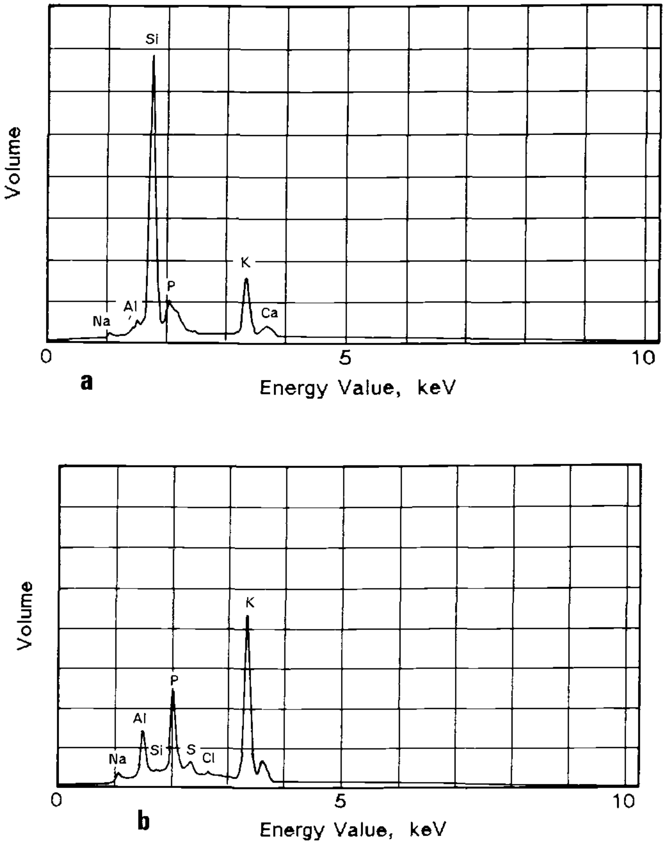


FIG. 5—*EPMA analysis of clusters* (a) *and filtrate* (b) *of LLC-A.*

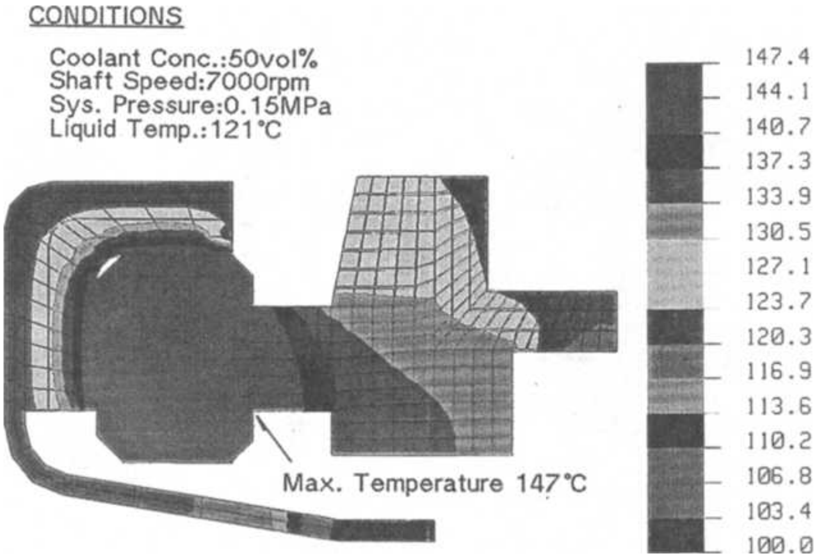


FIG. 6—*Temperature distribution of rubbing rings by FEM.*

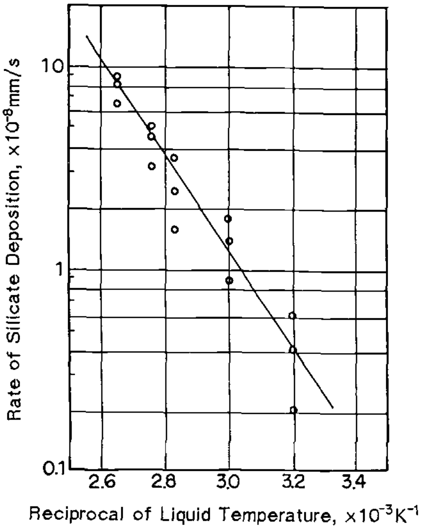


FIG. 7—*Effect of temperature on silicate deposition.*

severity of engine operating conditions (for example, increase in rotation speed and temperature rise of coolant) elevates the temperature of rubbing surfaces of mechanical seals, so that the silicate deposition is apt to occur in recent years.

Deposition of Phosphorus, Iron, and Copper

Figure 8 shows profiles of deposits formed on sealing surfaces in actual service of automotive water pumps using LLC-B, where excessive leakage was observed. In this case, the deposit height reaches approximately 20 μm on a C ring surface. The EPMA result shown in Fig. 9 indicates that the principal ingredients of the deposits are iron (Fe) and copper (Cu). The result

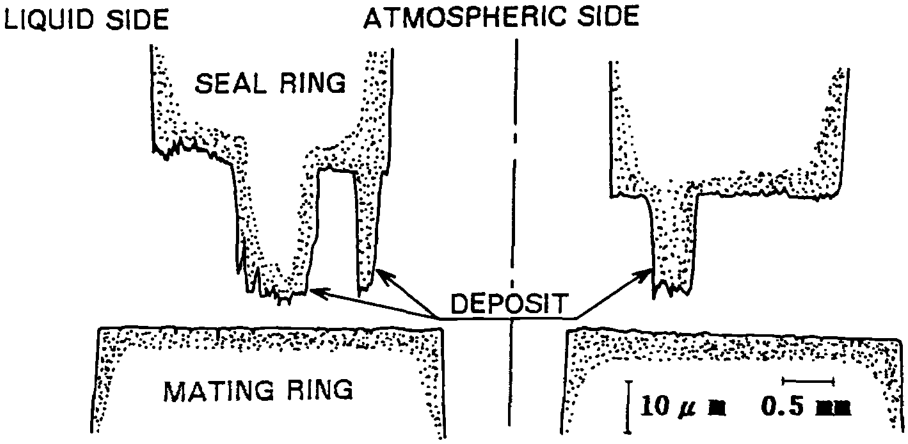


FIG. 8—*Profiles of P, Fe, Cu deposits in actual use.*

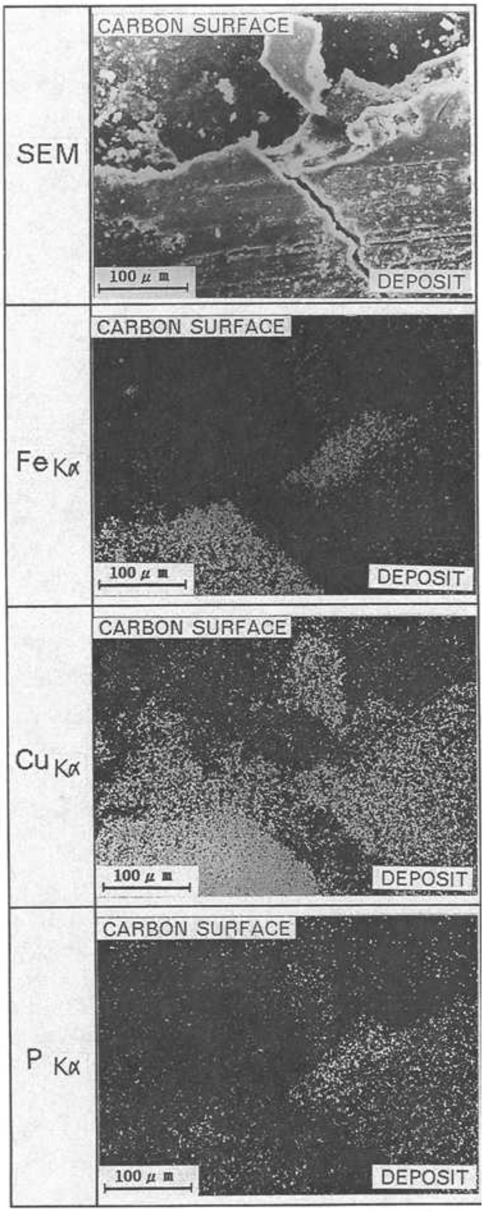


FIG. 9—*SEM image and X-ray mapping of P, Fe, Cu deposits.*

of electron spectroscopy for chemical analysis (ESCA) carried out by ion-sputtering the deposits and obtaining a concentration profile with depth is shown in Fig. 10. The ESCA results indicate that Cu concentrates mainly in an extremely thin layer within a few micrometers on the ferrous deposit.

This type of deposition was frequently observed in heavy-duty diesel engines running a long distance, for example, exceeding 10^5 km. Once encountered, even immediately after replace-

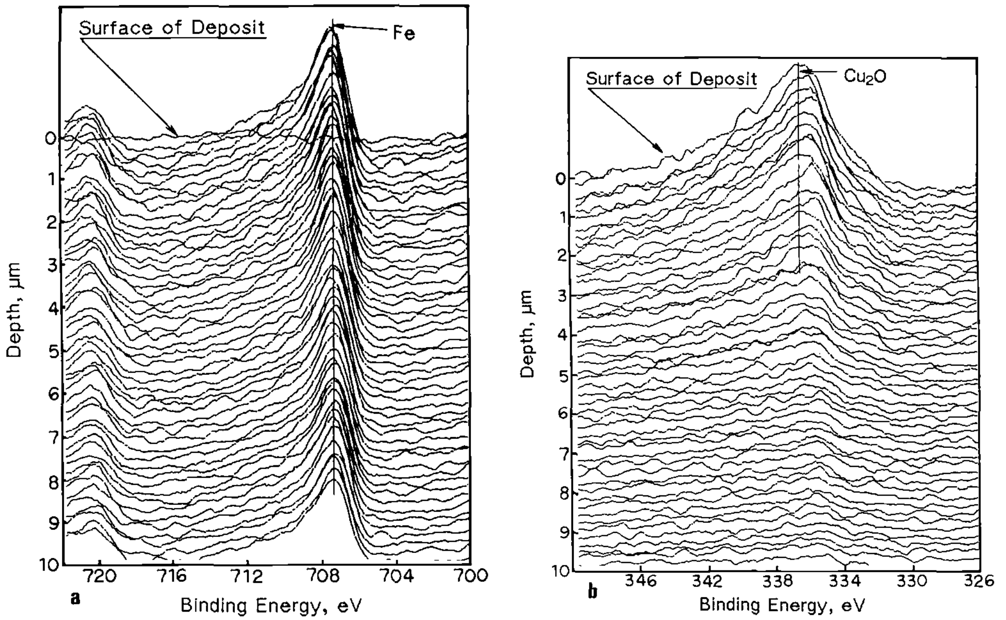


FIG. 10—*Distribution of Fe* (a) *and Cu* (b) *in depth direction.*

ment with a new seal, the deposition is apt to be reproduced. It is suggested that deterioration of LLC-B causes the deposition of this type.

According to Kikuchi and Tajima [*12*], who observed time changes in concentration of metal ions in LLC similar to the LLC-B type formulations, which was collected from engines in field service, Cu ions began to increase after a few months' operation and then Fe ions showed a rapid increase. Thompson and Lorking [*14*] considered the process of the change in these metal ions in connection with the deterioration of LLC.

Based on these viewpoints, the most probable mechanism of the deposit formation in LLC-B is explained in the following sequence: Formic acid as an oxidation product of ethylene glycol is formed and promotes corrosion of Cu parts. Cu ions dissolved in the LLC-B form galvanic cells on surfaces of Fe and Al parts by producing complex salt with amine. These galvanic cells act as triggers of corrosion of these metallic parts. The Fe ions dissolve into the LLC. As a result of an increase in concentration of ferrous ions, the self catalytic reaction promotes ferrous deposition on the sealing surfaces in the presence of phosphate as a corrosion inhibitor. Succeedingly, on the surface of ferrous deposit, a thin layer of Cu is formed.

Deposition of Dibenzothiazyl Disulfide (DM)

Figure 11 shows a rubbing seal ring surface that caused excessive leakage in actual field service using LLC-C. The deposit formation a few micrometers high is observed. EPMA analysis shows sulfur (S) as a main constituent (Fig. 12). Fourier transform infrared (FT-IR) microscopy was used to analyze the deposit. The infrared spectra found that the precipitate is composed of DM (Fig. 13). The molecular structure of DM is characterized by the existence of the S–S bond (Fig. 14). It is suggested that the deposit on rubbing surfaces is composed of DM. However, whereas LLC-C coolant contains MBT as a rust preventive for Cu parts, DM is not typically found in LLC formulations. This supposition is verified also by Kinisky and

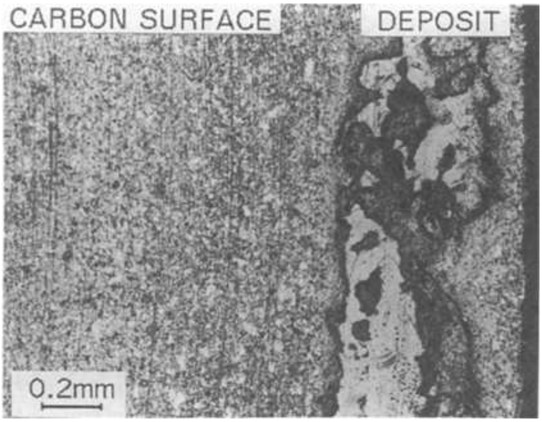


FIG. 11—*Appearance of seal ring surface with DM deposit.*

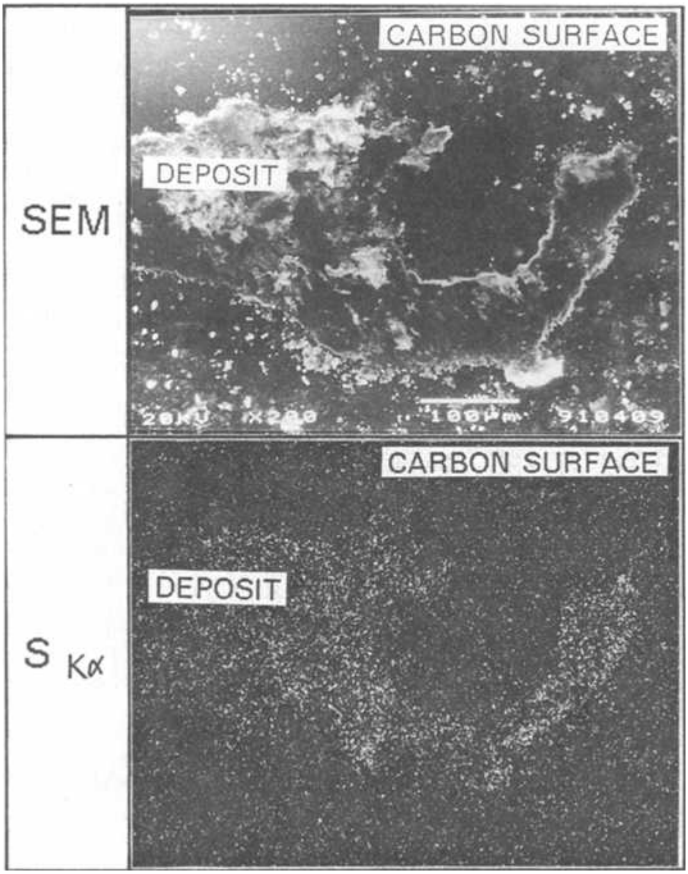


FIG. 12—*SEM image and X-ray mapping of DM deposit.*

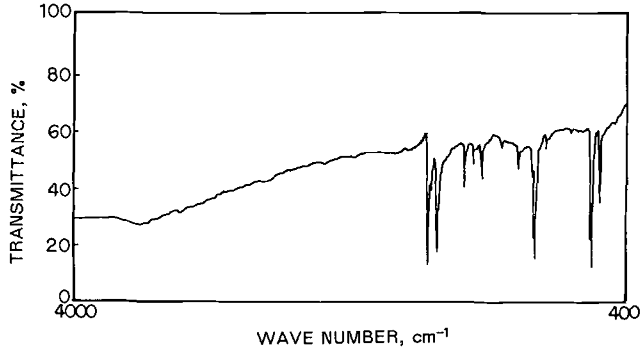


FIG. 13—*FT-IR analysis of precipitate in LLC-C.*

McKenzie [*6*] who used a similar analytical method. They found the same result in the case of LLC without MBT. Figure 15 shows the observed result by Yoshikawa et al. [*15*] who found that DM could be dissolved into LLC from rubber radiator hoses that included DM as a vulcanizer. In their study, the amount of DM dissolved into LLC from a new hose was approximately two times that from a used hose, which corresponded to approximately six times of initially added corrosion inhibitor. Using LLC-C in which a new rubber hose had been immersed, the result of running test deposit formation on seal ring surfaces was reconfirmed. This test result also coincides with Kinisky and McKenzie's study [*6*].

The above discussion can be summarized as follows: The precipitation of DM occurs as a result of the dissolution from rubber radiator hoses. The DM precipitate is concentrated by frictional heat and finally adheres on the sealing surfaces, causing seal leakage.

Countermeasures for Failures

The countermeasures for the deposition on sealing surfaces of mechanical seals should be established by considering suitable rubbing materials, surface roughness, and seal construction. Here, as a representative of the deposit types, the experimental results of silicate deposition are explained as follows:

Sealing Materials [*7*]

The authors attempted to reproduce the silicate deposition under laboratory conditions. Two types of C materials were used—graphitic C S1 causing the type 1 deposit formation and amorphous C S2 causing the type 2 deposition (Fig. 2). For the mating ring materials, alumina M1 with 92% purity and silicon carbide M2 with 97% purity produced by sintering at atmospheric pressure were selected. The mechanical and thermal properties of these four materials are listed in Table 2.

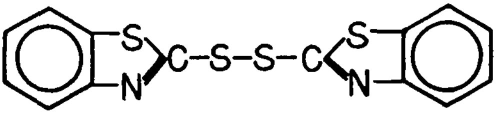


FIG. 14—*Structure of DM.*

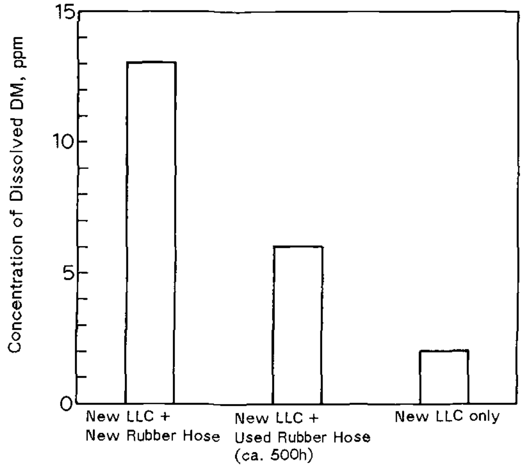


FIG. 15—*Amount of DM dissolved from radiator rubber hoses.*

Figure 16 illustrates the surface profiles after the laboratory tests. The results are indicated as follows:

S1 vs. M1—Deposition on the mating ring M1 surface
S2 vs. M1—Deposition on the seal ring S2 surface
S1 vs. M2—No deposition on both surfaces
S2 vs. M2—Deposition on the seal ring S2 surface

These marked differences in the deposit formation will be discussed from the viewpoint of interfacial chemistry, that is, a change of wetting free energy W_a for intensity of adhesion, where a contact angle Θ plays an important role. This relationship is expressed by Eq 1, where γ_{LV} denotes interfacial free energy between vapor and liquid [*16*]. Here, the liquid is distilled water.

$$W_a = \gamma_{LV}(1 + \cos \Theta) \tag{1}$$

TABLE 2—*Mechanical and thermal properties of rubbing materials.*

	Seal Ring		Mating Ring	
Parameters	S1	S2	M1	M2
Materials	resin bonded carbon		alumina	silicon carbide
Filler	graphite	amorphous carbon	Al_2O_3	SiC
Gravity	1.76	1.73	3.72	3.15
Hardness	54 HS	68 HS	1500 HV	2750 HV
Strength, MPa	45	75	350	490
Coefficient of linear expansion, 1/K	1.1×10^{-5}	3.1×10^{-5}	6.7×10^{-6}	4.0×10^{-6}
Heat conductivity, W/m · K	9.2	2.9	15.9	125.0

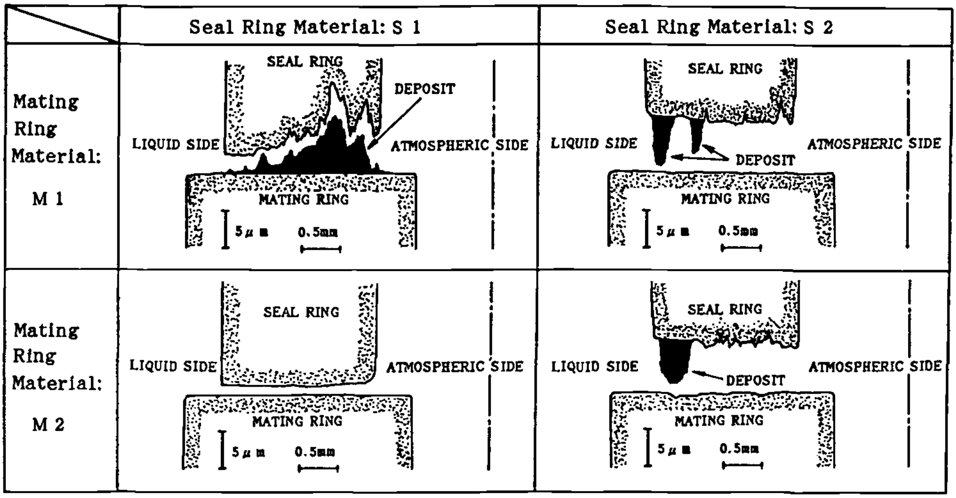


FIG. 16—*Surface profiles after reproducibility tests.*

Because in this test series the same liquid with the same γ_{LV} was used, the wetting energy W_a of each material can be estimated and compared by measuring the contact angle on each sealing surface (Table 3). The relationship between the deposit formation and the wetting energy W_a is plotted in Fig. 17. Deposits are preferably formed on the rubbing surface with higher wetting energy. And, in the case of the combination of rubbing materials where both showed lower wetting energy, no deposit is formed.

As a suitable countermeasure, a selection of both seal materials having lower wetting energy is required. In fact, graphitic C as the seal ring material and silicon carbide as the mating ring are the most desirable material combination.

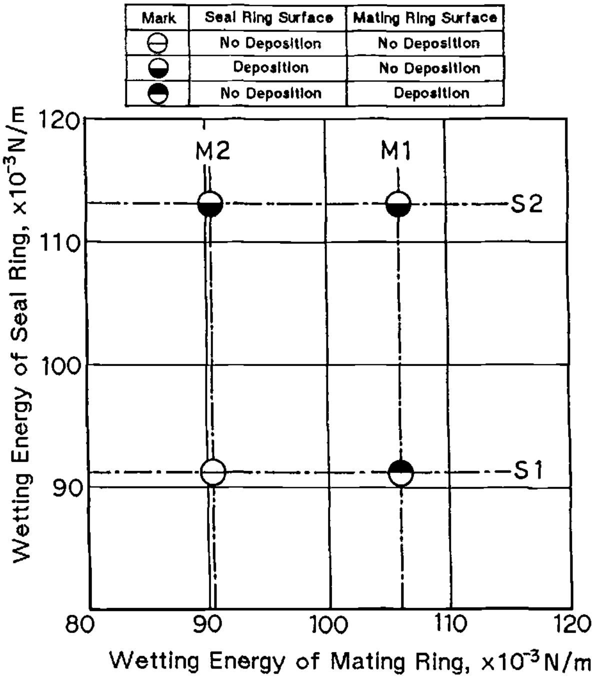
Surface Roughness of Mating Ring

Because the change of surface roughness of mating rings caused by rubbing is low because of high hardness, the sealing performance of the mechanical seal is considered to be affected by surface roughness of the mating rings over long durations. Consequently, it is important to control surface roughness of mating rings within an optimum range.

The laboratory tests were performed with the combination of S1 versus M2 in LLC-A, where surface roughness of the mating ring, M2, was varied within the range from 0.01 to 0.10 μmRa. Figure 18 shows the relationship between the surface roughness and the rate of silicate deposition. In the roughness range lower than 0.03 μmRa, the deposit is formed on the surface of the seal ring S1. In contrast, in the range exceeding 0.06 μmRa, the deposition occurs on the

TABLE 3—*Wetting energy of each rubbing materials.*

	Seal Ring		Mating Ring	
Parameters	S1	S2	M1	M2
Wetting free energy, × 10^{-3} N/m	91.1	113.0	106.0	90.3



Mark	Seal Ring Surface	Mating Ring Surface
⊖	No Deposition	No Deposition
◒	Deposition	No Deposition
◓	No Deposition	Deposition

FIG. 17—*Relationship between wetting free energy and deposition.*

mating ring surface. In the range from 0.03 to 0.06 μmRa, little or no deposition is generated on either seal surface.

These results can also be discussed from the viewpoint of interfacial forces. Figure 19 shows the relationship between the surface roughness and the wetting free energy of the mating ring M1 surface, which is calculated by Eq 1. As the surface becomes smoother, the wetting free

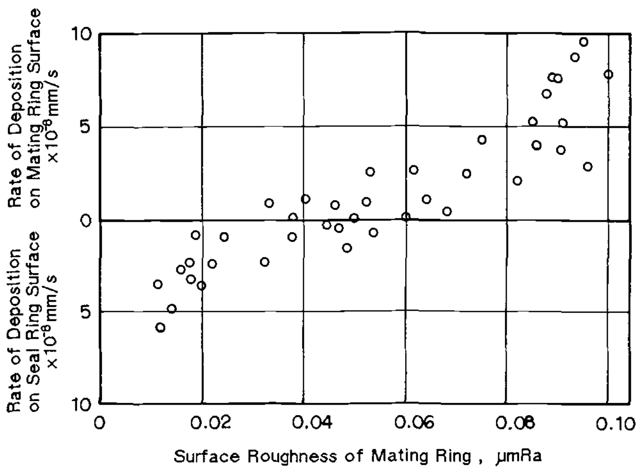


FIG. 18—*Effect of surface roughness on deposition of rubbing rings.*

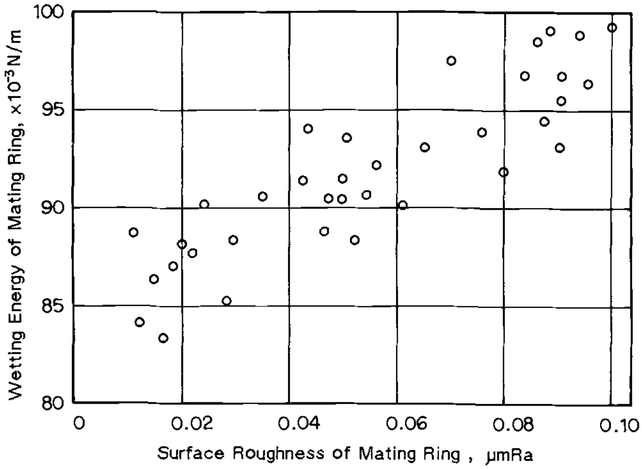


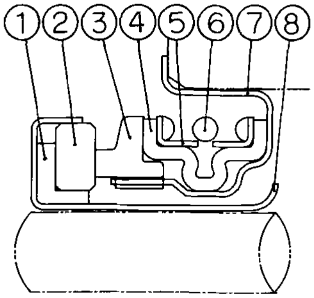
FIG. 19—*Relationship between surface roughness and wetting energy.*

energy of the mating ring becomes lower than that of the seal ring (Fig. 17). In the range of lower M1 surface roughness, the deposit is not formed on the mating ring surface but on the seal ring surface. However, in the range exceeding 0.06 μmRa, the deposit is not generated on the seal ring surface but on the mating ring surface, because the wetting energy of the mating ring M1 becomes higher than that of the seal ring S1.

It is very important not only to select the suitable combination of seal materials but also to control surface roughness within the optimum range to prevent the deposit formation.

Construction of Mechanical Seals

As shown in Fig. 7, the silicate deposition is accelerated by raising liquid temperature. Consequently, to suppress deposit formation, one must decrease the temperature of rubbing surfaces. In comparison with the conventional seal structure illustrated in Fig. 1, the authors recommend the improved seal structure shown in Fig. 20 to decrease the temperature of rubbing surfaces. In the conventional seal, the rubber cup gasket (part 1 in Fig. 1) disturbs transfer of frictional heat to the coolant. However, the frictional heat transfer in the recommended seal structure is much improved because the contact area of the mating ring to coolant increases according to transposition of the cup gasket to the inner side of the mating ring.



①- CUP GASKET : NBR
②- MATING RING : CERAMICS
③- SEAL RING : CARBON
④- BELLOWS : NBR
⑤- SPRING HOLDER : STAINLESS STEEL
⑥- COIL SPRING : STAINLESS STEEL
⑦- CARTRIDGE : STAINLESS STEEL
⑧- SLEEVE : STAINLESS STEEL

FIG. 20—*Improved seal structure.*

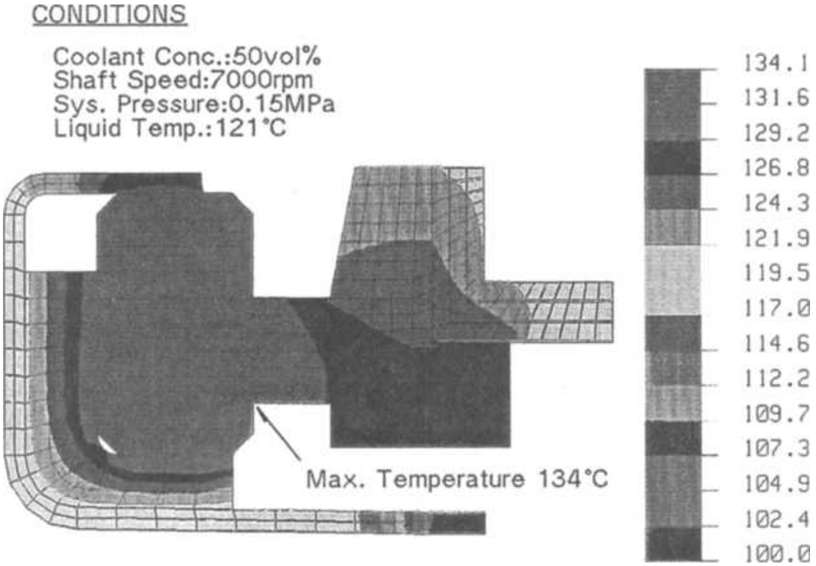


FIG. 21—*Temperature distribution of improved seal by FEM.*

FEM analysis was carried out again to confirm the effect of the transposition of the cup gasket on the temperature distribution of the improved seal. In comparison with the temperature of the sealing surfaces in the conventional type seal shown in Fig. 6, a lower temperature around 13°C is expected, as shown in Fig. 21. This is also confirmed by measuring the actual temperature of the rubbing surfaces.

Furthermore, one should also sufficiently consider the environmental condition near the seal faces, for example, quenching, aeration, and so forth, which can also affect the transfer of frictional heat.

Durability Tests of the Improved Seal

The durability tests in LLC-A were performed to confirm the effects of the countermeasures as mentioned above. Figure 22 shows time changes of total leakage including vapor. In Fig. 22, seal-α is the conventional seal and seal-β is the improved one, in which three types of countermeasures, that is, rubbing materials, surface roughness and seal construction, are applied. Seal-α generates abrupt leakage due to the deposit formation in a short period. On the other hand, seal-β maintains the satisfactory sealing performance for long duration. The result of the durability tests confirmed that these countermeasures show the sufficient effects on preventing the deposit formation.

The description in the above concerns the silicate deposition in LLC-A. However, the authors confirmed experimentally that seal-β shows similar good sealing performance also in LLC-B and LLC-C, that is to say, these countermeasures are also effective to prevent deposition of phosphorus (P), Fe, Cu, and DM.

Conclusion

The mechanisms and countermeasures of three types of deposit formation on sealing surfaces of water pump seals are summarized as follows:

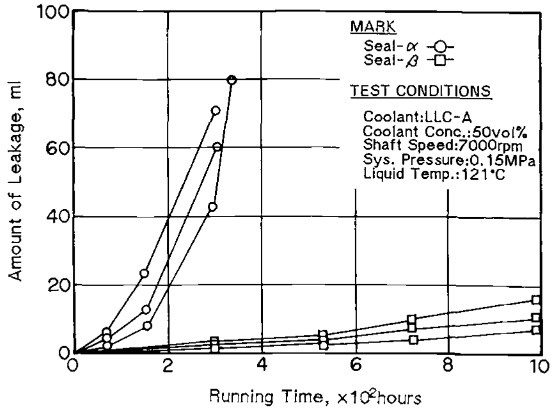


FIG. 22—*Time change of leakage in durability tests.*

Mechanisms of Deposit Formation

1. Deposition of silicate—Frictional heat of mechanical seals accelerates the process from a state of silicate gel into the solidified film as a result of the condensation reaction by dehydration. The solidified film adheres and grows on the sealing surface side with higher wetting free energy.
2. Deposition of P, Fe, and Cu—As a result of an increase in concentration of ferrous ions caused by deterioration of the LLC, the self catalytic reaction promotes ferrous deposition on rubbing surfaces in the presence of phosphate, and, subsequently, a thin layer of Cu is formed on the surface of the ferrous deposit.
3. Deposition of DM—The precipitation of DM occurs as a result of dissolution from rubber radiator hoses. The DM precipitate is concentrated by frictional heat and adheres to the sealing surfaces.

Countermeasures for the Deposition

1. *Rubbing materials*—Selection of combination of rubbing materials having lower wetting free energy.
2. *Surface roughness*—Finishing in an appropriate range of mating ring surface roughness in relation to wetting free energy of the seal ring surface.
3. *Seal construction*—Improvement of the seal construction to increase transfer of frictional heat.

Acknowledgment

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Stephen M. Woodward[1] *and Aleksei V. Gershun*[1]

Characterization of Used Engine Coolant by Statistical Analysis

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REFERENCE: Woodward, S. M. and Gershun, A. V., **"Characterization of Used Engine Coolant by Statistical Analysis,"** *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 234–247.

ABSTRACT: Since the 1950s, the most common choice of engine coolant has been a 50:50 mixture of ethylene glycol and water, with the ethylene glycol containing selected corrosion inhibitors and other additives such as nitrates, silicates, borates, phosphates, tolyltriazole (TTZ), mercaptobenzothiazole (MBT), antifoam, molybdates, silicones, dye, surfactant, and alkalinity builder. Manufacturers in Europe and Asia use a different corrosion inhibition technology than those used in North America.

The function of the engine coolant is simple, to remove the heat from the engine and to protect the engine from corrosion and pitting of the metal surfaces. As the coolant accumulates miles or hours in a vehicle cooling system, it develops many different types of problems. With time, the inhibitors deplete, the ethylene glycol degrades, the pH of the coolant solution decreases, and corrosion starts to take place. Silicates can combine with excessive levels of magnesium or calcium, thus losing their ability to protect aluminum; MBT is easily oxidized and results in loss of copper protection; and phosphates can combine with calcium and magnesium to form an insoluble sediment.

A consequence of this chemistry is that the coolant that comes out of an automobile after time and use can be significantly different than what went into it. With the increased emphasis placed on proper waste disposal and recycling of used coolant, it is important to understand what is coming out of the car.

During 1989 and 1990, a statistically valid survey and characterization of used engine coolant was taken from commercial automotive service centers. The purpose of the survey was to characterize the condition of a typical used engine coolant. The samples were evaluated for suspended matter, and analyzed for pH, reserve alkalinity (RA), percent ethylene glycol (EG), diethylene glycol (DEG), propylene glycol (PG); the presence of degradation acids (acetate, glycolate, formate, and ethylenediaminetetraacetate [EDTA]); the level of inhibitors (nitrites, nitrates, TTZ, MBT, benzotriazole [BZT], benzoate), oil, chloride, fluoride, sulfate concentrations, and 14 other elements (Al, B, Ca, Cu, Fe, K, Mg, Mo, Na, P, Pb, Si, Sn, Zn) in their soluble and insoluble forms. The samples were also tested following U.S. Environmental Protection Agency (EPA) guidelines to determine if the engine coolant would be considered a hazardous waste.

This paper presents the findings of this survey and shows the variation in the condition of engine coolant taken from automobiles at the time the average consumer decides to change the fluid.

KEYWORDS: automotive, antifreeze, engine coolant, characterization, used antifreeze

In the early 1980s, the Home and Automotive Products Division of Union Carbide, which later became First Brands Corporation, conducted a survey entitled "A One Thousand Car Assessment of the U. S. Car Population Cooling System" [*1*]. The objective of this survey was

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[1] Senior development chemist and project scientist, respectively, Coolant Group, First Brands Corporation, 55 Federal Rd., Danbury, CT 06108-4001.

to determine the quality of engine coolant in cars currently on the road and to compare that with the recommended procedures as published by the major U. S. auto manufacturers. The results showed that there was a "general state of neglect of the engine cooling system and the lack of proper attention being paid to the service recommendations of the car manufacturers" [*1*]. This survey is different in that the evaluation is made at the end of the coolant's life. In addition, the samples taken were analyzed for their basic chemical components using current techniques.

As chemical costs and disposal charges escalate, used coolant is slowly becoming a commodity as a resource for raw materials such as ethylene glycol (EG) and recycled engine coolant. In addition to the obvious environmental benefits, the magnitude of the potential source of recycled EG dictates that new technology be developed at a reasonable cost to take advantage of this opportunity.

As a result, it became necessary to identify the ingredients of the coolant at the end of its useful life defined by the consumer. This information will help develop a database to address other important questions: What is the legal classification of used coolant? How do analytical test methods impact hazardous classification? What is the environmental impact of used coolant disposal? What role does variation in used coolant composition have on efforts to recycle it? All of this leads back to the need for a detailed survey of the composition of typical used coolant.

First, we must address the question: "What is the definition of a used coolant?" For our purposes, used coolant is a material that has been functioning in the cooling system of an internal combustion engine and now has been removed because of a perceived lack of performance.

This survey, entitled "Characterization of Used Engine Coolant by Statistical Analysis," includes a variety of automobile makes and model years, and addresses population variation as well as averages for used coolant.

Survey Procedure

This survey deals with coolant that has been removed from vehicles during routine maintenance service. The owner has decided to replace the coolant in the car with a fresh fill, as a result of a scheduled mileage time table, a visual inspection by the vehicle owner, or an inspection by a service station attendant during a routine oil change. The engine coolant was removed and replaced by a service technician. This survey, therefore, does not necessarily represent do-it-yourselfers' changing habits. This survey is confined to used coolant from automobiles and light-duty trucks and does not address heavy-duty vehicles.

Interviews were conducted at several of the service centers while the coolant was changed. Figure 1 shows the breakdown of vehicle types that came in for an engine coolant change as a function of manufacturers. For comparison, Fig. 1 presents the percentage of the vehicles serviced against the ratio of vehicles sold in the U. S. during the last 6 years [*2,3*]. The survey test sample corresponds to the cross section of cars on the road. The average coolant change interval is shown in Fig. 2. It occurred every 2 to 3 years, with the most common period being every other year. It is interesting to note that the coolant age of at least 41.3% of the vehicles sampled was 3 years and older.

The coolant was collected over an 18-month period between April 1989 and September 1990. The samples were tested at the time of receipt.

The samples were collected from service stations along the eastern section of the country, ranging from New England to Georgia, from ten different sources (Table 1). The coolant was collected and stored as individual vehicle samples, as a combined sample of 15 to 25 vehicles (in 55-gal drums), or in a bulk truck (5000 gal). The breakdown indicates a solid cross-sectional

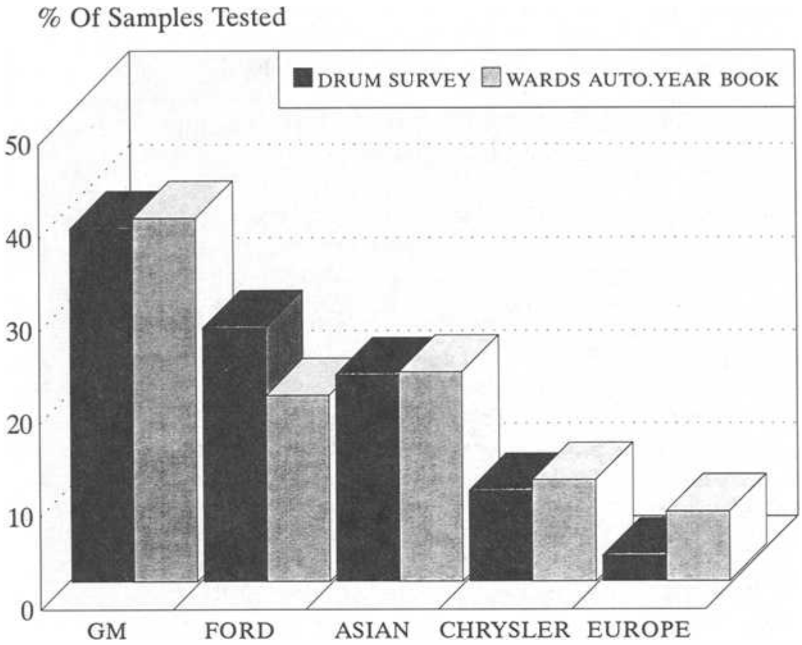


FIG. 1—*Population of samples by manufacturer share.*

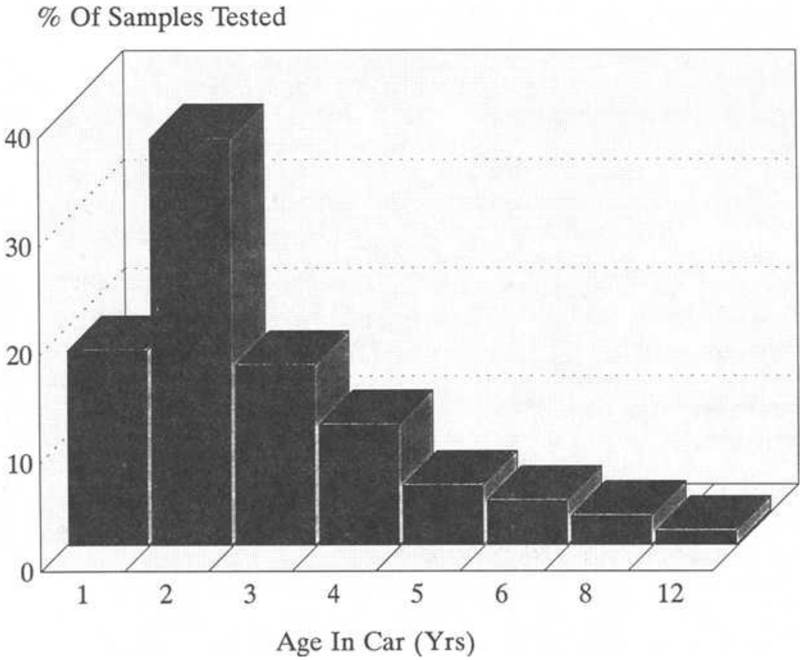


FIG. 2—*Population of samples by coolant age.*

TABLE 1—*Used engine coolant survey.*

Area	# Vehicles	# Samples	Sampled As
New England	2000	1	5000-Gal truck
	75	5	55-gal drum
	25	25	Individual car
	2100		
New York	135	9	55-gal drum
	33	33	Individual car
	168		
Georgia	240	16	55-gal drum
TOTAL	2508	89	6757 Gal

NOTE: 2 gal = 3.8 L.

base to allow generation of variance data, as well as a large sample size, which adds significance to the average data. The total sample includes the results of over 2500 cars.

Analytical Techniques

It is important to understand the techniques involved in quantifying used coolant. As seen on Table 2, gas chromatography was used to identify the glycols, high performance liquid chromatography was used to identify the organics, ion chromatography was used to identify the inorganic anions, and standard laboratory techniques were used for pH (ASTM Test Method for pH of Engine Antifreezes, Antirusts, and Coolants [D-1287]) and reserve alkalinity (ASTM Test Method for Reserve Alkalinity of Engine Coolants and Antirusts [D 1121]). One of the more critical tests was the elemental analysis completed by inductively coupled plasma emission spectroscopy (ICP). This is because it measures the concentration of heavy metals, which determines if a material should be classified as a hazardous waste. Recognizing the importance and sensitivity of this method, special care was taken to avoid errors caused from interferences by this complex matrix or by different coolant sample viscosities (caused by glycol concentration differences between the sample and the standards).

The EPA has set strict guidelines for characterization of a material as a hazardous waste [*4*]. The guidelines include a list of hazardous materials and upper limits for each listed material. In addition, sample preparation plays a key role in the characterization of the potential hazard level. The EPA has defined sample preparation methods. Table 3 shows the recent history of EPA test methods for heavy metals such as lead (Pb).

In 1989, one of the definitions for characterizing waste was called the extraction procedure toxicity test (EP Tox) [*5*]. For used engine coolant, the primary concern is the presence of

TABLE 2—*Lab methods.*

Analysis Required	Method Used
Physical properties	pH Meter, Karl Fisher
Oil	Babcock bottle method
Ethylene glycol, diethylene glycol, propylene glycol	Gas chromatography
Nitrite, nitrate, chloride, fluoride, sulfate, benzoate	Ion chromatography
TTZ, BZT, MBT, degradation	Liquid chromatography
Elemental analysis—Al, B, Ca, Cu, Fe, K, Mg, Mo, Na, P, Pb, Si, Sn, Zn	Inductively coupled plasma emission spectroscopy

TABLE 3—*EPA test methods, lead contamination.*

Contaminent	EP Toxicity	TCLP
Effective date	1986–Sept. 1990	Oct. 1990–?
Filtration size	0.45 μm	0.6–0.8 μm
Maximum lead allowed	5 ppm	5 ppm

EP Toxicity = extraction procedure toxicity test; TCLP = toxicity characteristic leaching procedure.

heavy metals, specifically Pb. The source of Pb in used coolant is from the solder used in copper/brass radiators and heater cores that have corroded. Sample preparation consisted of filtering the sample through a 0.45-μm filter and then conducting an analysis on the filtrate. The solids were extracted for analysis only if the solids exceeded 0.5% by weight of the original coolant. This served as the definition for soluble versus insoluble material.

In September 1990, the EPA replaced the EP Tox test with the toxicity characteristic leaching procedure (TCLP) [*4*]. The major difference is that the filter has been changed from 0.45 μm to a filter which has 0.6 to 0.8-μm pore size. The net effect of this change is that the soluble fraction has increased. TCLP was used to define solubles versus insolubles for this presentation.

Analysis of Components

The analysis of the used coolant samples has been broken into several groups as shown on Table 4. These groups include properties, residual inhibitors, corrosive contaminants, EG degradation products, corrosion products, and gravimetric analysis. Gravimetric analysis covers the characterization of the insoluble or suspended solids.

Properties

Table 5 presents the averages and standard deviation for pH, reserve alkalinity (RA), and the percent glycols, including EG, diethylene glycol (DEG), and propylene glycol (PG). The pH and RA are measures of the buffering capacity of the coolant, which maintains a stable inhibitor package. The glycols represent the freeze point protection. EG is the primary agent. DEG, a byproduct of the EG manufacturing process (with less freeze point depression characteristics), is added to extend the EG base. PG has also been used as an extender for EG during EG shortages and as a direct replacement for EG, although PG is not as effective for freeze point as EG [*6*]. The RA shown here is defined as the number of milliliters of one tenth normal hydrochloric acid required to neutralize 10 ml of the engine coolant. Based on a 50% solution

TABLE 4—*Used engine coolant characterization.*

- Properties
- Inhibitors
- Corrosive contaminants
- Degradation products
- Corrosion products
- Gravimetric analysis

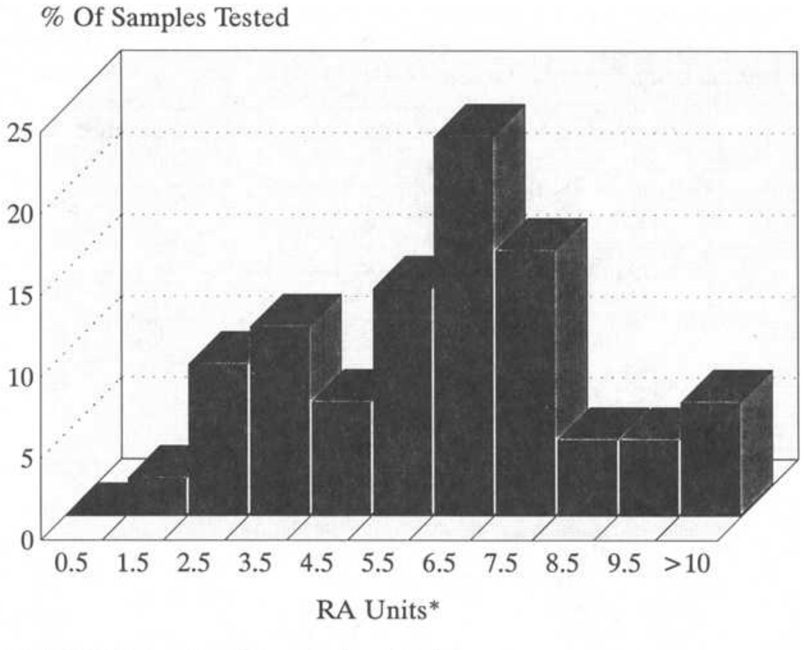
TABLE 5—*Typical used engine coolant, properties.*

Properties	Average	Standard Deviation
pH	8.48	0.62
Reserve alkalinity	6.10	2.51
Ethylene glycol, wt%	53.72	11.63
Diethylene glycol, wt%	2.76	1.07
Propylene glycol, wt%	0.37	1.02

of several leading national brands, the RA would be between 6.4 and 7.4 [*1*]. For the purposes of this paper, we considered a 50% depletion as one definition of an ineffective coolant. Figure 3, which is a summary of RA data, shows that over 13% of the samples tested fall into this category. Figure 4 represents the percent EG of the samples. On average, the percent glycol was 53.7% by volume, which is acceptable. However, the range is wide with values as low as 11.5% by volume to as high as 76.6% by volume EG. There was very little evidence of PG.

Residual Inhibitors

The most commonly used inhibitors are listed in Table 6. The inhibitors listed include those found in vehicles in this country from North American, European, and Asian formulations. As you can see, the variation (defined as plus or minus two standard deviations) of each material measured is at least equal to the averages. You could predict with 95% confidence that the



* ml of 0.1N HCl titrating 10 ml AF to pH 5.5

FIG. 3—*Reserve alkalinity distribution.*

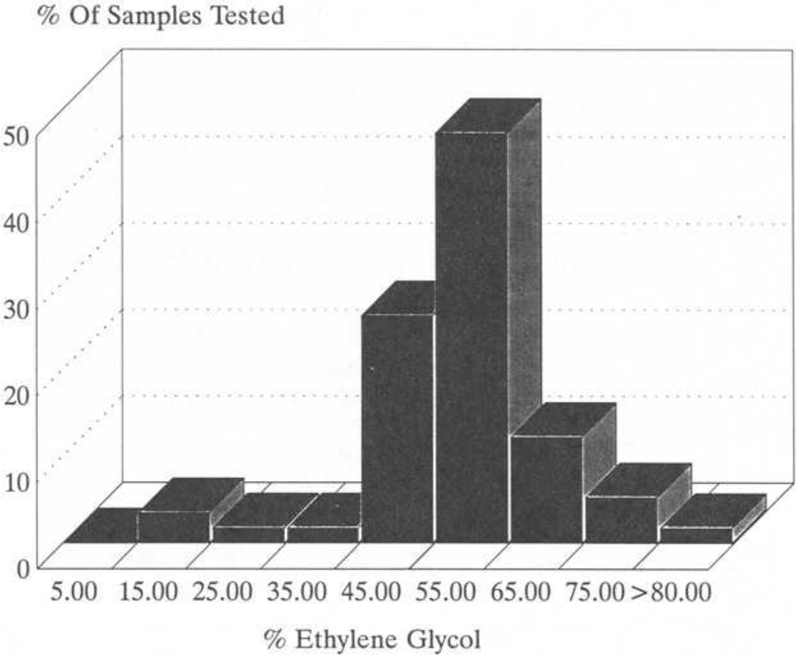


FIG. 4—*Percentage ethylene glycol distribution.*

value of any inhibitor could be between 0 and twice the average listed here. Anyone skilled in the art recognizes that an effective coolant formulation (either original or recycled) requires the correct inhibitors, the correct amount of those inhibitors, and the correct balance of those inhibitors. The advantages and disadvantages of each inhibitor must be understood and balanced. Let's take a look at some examples of the variation of some commonly used coolant additives.

Figure 5 shows the distribution found for nitrate (NO_3^-). It is an inhibitor commonly used

TABLE 6—*Typical used engine coolant, inhibitors (soluble).*

Inhibitors	Average	Standard Deviation
Nitrite	77.99	214.59
Nitrate	981.94	503.96
Tolyltriazole	395.87	238.94
Benzotriazole	91.29	51.61
Mercaptobenzothiazole	14	86.26
Benzoate	2347.57	3890.95
Borate (as B)	403.04	271.16
Molybdate (as Mo)	44.19	115.22
Phosphate (as P)	656.51	550.98
Silicate (as Si)	48.98	25.94
Potassium	1180.6	1349.94
Sodium	2706.19	1028.4

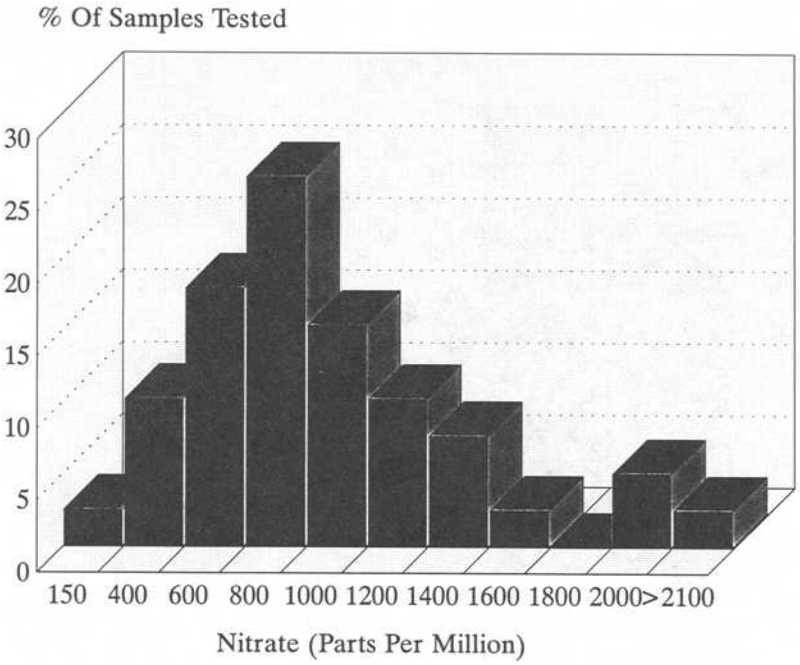


FIG. 5—*Nitrate distribution.*

to prevent pitting corrosion on aluminum (Al) [*7*]. The histogram shows a bimodal distribution with one center around 800 to 900 ppm and the second smaller one around 2000 ppm. Figure 6 shows the distribution for boron (B). Boron is commonly used in the form of sodium borate, borax, or boric acid. It buffers the solution at a desired pH and prevents the pH from dropping to a range where the corrosion of cast iron and steel is unacceptably high [*7*]. There are wide ranges and non-normal distributions for these various inhibitors found in engine coolant.

Corrosive Contaminants

Table 7 lists some of the corrosive contaminants found in a coolant system. Chloride, sulfate, and fluoride can be introduced into the cooling system by way of the water used to adjust the freeze point, during cleaning, or during conditioning of the cooling system. Another potential source of sulfate is the degradation of mercaptobenzothiazole (MBT; if present in significant quantities). Because these contaminants are common, the performance test methods for evaluating engine coolant outlined in ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light Duty Service (D 3306) define a corrosive water, which contains set amounts of these anions to dilute the concentrated coolant samples to the proper concentration before testing. Corrosive water is defined by ASTM as deionized water containing 100 ppm each of sulfate, chloride, and bicarbonate introduced as sodium salts.

The chloride level found in these vehicles is similar to the level that would be achieved with corrosive water as used in ASTM D 3306. However, the sulfate level is significantly higher than in the standard. These water quality levels were consistent in all the samples taken.

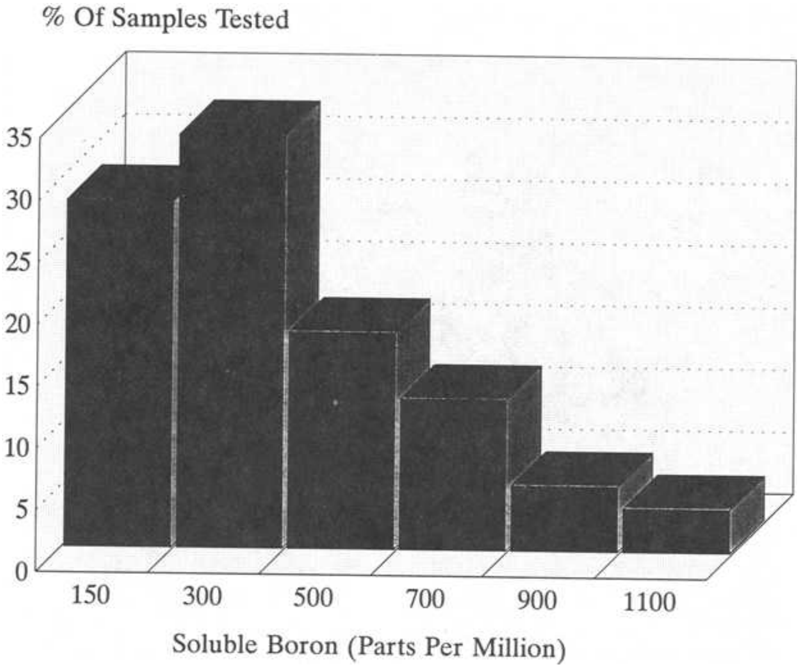


FIG. 6—*Boron (soluble) distribution.*

Degradation Products

Table 8 lists some of the degradation products found in used coolants. This list includes the soluble salt forms of the carboxylic acids generated by the thermal decomposition of ethylene glycol. The formation of acetates, glycolates, and formates depletes the reserve alkalinity when the acids are formed. The level of glycol degradation products varied from sample to sample; however, the ratio of glycolate to formate to acetate remained relatively stable at 29:11:6, respectively. They all are soluble at this level in 50% glycol/water mixtures.

Also included are the insoluble or precipitated corrosion and deposition products of the interaction of inhibitors with the coolant system and with calcium (Ca) and magnesium (Mg) found in the dilution water. The concern with insoluble inhibitor products is that, at certain levels, they could have two negative results. The first is that they reduce the desired effectiveness of the inhibitors, which can create a system imbalance promoting corrosion and can act as a physical catalyst for further precipitation. The second result is that these insolubles may reduce the efficiency of cooling system components (that is, reduce or restrict the flow through the heater core and radiator, and so forth).

TABLE 7—*Typical used engine coolant, corrosive contaminants, ppm.*

Contaminents	Average	Standard Deviation
Chloride	54.40	74.86
Sulfate	269.45	199.30
Fluoride	146.00	101.00

TABLE 8—*Typical used engine coolant, degradation products, ppm.*

Products	Average	Standard Deviation
Acetate	147.55	77.50
Glycolate	722.17	918.1
Formate	278.37	155.6
Insoluble		
B	29.07	12.4
Ca	9.66	58.35
K	19.91	50.61
Mg	4.35	5.69
Mo	1.04	1.58
Na	76.64	35.58
P	28.28	28.64
Si	19.94	94.03

Corrosion Products

Table 9 lists the soluble and insoluble corrosion products found in the used coolants tested. These materials represent the metals commonly found in cooling systems. As discussed earlier, the soluble data are identified by measuring the ion level of a coolant that has been filtered through a 0.7-μm filter, and the insoluble measurement was made on the material trapped on the filter, which is then acid digested [*4*]. There are two implications from the generation of soluble and insoluble metals suspended in the coolant. The first concern is that, as the concentration of suspended solids increases, this can cause abrasion of surfaces and dramatically increase the chance of water pump failures, radiator clogging, and insulating barriers. The second concern is based on the regulatory impact of dissolved heavy metals in used coolants.

The most common way that a used coolant could be classified as a hazardous waste by the federal government is if it is characterized as containing heavy metals such as Pb. Used engine

TABLE 9—*Typical used engine coolant, corrosion products, ppm.*

Products	Average	Standard Deviation
Soluble		
Aluminum	2.68	2.22
Copper	0.69	7.27
Iron	2.73	17.52
Zinc	4.65	20.34
Lead	2.85	3.6
Insoluble		
Aluminum	10.71	15.15
Copper	1.98	7.91
Iron	43.53	29.53
Zinc	6.13	8.58
Lead	15.49	23.78

coolant is not listed by the federal government as a hazardous waste. We have conducted studies on data from 55-gal drum quantities of used coolant including EP Tox and TCLP methods [*4,5*]. Each drum typically contained coolant from 15 to 25 different vehicles. Using the soluble portion of the coolant, it is predicted that 20% of used engine coolant will have Pb in excess of 5 ppm. The impact of this issue on engine coolant recycling has not been fully addressed, but it is clear that all disposal options are important and that recycling efforts should not be discouraged.

Gravimetric Analysis

The final means that we have used to characterize used coolant is gravimetric analysis. The functionality of a fluid can be identified by concentrating on the suspended or insoluble fraction of a used coolant. Usually, a visual inspection of a sample allows conclusions to be drawn based on its color and turbidity. Determining the total suspended solids analytically provides a better determination of the deterioration of a coolant's effectiveness. After the solids are collected on a 0.7-μm filter, the filter is dried at 180°C until the weight loss stabilizes. Figure 7 shows that there is a significant range of values in the samples tested. We believe that a high level of suspended solids indicates a failed coolant. Over 25% of the samples tested contained more than 500 ppm suspended solids.

The suspended solids were further characterized by particle size (Table 10). The objective was to determine the theoretical effectiveness of different filtration techniques on the removal of particulate matter. It was found that over 10% of the suspended matter was less than 5 μm in diameter.

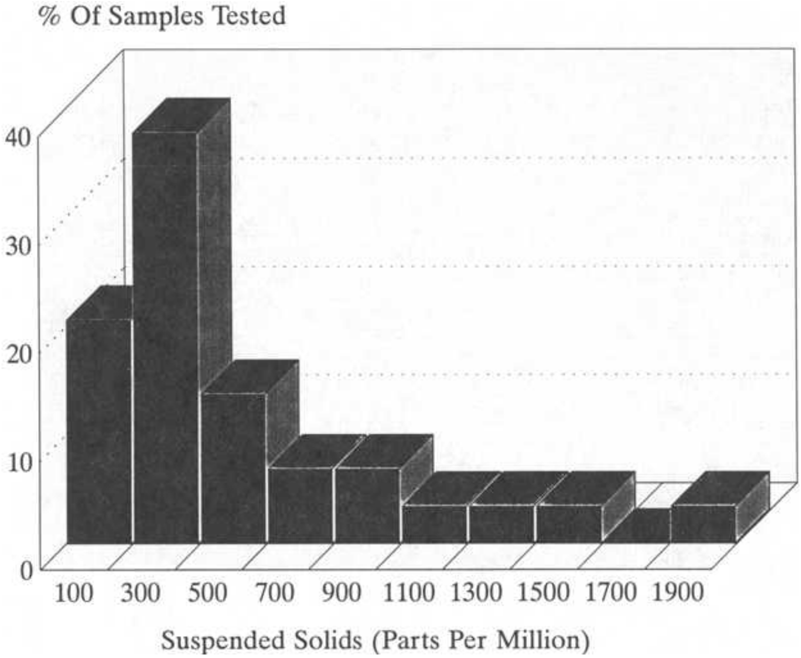


FIG. 7—*Total suspended solids.*

TABLE 10—*Typical used engine coolant, particle size distribution.*

Particle Size, μm	Percent
< 0.1	0.1
0.1–.45	0.3
0.45–.7	0.4
0.7–1.0	0.8
1.0–2.5	4.0
2.5–5.0	7.0
5.0–15.0	9.0
15.0–25.0	13.0
25.0–50.0	15.4
50.0–100.0	13.0
>100.0	37.0

Summary and Conclusions

This 1989/1990 survey has shown that in many cases, the point at which the consumer decides to change engine coolant is well beyond its useful life. Over 41% of consumers have the same coolant for more than 2 years in vehicles. The inhibitors have been significantly depleted. Corrosion is evident to some degree in a majority of vehicles. In addition to the damage to the cooling system, the lack of good maintenance has generated soluble heavy metals such as Pb, which represents a hazardous waste situation. The survey also shows the continuing problem with consumers' lack of appreciation for having the recommended engine coolant concentration, as pointed out in the earlier survey [*1*]. This not only increases the risk of damage from boilovers and freezeups, but it also accelerates the rate of corrosion due to lower inhibitor levels.

This survey indicates a significant variation among coolants at the perceived end of their functionality. Treatment of used coolant for the purposes of recycling either on-site or off-site presents many challenges. The variety of engine coolant formulations on the market as well as the variation of coolant condition requires careful consideration when evaluating different recycling techniques.

The engine coolant industry must be environmentally conscious and proactive in addressing the issues of used coolant, but, at the same time, they must preserve the integrity and performance standards of engine coolant for automotive and heavy-duty cooling systems.

References

[*1*] Cooper, N. R., Hannigan, H. J., and McCourt, J. C., "A One Thousand Car Assessment of the U.S. Car Population Cooling Systems,"; SAE Report 831821, Society of Automotive Engineers, Warrendale, PA, 5 Dec. 1983.

[*2*] *Ward's Automotive Yearbook 1990,* Ward's Communications, Detroit, 1990.

[*3*] *Ward's Automotive Yearbook 1987,* Ward's Communications, Detroit, 1987.

[*4*] "Hazardous Waste Management System: Identification and Listing of Hazardous Waste, Environmental Protection Agency," 40 CFR Part 261, *Federal Register,* Vol. 55, No. 61, March 29, 1990.

[*5*] "Hazardous Waste Management System: Identification and Listing of Hazardous Waste; Environmental Protection Agency," 40 CFR Part 261, Test Methods for Evaluating Solid Waste, SW-846, U.S. Environmental Protection Agency, National Technical Information Service, Springfield, VA, 3rd ed., Nov. 1986, pp. 1310–1311.

[*6*] Curme, G. O., Jr, Ed., "Glycols," American Chemical Society Monograph Series, Reinhold Publishing Co., New York, 1952.

[*7*] Chiasson, B. A., "An Overview of Antifreeze Chemistry," internal First Brands Corp. memo, May 10, 1988.

DISCUSSION

P. Dittmar[1] *(written discussion)*—My questions relate to the issue of proper disposal under RCRA:

1. What conclusions has First Brands reached regarding whether used antifreeze should generally be considered TCLP-Hazardous?
2. Of the samples analyzed, how many were taken directly from vehicles? Is there any statistically significant difference between the sample sets taken from vehicle versus others, perhaps revealing the effects of cross-contamination with other shop wastes?
3. What fraction of samples showed TCLP soluble lead in excess of the EPA 5-ppm threshold?
4. Do the lead data follow a normal definition? If so, what is the upper limit of the data as defined in EPA Method SW846?
5. To what extent was perchloroethylene observed and to what detectability limit?

Stephen M. Woodward (author's response)—1. First Brands has not made any conclusions about the classification of used antifreeze as an EPA Hazardous waste. We do recommend that if any one or more of the following apply, then the material should be treated as if it were hazardous:

(a) State and/or local regulations require it.
(b) A representative sample of the material on hand has been analyzed and has been found to contain lead above the standard.
(c) A history of representative samples shows that lead levels have exceeded the standards for that specific location on a regular basis.
(d) No sampling has been done and no recognized form of recycling is being used that would remove the hazardous material or deactivate it.

2. Fifty-eight of the coolant samples were taken directly from the vehicles. The only cross-contaminant that was identified in our samples was oil. There was only a slight difference found, but no test for significance was conducted.

3. We did not conduct TCLP analysis on every sample, however, based on our data, it is predicted that at least 80% of the vehicles will not exceed 5-ppm soluble lead (after filtration through a 0.7-μm paper).

4. The distribution of data for lead was not a normal distribution because the lower limit is bound by zero. At this time, the upper statistical limit based on EPA Method SW846 is not known.

5. Perchloroethylene was not part of the initial list of materials to analyze for because it is not in any known antifreeze formulation and it is not part of any OEM cooling system preparation. As a result of a Safety-Kleen letter stating that it was used by OEMs in the preparation of radiators, several samples of used coolant and several samples from vehicles with less than 50 miles (80 km) on the odometer were tested and perchloroethylene was not detected in any samples by our methods (2-ppm limit of detection).

J. A. Lima[2] *(written discussion)*—One of your specimens was from a system that had not been changed in 12 years, if I understand correctly. I assume that it was a standard North

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[1] Safety Kleen Corp., 1255 W. Old Higgins Rd., Elk Grove Village, IL 60007.

[2] Houghton Chemical Corp., Allston, MA.

American coolant, and am wondering what you think the practical life of a North American coolant might be, if proper charging procedures and de-ionized water were used in the initial fill?

Stephen M. Woodward (author's response)—The intent of this survey was not to determine the theoretical life of a coolant that was under ideal conditions, but rather, the objective was to characterize the quality of the used coolant under "real" conditions. The 12-year-old coolant that was collected was mixed in a drum at the service station and could not be segregated and analyzed.

Richard D. Hercamp[1] *and Robert A. Remiasz*[2]

Coolant Maintenance and Extension of Coolant Life for Light Duty Vehicles

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REFERENCE: Hercamp, R. D. and Remiasz, R. A., "**Coolant Maintenance and Extension of Coolant Life for Light Duty Vehicles,**" *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 248–257.

ABSTRACT: For many years coolant has been maintained and coolant life extended for heavy duty vehicles by using periodic additions of supplemental coolant additives (SCAs) and, in many cases, use of on-board by-pass filtration of the coolant. This concept has now been applied to light duty vehicles using a system consisting of coolant testing, off board full flow coolant filtration, and SCA addition to the coolant. In this manner, coolant life in light duty vehicles may be safely extended.

The system used to maintain and extend the life of the coolant is described. Glassware, bench, and simulated service testing data are reported, which support this approach.

KEYWORDS: engines, light duty vehicles, engine coolant, life extension, recycling, additives, filtration, corrosion, filling and flushing, maintenance

Several years ago the combination of an ethylene glycol shortage and increasingly stringent environmental laws caused vehicle service organizations to investigate methods of conserving automotive light duty antifreeze. The ethylene glycol shortage was short-lived, but disposal regulations continued to become tighter. The interest in reducing the volume of coolant disposal is expected to continue.

The current issue concerns itself with disposal of light duty (LD) antifreeze. The Environmental Protection Agency's (EPA) guidelines for reducing waste disposal volume consists of a hierarchy of approaches [*1*]. In descending order of desirability, they are as follows:

1. Design the product to last longer.
2. Extend the useful life of the product.
3. Recycle the product.
4. Properly dispose of the product.

Consistent with the EPA's primary approach, original equipment manufacturers (OEM) have become more interested in longer life LD coolants. Work has been underway at several laboratories. Texaco, for example, has reported on a portion of their work [*2*]. Additionally ASTM D 15 on Engine Coolants has formed a task force to start work to develop a specification for a long-life coolant for light duty engines.

Consistent with the EPA's secondary approach, heavy duty (HD) engine OEMs have used periodic addition of supplemental coolant additives (SCAs) and on-board coolant filtration

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[1] Consultant, Daubert Industries, 55E 1100S, Columbus, IN 47201.
[2] ECP Inc., Daubert Industries, 4700 S. Central Ave., Chicago, IL 60638.

for over 30 years [3]. The lives of HD coolants are routinely extended to 290 000 km (180 000 miles) or more [4].

For the last ten years, the U.S. military has successfully used their MIL-A-53009 SCA to extend coolant life in LD vehicles [5]. More recently, several commercial ventures have offered LD SCAs for coolant life extension. This paper offers data developed to support one of these programs.

Coolant or ethylene glycol recycling (EPA's tertiary approach) is often confused with coolant extension. In March 1989, the National Automotive Radiator Service Association sponsored an all day Forum on Coolant Recycling and Disposal. Shortly thereafter ASTM formed a Subcommittee on Recycled Coolant (D 15.15). As would be suggested by the titles, both groups focused on the recycling of spent coolant.

It is worth noting that it is not the intention of the authors to suggest that any coolant, regardless of its condition, is extendable. A coolant that has, or is about to fail, is not considered extendable. It should be recycled or disposed of.

A comparison of HD and LD systems is provided in Table 1.

A System to Maintain and Extend the Useful Life of Coolants for Light Duty Vehicles

A system has been developed to effectively extend the useful life of LD coolants. This system includes qualification of the coolant by chemical, physical, and visual means; and extension of the coolant life by filtering and the addition of an SCA. If the coolant does not qualify, it is removed for recycling or disposal.

The following quick checks are made to determine whether or not the coolant is extendable. Since the concept of the system is to extend the coolant life and keep it in good condition, it is vital to perform the maintenance at about the same mileage that light duty vehicle manufacturers have recommended that the coolant be replaced with new coolant, generally about 50 000 to 65 000 km. Therefore, the first criteria to determine if the coolant is maintainable is that the coolant shall not have more than 65 000 km of use since new, or since its last maintenance with this system.

Second, if the coolant is oily, murky, or rusty, it indicates that the coolant has been contaminated by foreign material or that excessive corrosion has already occurred. In either case the coolant must be removed, the cooling system cleaned thoroughly, and repairs made to correct any cooling system problems.

Third, if the glycol level is less than 25% or the reserve alkalinity (RA) less than 3 (for domestic vehicles), it can be concluded that corrosion, scaling, and so forth, has already occurred to the extent that the coolant should be removed, the cooling system cleaned, and the cause for the dilution or loss of RA determined and corrected. The glycol level and RA level can be

TABLE 1—*A comparison of HD and LD cooling systems.*

HD	LD
OEM recommends draining and flushing at ≈ 300 000 km	OEM recommends draining the system at 50 000 to 65 000 km
Typically 90% of the coolant can be drained	Typically 50 to 75% of [6] the coolant can be drained
Typical capacity of cooling system is 32 to 56 L	Typical capacity of cooling system is 8 to 14 L
Routinely extended to 290 000 km or more, with maintenance and SCA addition	Extendable with proper maintenance and SCA addition
Life of vehicle typically 1 600 000 km, or more	Life of vehicle typically 200 000 km or more

FIG. 1—*Coolant filtration device.*

conveniently determined using a 2 pad test strip [*7*]. If these 3 checks are positive, the coolant is deemed extendable and is maintained. If not, the coolant is removed for recycling or disposal.

The device described in the Appendix is attached to circulate and filter the coolant (Fig. 1). (The benefits of filtration for HD engine coolants have been shown [*3*], and it can be assumed that filtration is also beneficial for LD engine coolants.) SCA is then added to reinhibit and extend the life of the coolant, and glycol or water is added to achieve a 50% glycol final mixture. The SCA is also described in the Appendix.

Performance Testing

Since extension of LD engine coolant life is relatively new and no industry standards of performance exist, it was decided to run modified performance tests listed in ASTM Specification for Ethylene Glycol Base Engine Coolant for Automobile and Light Duty Services (D 3306). These tests were run on used coolant both as received and after treatment. The tests were modified in that the same amount of corrosive agent added to new coolant concentrate, for which the tests procedures are written, was added to the sample coolants. A somewhat different approach using simulated depleted coolant has been reported which was used to evaluate proposed SCA's for LD engine use [*8*]. Since the SCA we use had already been developed with chemistry similar to the additive specified for the GM 6043 [*9*] coolant concentrate (antifreeze), we chose to test used coolant from the field rather than simulated depleted coolants.

A test using six domestic light duty vehicles with mileages exceeding the 65 000-km criteria mentioned previously was designed to measure the performance in ASTM Test Method for Corrosion Test for Engine Coolants in Glassware (D 1384) and ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions (D 4340) corrosion tests, both before and after coolant maintenance. The higher mileage coolants were used to make the test more severe. Unfortunately, a mixup occurred, and one set of data had to be discarded. The performance data for the other 5 are shown in Tables 2 through 6. Coolant analysis results are shown in Table 7.

TABLE 2—*1986 Mustang, 46 959 miles, pump replaced at 9916 miles, 1 gal antifreeze added, no other maintenance, 2.3 L.*

	Results of ASTM D 1384 Glassware Testing on ECP 524122					D 4340
	Weight Loss, mg/Sample					Average of 2 Tests
Coupon Type	1	2	3	Average	Maximum Allowed*	Maximum (1)
			As-Received			
Copper	2	2	2	2	10	
Solder	3	3	5	4	30	
Brass	5	5	2	4	10	
Steel	0	3	0	1	10	
Cast iron	120	106	115	^114^	10	
Cast aluminum	93	75	103	^90^	30	^9.99^
			After Treatment			
Copper	1	2	2	2	10	
Solder	5	6	6	6	30	
Brass	2	1	2	2	10	
Steel	0	0	2	1	10	
Cast iron	5	2	5	4	10	
Cast aluminum	8	2	3	4	30	0.028

NOTES: *: ASTM Specification for Ethylene glycol Based Engine Coolants (D 3306). ^: Exceeds ASTM D 3306 maximum weight loss. 1 mile = 1.609 km.

TABLE 3—*1985 Celebrity, 68 281 miles, Car 425.*

	Results of ASTM D 1384 Glassware Testing on ECP 524124					D 4340
	Weight, mg/Sample					Average of 2 Tests
Coupon Type	1	2	3	Average	Maximum Allowed*	Maximum (1)
			As-Received			
Copper	2	2	2	2	10	
Solder	6	7	7	7	30	
Brass	2	3	2	2	10	
Steel	0	2	1	1	10	
Cast iron	0	6	7	4	10	
Cast aluminum	11	6	5	7	30	^16.13^
			After Treatment			
Copper	2	2	2	2	10	
Solder	4	4	4	4	30	
Brass	2	2	2	2	10	
Steel	1	2	1	1	10	
Cast iron	5	4	1	3	10	
Cast aluminum	5	4	6	5	30	0.11

NOTES: *: ASTM Specification for Ethylene Glycol Based Engine Coolants (D 3306). ^: Exceeds ASTM D 3306 maximum weight loss. 1 mile = 1.609 km.

TABLE 4—*1985 Celebrity, 57 699 miles, Car 426.*

Results of ASTM D-1384 Glassware Testing on ECP 524126						D 4340
	Weight, Loss in mg/Sample					Average of 2 Tests
Coupon Type	1	2	3	Average	Maximum Allowed*	Maximum(1)
			As-Received			
Copper	4	4	3	4	10	
Solder	7	10	8	8	30	
Brass	3	3	3	3	10	
Steel	3	3	3	3	10	
Cast iron	6	11	9	9	10	
Cast aluminum	10	7	8	8	30	ˆ16.10ˆ
			After Treatment			
Copper	3	3	3	3	10	
Solder	4	5	5	5	30	
Brass	2	3	3	3	10	
Steel	2	3	3	3	10	
Cast iron	2	4	3	3	10	
Cast aluminum	6	8	6	7	30	0.59

Notes: *: ASTM Specification for Ethylene Glycol Based Engine Coolants (D 3306). ˆ: Exceeds ASTM D 3306 maximum weight loss. 1 mile = 1.609 km.

TABLE 5—*1986 Blazer, 61436 miles, 2.8 L V-6, no maintenance except water addition.*

Results of ASTM D 1384 Glassware Testing on ECP 524128						D 4340
	Weight Loss in mg/Sample					Average of 2 Tests
Coupon Type	1	2	3	Average	Maximum Allowed*	Maximum (1)
			As-Received			
Copper	3	3	2	3	10	
Solder	7	7	7	7	30	
Brass	2	3	2	2	10	
Steel	3	4	4	4	10	
Cast iron	61	79	78	ˆ73ˆ	10	
Cast aluminum	11	11	7	10	30	ˆ12.48ˆ
			After Treatment			
Copper	2	2	2	2	10	
Solder	4	5	4	4	30	
Brass	2	2	2	2	10	
Steel	5	5	5	5	10	
Cast iron	11	13	9	ˆ11ˆ	10	
Cast aluminum	4	4	5	4	30	ˆ19.58ˆ

Notes: *: ASTM Specification for Ethylene Glycol Based Engine Coolants (D 3306). ˆˆ: Exceeds ASTM maximum weight loss (D 3306). 1 mile = 1.609 km.

TABLE 6—*1986 Chrysler Laser, 45 461 miles, 2.2 L Turbo, no known maintenance.*

Results of ASTM D 1384 Glassware Testing on ECP 524130						D 4340
	Weight Loss, mg/Sample					Average of 2 Tests
Coupon Type	1	2	3	Average	Maximum Allowed*	Maximum (1)
			As-Received			
Copper	3	3	3	3	10	
Solder	7	7	6	7	30	
Brass	3	2	3	3	10	
Steel	5	3	4	4	10	
Cast iron	50	48	66	^55^	10	
Cast aluminum	10	6	5	7	30	^6.12^
			After Treatment			
Copper	2	2	2	2	10	
Solder	6	3	5	5	30	
Brass	2	2	2	2	10	
Steel	3	2	1	2	10	
Cast iron	14	12	14	^13^	10	
Cast aluminum	3	1	3	2	30	0.145

Notes: *: ASTM Specification for Ethylene Glycol Based Engine Coolants (D 3306). ^^: Exceeds ASTM D 3306 maximum weight loss. 1 mile = 1.609 km.

All five untreated coolants failed D 4340 by a wide margin, while 4 of the 5 maintained and extended coolants readily passed. Of the untreated coolants, 3 of 5 failed D 1384 by a wide margin, while 3 of the 5 maintained and extended coolants passed. The performance of the remaining 2 maintained and extended coolants was substantially improved, but they did not meet ASTM standards.

TABLE 7—*Coolant analysis results.*

Parameter	1986 Mustang		1985 Celebrity		1985 Celebrity #2		1986 Blazer		1986 Laser	
Treated	no	yes	no	yes	no	yes	no	yes	no	yes
pH	9.3	9.3	10	9.8	9.8	10	9.4	9.4	8.2	8.8
Reserve	5.15	5.1	6.2	7.2	4.2	7.8	4.0	6.3	3.8	5.1
Percent	48%	49%	58%	53%	40%	52%	54%	52%	59%	53%
Freeze	−30	−30	−56	−40	−12	−37	−44	−37	−60	−40
Gly./Formate	240	208	78	97	300	300	460	520	770	611
Chloride	70	75	74	200[a]	80	60	80	84	48	50
NO_2	0.0	0.0	280	260	350	350	0.0	0.0	0.0	0.0
NO_3	1000	830[a]	1000	1500	890	1800	580	1100	2700	2700
PO_4	500	415[b]	2200	3400	1300	3500	960	2200	3300	4000
SO_4	700	600	340	460	500	610	540	550	1400	1100
SiO_3	20	620	200	700	290	1160	120	550	300	800

[a] These results also are not logical, based on the SCA composition. Nitrate should increase appreciably while chloride should remain nearly constant.

[b] When checked by another lab, the phosphate showed an increase of 180% rather than the 17% decrease shown here. The 17% decrease is not logical, based on the SCA composition.

TABLE 8—*ASTM D 4340 test results.*

Coolant	Weight Loss, mg/cm^2/Week
NEW coolant	0.1
NEW coolant with additive	0.0
USED coolant	2.8
USED coolant with additive	0.06

In addition to the above tests, the effect of adding the SCA, without filtration, was studied in the following series of tests with new and used coolant: D 4340, ASTM Test Method for Caviation Erosion—Corrosion Characteristics of Aluminum Pumps with Engine Coolants (D 2809), and a modified 1500 h ASTM Method for Simulated Service Corrosion Testing of Engine Coolants (D 2570). Table 8 shows the improved performance with the additive in D 4340 tests. Table 9 shows the improved performance with the additive in D 2809 tests. Figures 2 and 3 show the improved performance with the additive in the modified 1500-h D 2570 test.

Taken as a whole, these data indicate that coolant, which meets all the criteria, including the 65 000-km limit, will generally be maintainable so that its life can be extended.

Commercial Experience

After 4 years of commercial use of this system to extend the life of coolant in 115 000+ vehicles, warranty figures show that only 28 claims have been filed for cooling systems failures.

Conclusions

Both lab tests and field experience show that, with proper maintenance at 50 to 65 000-km intervals, coolant life in light duty vehicles can be safely extended.

Proper maintenance includes coolant analysis, filtration, and addition of a well formulated SCA.

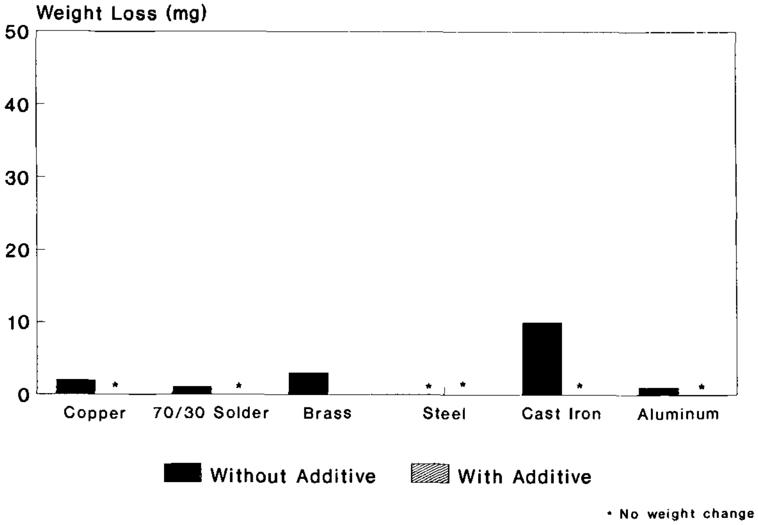

FIG. 2—*Average weight loss of coupons from 1500-h simulated service tests (new coolant).*

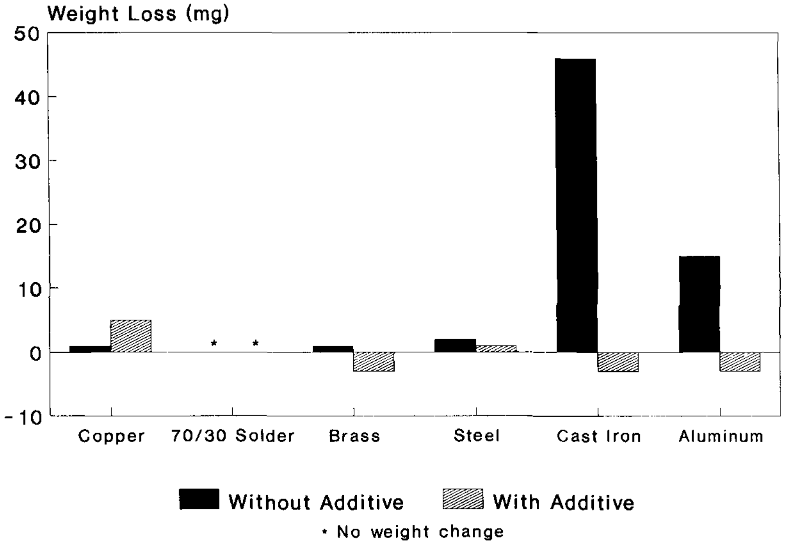

FIG. 3—*Average weight loss of coupons from 1500-h simulated service tests (used coolant).*

APPENDIX

Description of the Circulation and Filtration Device and the SCA

The Circulation and Filtration Device

The device is described in detail in U.S. Patent No. 4,996,874 [*10*]. The coolant flushing is performed by a diaphragm pump operating at 8 gal/min (30 L/min). The complete cooling system is flushed in a closed-loop fashion by manipulating hose pliers. The push/pull action of the pump creates less than 15-psi (103 kPa) pressure on system components. The system is further protected by a liquid pressure relief valve. Simultaneous to flushing, the coolant is filtered through a full-flow filter manifold. Circulating the coolant for 15 min removes 95% of the particles larger than 5 μm.

In addition, the device contains a venturi pump that allows the user to vacuum test the cooling system. The vacuum also allows for the elimination of air pockets when the system is refilled with coolant by vacuum. This eliminates the need to run the engine and make several coolant additions.

TABLE 9—*ASTM D 2809.*

Coolant	Rating
New coolant	9
New coolant with additive	9
Used coolant	8
Used coolant with additive	9

Supplemental Coolant Additive

The supplemental additive uses chemistry similar to the GM 6043 antifreeze additive. It is a colorless liquid with sufficient additive in a 12-oz (0.35-L) bottle to treat 12 qt (11.35 L) of coolant in a typical light duty cooling system.

The additive uses both borate and phosphate to boost and restore reserve alkalinity and to buffer pH in the preferred 8.5 to 10 range. The stabilized silicate is present in a sufficient amount to protect all of the aluminum components in the system, but the amount used is not so much as to cause gel formation [*11*]. Nitrate is included to insure against aluminum pitting corrosion and the resulting failure of aluminum radiators [*12*]. Azoles are included to give yellow metal corrosion protection [*13*]. Additionally, molybdate is included, which is an excellent multimetal corrosion inhibitor [*14*]. Molybdate also shows synergistic effects with other inhibitors for reducing corrosion of iron [*15*], aluminum [*14,16*] and yellow metals [*17*]. Furthermore, molybdate depletion rates are low compared to those of many of the corrosion inhibitors used in engine coolants. Its durability will provide corrosion protection after other inhibitors have been depleted [*18*]. This is a very well balanced and complete package which is designed for all the needs of LD engine coolants.

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DISCUSSION

S. Woodward[1] *(written discussion)*—How can a filtration/reinhibition process that yields coolant that fails the ASTM D 3306 specification 20% of the time be recommended for use?

R. Remiasz and R. D. Hercamp (authors' response)—We stated that the system is designed for use at intervals of 65 000 km, maximum. However, the average usage of the coolants in the 5 vehicles tested was 55 967 miles or 90 050 km. These used coolants at much higher mileages were chosen to make the test more severe. The results demonstrate that the system performs relatively well even when usage recommendations are exceeded. Even though the treated coolant failed to meet ASTM D 3306 20% of the time for coolants that had been used 38% longer than recommended, it is reasonable to conclude that the system, when used as recommended at 65 000 km maximum, will provide coolant meeting D 3306 performance.

S. Woodward[1] *(written discussion)*—It was stated that the on-vehicle recycle equipment attached directly to one of the heater hoses. Can you comment about the future ability of your system to work because of the increasing difficulty of accessing heater hoses due to underhood clutter?

R. Remiasz and R. D. Hercamp (authors' response)—This concern exists today. Some vehicles are much more difficult to service. We continually provide customers with new connection adaptors and procedures to be used as new vehicle configurations are introduced. We are not aware of any that cannot be serviced, but the more difficult models require special adaptors and special procedures. They also may take more time to service.

[1] First Brands Corporation, Danbury, CT 06810.

Robert C. Richardson[1]

A Multi-Stage Process for Used Antifreeze/Coolant Purification

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REFERENCE: Richardson, R. C., "**A Multi-Stage Process for Used Antifreeze/Coolant Purification,**" *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 258–275.

ABSTRACT: Today, the subject of recycling used antifreeze/coolant is a popular and very complex issue. Legislation has forced users in some areas of the United States to either recycle or to pay for proper disposal through a licensed facility. Recycling represents a viable alternative to disposal but poses technical challenges never before attempted. This paper describes a unique, multi-stage purification process (MSPP) based on dual-bed deionization. The process can be effectively utilized in automotive or heavy-duty applications to remove inhibitors and contaminants in both ionic and particulate form. This paper presents (1) analysis of several used coolants before and after the process, (2) comparison of other recycling processes, (3) hazardous waste characterization testing of process components and finished product, and (4) complete corrosion/performance testing of the finished coolant.

KEYWORDS: ion, ion-exchange, total dissolved solids, glycolate, formate, recycling, multistage purification process

Recycling used engine coolant, while providing a solution for hazardous waste disposal, poses technical challenges never before attempted. Characterization of the constituents present in used engine coolant and their concentrations has created more questions than it has answered thus far. However, this paper attempts to answer some of those questions and will provide a platform from which future research can grow. The end result of the recycling effort should be higher quality engine coolants, both virgin and recycled, as well as a better understanding of engine coolants and cooling systems in general.

A unique, multi-stage purification process for used engine coolant has been developed that is based on dual-bed deionization. This paper examines the efficiency of the process for removing inhibitors and contaminants in both particulate and ionic form. Data from corrosion and performance testing of the finished, prediluted engine coolant shows that this recycled product meets all current ASTM standards and is being successfully evaluated by at least one major U.S. Original Equipment Manufacturer (OEM). Hazardous waste characterization testing, according to Environmental Protection Agency (EPA) standards, of process components and finished product is also presented.

One of the greatest challenges facing today's automotive and industrial shops is complying with governmental regulations concerning the proper disposal of hazardous waste. In recent years, world attention has increasingly focused on the earth's delicate ecology and ways to restore and preserve the natural environment. This attention has been aimed at reducing sources of waste, producing more biodegradable materials, and recycling a larger portion of the materials we use. We have seen massive changes in business and industry to adapt and to

[1] Laboratory manager, BG Products, Inc., 701 South Wichita, Wichita, KS 67213.

provide products designed for these new markets. The transportation industry has offered one of the largest and most visible of these new markets, one created mainly by more rigorous environmental legislation. These changes include the phase-out of chlorofluorocarbons (CFC), such as dichlorodifluoromethane (R-12), for use in automotive air conditioners, mandatory use of oxygenates in gasoline to lower exhaust emissions in large urban areas, and proper disposal of used fluids such as motor oil and engine coolant. The aforementioned environmental mandates have culminated in the introduction of many types of recycling that provide viable alternatives to disposal. This stems the flow of hazardous materials to toxic waste sites or landfills, or both, and provides a cost-effective, often profitable, solution for end users.

Legislation

On October 17, 1986, the Superfund Amendment Reauthorization Act (SARA) Title III was signed into federal law by the U.S. Congress. Section 313 of this legislation designated ethylene glycol, the major component in most engine coolants, as a toxic chemical. Furthermore, the EPA defines ethylene glycol as hazardous waste under 40 CFR 414.60 and 40 CFR 261.24 if it contains any regulated heavy metals, such as lead, in concentrations above 5 mg/L (Waste D008). Section 311 of the Clean Water Act prohibits the disposal of hazardous waste in any sewer system. Although some states allow used engine coolant to be discharged to a sanitary sewer, provided it goes to a treatment-for-disposal plant, others have set more stringent guidelines than the federal laws.

All of this has led to massive confusion and problems for shops who must service vehicle cooling systems and periodically replace the used or spent engine coolant.

Commercial Technologies

In the three to four years since recycling engine coolant has become commercially available, as many as seven different methodologies have been offered. A list of these might include filtration, chemical filtration, chemical filtration/oxidation, centrifugation/filtration, vacuum distillation, reverse osmosis, and ion-exchange/filtration. Table 1 lists each process in general terms and comments on the ability of the process to separate inhibitors, contaminants, and degradation products from the reuseable water/glycol mixture.

As can be seen in Table 1, there are large differences in separation efficiencies between the various processes. When used alone, conventional filtration (>1 μm) is not adequate to provide complete purification of spent coolant, since it cannot remove contaminants, degradation products, and dissolved solids and provide a consistent finished product with a known inhibitor balance. Dissolved solids, for these purposes, are defined as compounds that will pass through a 0.7-μm filter. They include water impurities, such as chlorides and sulfates, inhibitors, such as borate, phosphate, silicate, and some corrosion metals.

TABLE 1—*On-site engine coolant recycling process comparison.*

Process	Purification Efficiency
Filtration	very low
Chemical filtration	low
Chemical filtration/oxidation	low
Centrifugation/filtration	low
Vacuum distillation	high
Reverse osmosis	high
Ion-exchange/filtration	high

Background

Chloride and Corrosion Metals

Chloride is known to promote pitting corrosion of aluminum, as does soluble corrosion metals (for example, copper) albeit by different mechanisms. Chloride promotes pitting by setting up a localized corrosion cell within a crevice, casting pore, or other microcell [*1*] while soluble corrosion metals, such as copper (Cu^{2+}) and zinc (Zn^{2+}), function by coupling with metals, such as aluminum, to set up active galvanic cells [*2*].

There has been some disagreement as to whether or not "soluble" corrosion metals (cations) actually exist in used engine coolant. This is primarily questioned because it is known that cations will readily form insoluble hydroxides at a pH of 8 to 10. Therefore, the author sampled some representative used automotive coolants and analyzed each before and after a 0.7-μm filtration. Cations remaining in the coolant after filtration would be considered soluble. Results are shown in Table 2.

The D15.15 samples represent coolant from approximately 2100 vehicles and were from bulk collection in California. The three vehicles sampled were from the Midwest region, and the D15.15 used (simulated) was a coolant made in the author's lab in an attempt to simulate the physical/chemical properties of the average used coolant more fully outlined in Table 3. As can be seen in Table 2, some soluble corrosion metals, including zinc and copper, do exist even at elevated pH.

Glycol Degradation

Another ionic species that cannot be removed by conventional filtration is the oxidative/thermal degradation products of glycol. For the purpose of this paper, this is limited to glycolate, formate, and acetate, which are the major by-products of ethylene glycol (EG) breakdown. EG is still the most widely used freezing point depressant in commercial engine coolant formulations. Propylene glycol, although not inert, is much more resistant to thermal/oxidative stresses and is gaining ground as a replacement freezing point depressant [*3*]. EG degradation has been well studied in simple systems with relatively few inhibitors [*4*], but it has not been well established whether the degradation products pose corrosion problems at concentrations found in a typical used engine coolant. In a recent effort by ASTM Subcommittee D15.15 on Recycled Coolants to document the condition of the "average" used coolant, the following properties (Table 3) were found in a used coolant population of 28 to 100 samples.

As shown in Table 3, glycolate/formate levels in used coolant range from 123 to 1172 mg/L with a mean of 647 mg/L. Since these are average levels only and would not represent a

TABLE 2—*Soluble corrosion metal evaluation in used engine coolants before/after 0.7 μm glass fiber filter-metal concentrations.*

Sample	pH	Al	Cu	Fe	Pb	Zn
D15.15 Round Robin #1	8.61	0/0	0/0	0/0	0/0	18.0/0
D15.15 Round Robin #2	8.34	0/0	0/0	17.0/0	8.0/0	10.0/4.0
'89 Olds Calais	8.07	12.3/10.3	0.2/0.2	42.5/1.5	2.4/0.7	17.0/1.0
'83 Honda Accord	10.70	2.7/2.6	4.6/4.1	0.1/0	4.7/0.4	0.8/0
'80 Chevy Malibu	8.5	4.4/2.6	4.9/0.2	1.8/0	5.9/0.9	6.7/0
D15.15 Used (simulated)	8.74	0/0	15.1/0	69.5/1.5	34.3/17.9	31.4/0.2

NOTE: Analysis performed by inductively coupled plasma atomic emission spectroscopy (ICPAES) using a 1:10 sample prep in a 1% nitric acid aqueous matrix. All metal concentrations in mg/L w/w. Detection limit 0.1 mg/L.

TABLE 3—*ASTM D15.15 summary sheet: used coolants frequency distribution charts.*

General Properties	Number of Samples	Mean	Standard Deviation (±)
pH	88	8.82	±0.94
RA	74	5.13	±2.57
% Glycol	72	41.10	±17.00
Freeze point, °F	44	−27.4	±27.30
Total dissolved solids, mg/L	34	15 581.60	±17 713.20
Inhibitors, mg/L			
phosphorus	56	899.98	±1 179.33
nitrate	67	791.94	±675.43
boron	60	213.83	±203.74
silicon	34	137.62	±137.00
tolyltriazole	52	258.67	±118.18
Contaminants (mg/L)			
glycolate/formate	58	647.45	±524.78
Chloride	80	48.01	±63.11
Corrosion Metals (mg/L)			
lead	100	13.95	±15.29
copper	98	9.11	±11.59
iron	83	48.19	±84.24
zinc	28	33.69	±46.40
aluminum	47	2.26	±5.02

worst-case scenario, it was decided to examine potential deleterious effects of these species. ASTM Corrosion Test For Engine Coolants in Glassware (D 1384) was utilized for this purpose. A modern phosphate/silicate based coolant, known to perform well in the test, was used as the control, and a second, triplicate test using the control coolant spiked with 450 mg/L of glycolic acid (99+% $HOCH_2CO_2H$) and 195 mg/L of formic acid (95% to 97% HCO_2H) served as the experimental samples. Results are shown in Table 4, and it is obvious that glycolate and/or formate aggravated aluminum corrosion.

Figure 1 shows the severe pitting induced on the aluminum coupon. This suggests that aluminum may be particularly susceptible to pitting corrosion from these species and that heat exchangers would be of particular concern.

TABLE 4—*Glycolate/formate corrosivity evaluation as measured by ASTM D 1384.*

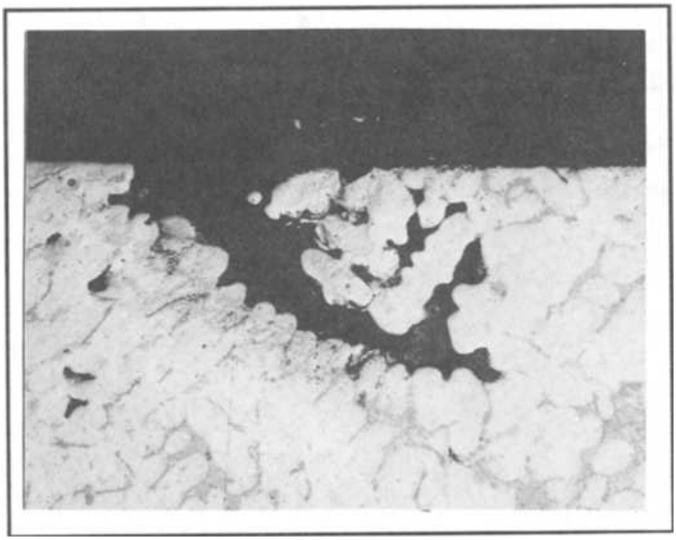
Specimen	Sample #1[a]	Sample #2[a]	D 4656 Limits[b]
Copper	2	2	10
Solder	3	4	30
Brass	2	2	10
Steel	1	1	10
Cast iron	2	1	10
Aluminum	1	14[c]	30

NOTE: **Sample #1:** 50/50 prediluted automotive coolant. **Sample #2:** 50/50 prediluted automotive coolant with 450-mg/L glycolic acid and 195 mg/L formic acid added.

[a] Solutions prepared in accordance with ASTM specification for prediluted automotive antifreeze/coolant D 4656.

[b] Average (3) weight loss in milligrams.

[c] Evidence of severe nonlocalized pitting corrosion.



Specimen:	D1384 Cast Aluminum Specimen
Description:	Magnification of pit formed in casting void and propagating through intergranular galvanic corrosion.

FIG. 1—*Photomicrograph of D 1384 specimen.*

Although Hercamp et al. [*3*] showed in D 1384 tests with uninhibited EG/corrosive water solutions that EG breakdown products were corrosive toward lead, no significant increase in solder corrosion was apparent upon the addition of glycolic/formic acid.

To more fully understand the thermal/oxidative degradation of EG, a test was designed to measure the separate and combined effects of common corrosion inhibitors. The test utilized ASTM Oxidation Stability of Steam Turbine Oils By Rotating Bomb (D 2272) apparatus with the following adaptations for consideration of glycol solutions:

- 50/50 v/v glycol solutions in deionized water
- 380 minute test duration
- 101°C test temperature
- 620 kPa oxygen pressure
- Electrolytic copper wire catalyst

The following properties of the glycol solutions were evaluated before and after each test to evaluate the extent of oxidation and the success of inhibitors:

- pH change
- Reserve alkalinity loss and % additive depletion (calculated)
- Conductance
- Degradation product concentration (by ion chromatography exclusion)
- Dissolved copper concentration (by inductively coupled plasma atomic emission spectroscopy)

Interestingly, initial runs at the chosen test length of 380 min with a known, fully formulated coolant, produced well over the maximum glycolate/formate levels found in typical used coolants and additive depletion ranging from 9.28 to 60.0%. Twenty-five percent depletion is the specified maximum in the GM 1825M standard after 1000 h in the simulated service test. Therefore, it was decided that the test apparatus and conditions were right for the desired screening of corrosion inhibitors and that glycols may provide insight into the comparative service life of various formulations in service. Results of the test are outlined in Table 5, Fig. 2, and Fig. 3.

It is interesting to note that most inhibited glycol solutions oxidized to a greater extent than the uninhibited glycol solution. The exceptions were the glycol solutions with copper inhibitors such as various azoles (for example, mercaptobenzothiazole). This could be partially due to the fact that glycol degradation products can inhibit further oxidation by the common-ion principle as has been previously demonstrated [*4*]. The most common engine coolant pH buffers, borate and phosphate, seemed to aggravate the oxidation of EG more than any single inhibitor evaluated, although simple combinations of mono and dicarboxylic acids, which are becoming of interest as inhibitor systems [*5*], were worse. However, in the presence of sufficient copper inhibitor, mono/dicarboxylic acid formulations performed far better than conventional borate/phosphate formulas with respect to end of test (EOT) glycolate/formate levels.

TABLE 5—*Glycol oxidation study, sample legend.*

Sample ID	Description	ΔpH	Δ*R.A*	ΔCondition, µS/cm	Formic, mg/L	Glycolic, mg/L	Copper, mg/L
PG1	PG/DI H_2O 50/50	−1.18	...	...	0.7	<0.3[1]	94.0
EG1	EG/DI H_2O 50/50	−1.18	...	...	27.0	73.0	111.0
EG2	PLUS 900 mg/L P as K_2HPO_4	−1.52	−1.0	34	136.0	1210.0	5.1
EG3	PLUS 213 mg/L B as $Na_2B_4O_7$	−1.78	−1.1	76	220.0	1430.0	308.8
EG4	PLUS 750 mg/L $NaNO_3$	−1.72	−0.1	37	53.0	120.0	105.4
EG5	PLUS 980 mg/L sodium silicate 28.7% $SiO_2^=$	...	−0.2	17	43.0	220.0	38.7
EG6	PLUS 2500 mg/L Na mercaptobenzothiazole 50%	−1.44	−0.4	18	10.0	30.0	0.0
EG7	PLUS 1000 mg/L Na tolyltriazole 50%	−0.69	−0.2	67	14.0	43.0	0.0
EG8	PLUS 1000 mg/L Na dimercaptobenzothiazole	−2.84	−0.2	3	11.0	<0.5	1.7
EG9	PLUS 1.772% octanoic acid/0.772% sebacic acid	−0.59	−0.8	−370	170.0	2800.0	169.0
EG10	PLUS 1.89% octanoic acid/0.61% adipic acid	−0.67	−0.9	−70	180.0	3400.0	99.0
EG11	PLUS phosphate based inhibitor system	−2.50	−0.8	...	41.0	1686.0	8.0
EG12	PLUS GM 6043-M inhibitor system	−3.05	−3.0	64	130.0	1420.0	2.6
EG13	commercial long life coolant 50/50 DI H_2O	−0.12	−0.4	0	115.0	110.0	0.0
EG14	commercial recycled antifreeze/coolant[2]	−2.97	−1.8	−20	520.0	3100.0	62.7

[a] Lactic acid.

[b] Produced by a process other than ion-exchange, distillation, or reverse osmosis.

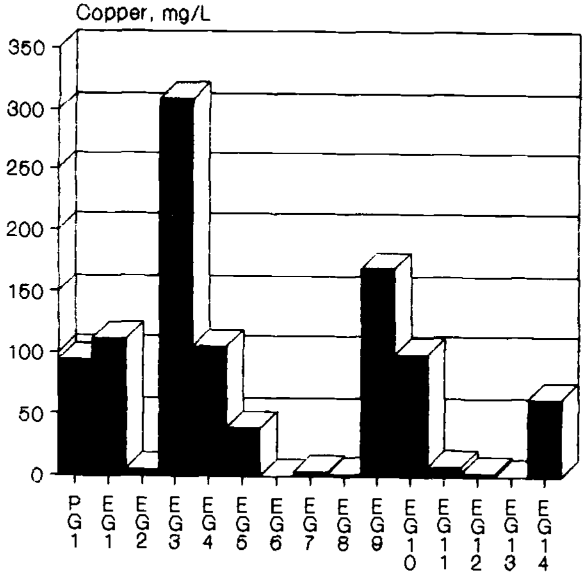


FIG. 2—*EOT soluble copper.*

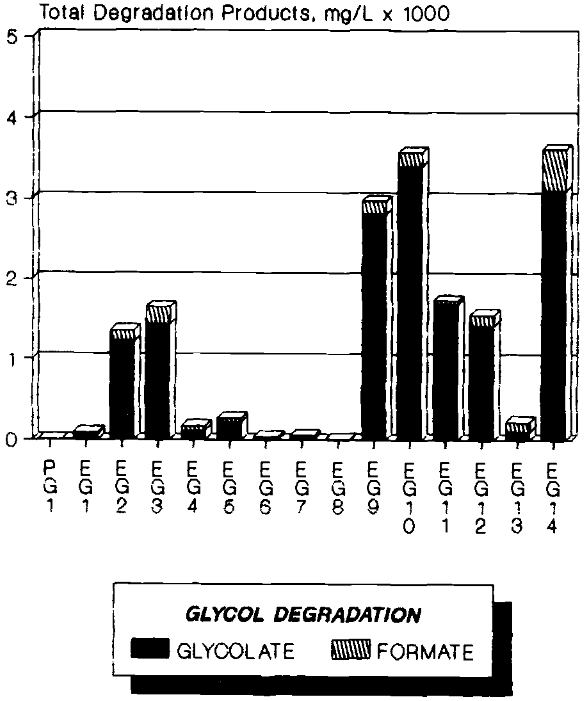


FIG. 3—*EOT degradation products.*

It has been generally established that elevated levels of dissolved solids can be detrimental to cooling system performance. Hercamp [*6*] reported that a heavy-duty coolant with a calculated total dissolved solids (TDS) level of 3.4% w/w promoted water pump seal leakage in a simulated service rig. The 3.4% corresponds to approximately 41 000 mg/L using an acceptable gravimetric method (EPA 209B). While water pump seal failure is not univariate, McKenzie and Kinisky [*7*] found that the primary mechanism by which water pump seal leakage occurs is by face seal filming. Coolant is subjected to high temperature between the mating surfaces of the mechanical seals resulting in nucleate boiling, which leaves patchy films, 5 to 10 μm thick, of solid matter on the seal face. This separates the face seals providing a leak path for the coolant to escape.

High levels of TDS can also promote reduced heat transfer. When solubility limits of the various inorganic salts are exceeded or when incompatibilities between these salts occur, the result is precipitates or gels coming out of solution. These usually collect in low temperature, low flow areas of the cooling system, or they can deposit on cooling system components, characterized by high heat flux causing an insulating scale such as calcium phosphate. Silicate is an inhibitor of particular concern with respect to solubility problems because of its known propensity to gel and cause flow restriction [*8*].

This data collectively suggest that processes designed to adequately purify spent engine coolant and provide a consistent finished product must remove a majority of the TDS fraction; this includes inhibitors, glycol degradation products, water impurities, and corrosion metals.

Description of the Multi-Stage Purification Process (MSPP)

The MSPP was designed to purify used antifreeze/coolant by combining successive stages of suspended solids and dissolved solids removal. Figure 4 is a simplified flow diagram of the MSPP where the graduated shading depicts the successive stages of purification.

Filtration begins with a basket strainer (1) removing large particulates such as stop leak materials that are greater than 115 μm in size. The strainer's main purpose is to protect the system pump (2) and to extend cartridge filter (3, 4) life. Next is a cartridge filter (3), which

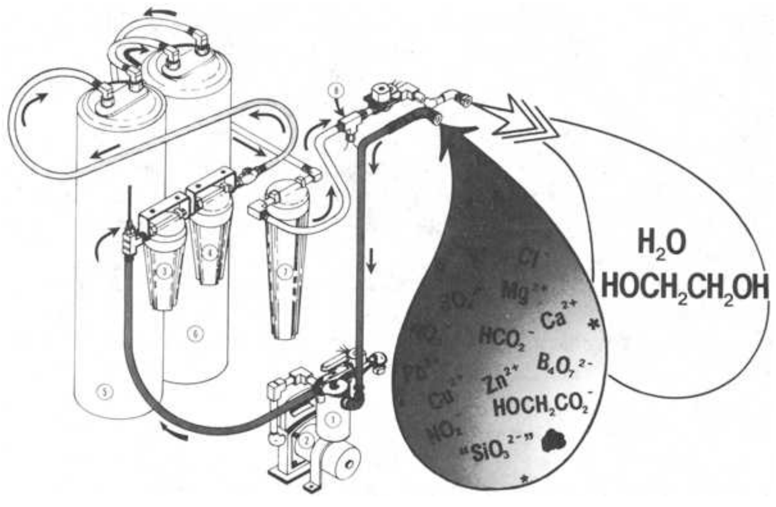


FIG. 4—*MSPP flow diagram.*

removes suspended solids greater than 25 μm, followed by a 5-μm cartridge filter (4) with a core employing granular 20 × 40 mesh activated carbon to adsorb organics. This protects the ion-exchange resins from organic fouling, which renders the resins ineffective. Since oil can be a common engine coolant contaminant [9], this is an important design concept.

After filtration in Stages 1, 2, and 3, the coolant, now free of particulates and heavy organics, flows into the cation exchange tank (5) through a tube to the bottom of the tank where it flows evenly upward contacting the ion-exchange resin. All positively charged ions (cations) are replaced by hydrogen (H^+) ions during this stage. In stage 6, all negatively charged ions (anions) are exchanged for hydroxide ions (OH^-). The H^+ and OH^- ions exchanged in Stages 5 and 6 combine to form water (H_2O) in an amount depending on the number of equivalents (moles of charge) of ions removed from the used engine coolant. The resulting purified fluid flows into a final activated carbon filter (7) whose purpose is to remove any entrained gases from the liquid stream. A more detailed explanation of the justification for this filter follows later in this paper.

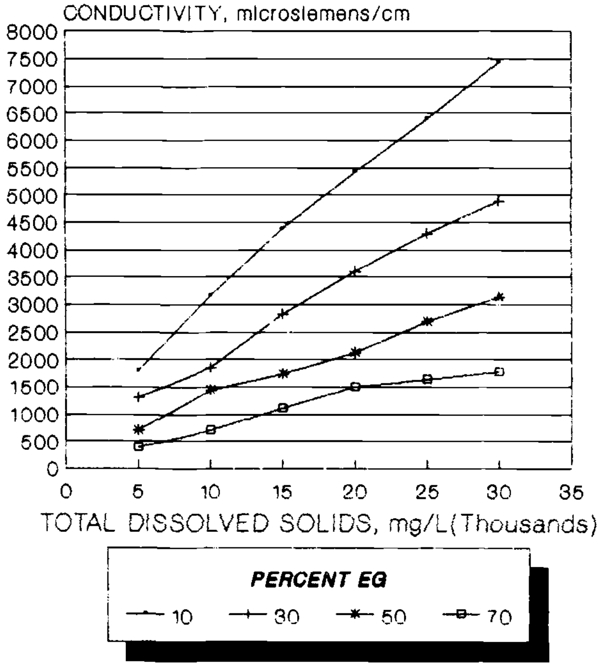
Finally, the completely purified EG/H_2O mixture passes through an in-line conductivity probe (8) which measures the conductivity of the solution as an indication of the degree of purification by the ion-exchange system in Stages 5 and 6. The probe is designed to show a green light when the conductivity is below 50 μS/cm. This ensures high-quality effluent and also gives the operator a visible indication that the process is under control and that the ion-exchange beds have not exceeded their capacity. When the ion-exchange resins are exhausted, dissolved solids remain in solution and the conductivity of the effluent rises and quickly exceeds the set point of the probe assembly at 50 μS/cm. This trips the green light off and lights a red light, indicating to the operator that the ion-exchange tanks must be removed for regeneration and replaced with a fresh set. The 50-μS/cm set point is normally reached within a few seconds after the beds have been exhausted, and maximum TDS at the 50-μS/cm point is 53 mg/L (as NaCl). Since glycol suppresses the conductivity of ions in solution, as can be seen in Fig. 5, this suppression must be taken into consideration in all TDS calculations.

These data stem from an evaluation in the authors lab to investigate the effect of glycol on conductivity derived calculation of TDS versus purely aqueous systems. TDS levels were achieved using a phosphate/silicate based inhibitor package in deionized water and antifreeze grade EG.

One set of ion-exchange tanks will generally purify 378.5 to 832.8 L (100 to 200 gal) of used engine coolant before regeneration is necessary. At the average of 567.8 L (150 gal) and an average TDS level of 15 581.6 mg/L, the capacity of the ion-exchange resins can be calculated at 3.5 mEq/mL.

The efficiency of the ion-exchange resins at removing dissolved solids depends largely on two factors: flow rate of the engine coolant through the resin and the ionization constant of the cation or anion to be removed. However, at an adequate flow rate (0.21 to 0.54 $L \cdot min^{-1}/m^{-3}$), most of the ionic species found in used engine coolant do not exceed the acid strength limits (Table 6).

Table 7 gives a good theoretical image of what should be possible to remove from the used engine coolant using ion-exchange technology. As can be seen, borate and silicate, due to their low acid strength, are the most difficult species to remove from conventional North American engine coolants and are the first to be detected as the ion-exchange tanks approach their capacities. Also, it suggests that European, Japanese, and new "long-life" coolants utilizing different inhibitor systems (that is, benzoate-nitrite and sebacic/adipic acid) may be effectively purified using the type of ion-exchange system used by the MSPP. This is assuming that these acid strengths, which were calculated in purely aqueous systems, are somewhat similar in water/glycol solutions.



* Specific conductance at 25°C
pH 10.8

FIG. 5—*Conductivity suppression in glycol-aqueous EG based engine coolant solution.*

Complications

With any research and development effort, unforeseen complications seem to arise. Two different undesirable chemical reactions occurring in the cation exchange bed were realized during the development of the MSPP. Both created products that were either removed or dealt with using more process equipment or chemical additives, or both.

TABLE 6—*Dissociation constants versus ion-exchange limitations.*

	Dissociation Constant		
Species, Anions	*T*, °C	pKa	Resin Limit
Adipic acid	25	4.63[a]	9 to 10
Acetic acid	25	4.75	9 to 10
Benzoic acid	25	4.19	9 to 10
Boric acid	50	9.08	9 to 10
Citric acid	20	3.14	9 to 10
Formic acid	25	3.83	9 to 10
Glycol	25	14.22	9 to 10
Glycolic acid	25	3.83	9 to 10
Oxalic acid	50	4.417	9 to 10
Phosphoric acid	50	2.260	9 to 10
m-silicic acid	. . .	9.70	9 to 10

[a] pKa for first ionization.

TABLE 7—*GM evaluation: coolant properties before and after MSPP.*[a]

Chemical Properties	Before MSPP	After MSPP	Reinhibited #1	Reinhibited #2
Contaminants				
chloride (Cl)	64	28	17	28
sulfate (SO_4)	290	6	82	100
formic acid	780	0	0	0
glycolic acid	1 800	28	15	0
acetate	21	0	0	0
calcium, mg/L	0	1	0	1
magnesium, mg/L	0	0	0	0
Corrosion metals				
aluminum, mg/L	3	0	3	3
copper, mg/L	7	0	0	0
iron, mg/L	0	0	1	2
lead, mg/L	1	0	0	0
zinc, mg/L	0	0	0	0
Inhibitors				
boron, mg/L	516	0	0	0
molybdenum, mg/L	249	1	181	149
phosphorus, mg/L	990	28	2 612	2 421
potassium, mg/L	1 203	52	4 474	5 315
silicon, mg/L	20	7	86	92
sodium, mg/L	3 014	7	318	380
nitrate (NO_3), mg/L	760	27	450	450
nitrite (NO_2), mg/L	35	14	14	0
General Properties:				
pH	8.37	8.46	10.38	10.38
freezing point, °F[b]	−60	−36	−35	−34
glycol, wt%	58	52	50	50
reserve alkalinity, ml	7.5	0.3	6.4	6.3
conductivity, μS/cm	1 879	21	2 769	2 810
TDS (calculated), mg/L	7 500	200	8 300	8 000
TDS (209B), mg/L	16 638	110	11 362	10 703
TSS, mg/L	1 318	90	356	419
visual	brown-green	clear/colorless	bright green	bright green

[a] Analysis performed by BG research laboratory.

[b] $t°C = (t°F - 32)/1.8$.

The first reaction was the conversion of nitrite (NO_2^-) ions, which are commonly found in most heavy-duty engine coolants, into nitrous acid (HNO_2). This reaction occurs via protonation of the NO_2^- ions as they pass through the strong acid (sulfonic) cation exchange resin. HNO_2, which is highly unstable, quickly decomposes into nitric oxide [$NO_{(g)}$] which is oxidized by the oxygen in the aerated coolant solution to form nitrogen dioxide [$NO_{2(g)}$], a toxic, reddish-brown gas. The reaction is summarized below

$$NO_2^- \xrightarrow[{[H^+]}]{EG/H_2O} HNO_2 \xrightarrow{\text{decomp.}} NO_{(g)} + OH^- \xrightarrow{O_2} NO_{2(g)}$$

Since $NO_{2(g)}$ is toxic, careful work was done using different process techniques and monitoring $NO_{(x)}$ gases with sensitive gas detection equipment. The problem was eliminated with a special filter (see #7 on Fig. 4) employing a special grade of activated carbon that removes most of the gas from the liquid stream.

The second reaction involved the oxidation of glycolate, formate, and acetate to carbon dioxide (CO_2). This was again found to be occurring in the cation exchanger because of a combination of the strong acid nature of the resin type being used and an unidentified oxidant. The CO_2 produced created some difficulties in obtaining a balanced pH in the finished engine coolant. The presence of CO_2 was usually noticed upon taking a pH measurement of the purified coolant solution before any inhibitor addition. The pH usually fell between 3.2 and 4.2, which is precisely the expected pH for a saturated H_2O/CO_2 solution. With no CO_2 present, the solution would exhibit a near neutral pH after the ion-exchange stage of the MSPP. More careful measurements found the pre-ion-exchange CO_2 concentration was typically 50 mg/L and the post-ion-exchange concentration around 260 mg/L. After the two-part MSPP inhibitor package is added to a near neutral solution of glycol/water, the pH will be 10.3 ± 0.1. However, with the CO_2 present, the pH would typically fall well below this to around 8.9. Our hypothesis is that CO_2 is converted to carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) when the purified coolant is made alkaline with the two-part additive addition. At a pH of 9 to 11, the HCO_3^- would dominate. This sets up a bicarbonate buffering system that shifts the desired pH from 10.0 to 8.9.

The solution to this problem is to make a simple pH check after additive addition. If necessary, an adjustment to the desired 10.0 pH is made with the alkaline portion of the two-part MSPP inhibitor package. Any extra buffering capability derived from the CO_3^{2-}/HCO_3^- is viewed as beneficial and foaming was shown to not pose a problem.

Corrosion Tests and Performance Data

The best purification process in the world would be useless without a well-formulated, balanced inhibitor package to restore the necessary corrosion inhibitors and performance additives to the engine coolant. A balanced pH; all system metals protection; foam inhibition; scale dispersants, sludge dispersants and detergents; buffering capability; and elastomer compatibility are all important performance targets that must be met.

A novel, two-component, phosphate-silicate-molybdate based inhibitor system was developed for the MSPP in automotive/light-duty applications. In mixed-fleet and heavy-duty applications, a similar two-component, low-silicate, phosphate-nitrite inhibitor system is used. The two-component system was developed out of necessity due to storage stability problems incurred with a concentrated, one-component package. However, the two-component approach allows a more foolproof design for recycled coolant re-inhibition. The two separate inhibitor concentrates are dyed different colors: one yellow and the other blue. Since all color (dye) is removed by the MSPP in most cases, the desired blue-green coolant coloration is produced and provides a visual indicator that both components have been added. Furthermore, the two components allow for adjusting the pH, since one is acidic and the other is basic. In normal operation, the two components produce a coolant with a balanced pH of 9.5 to 10.5 when used at a treat rate of 1 oz/qt of coolant or cooling system capacity (3.125% v/v) each.

General Motors—Service Technology Group Evaluation

This program was designed to supply service dealerships with accurate information as to what commercial processes could be safely used to recycle used coolant without voiding warranty. It was developed out of response to a desperate need of recycled coolant standards in the field. The Service Technology Group (STG) of GM organized and performed the initial evaluation while the actual testing of the resultant finished engine coolants was performed by a leading independent laboratory. The GM standard 1825-M was used as the target for passing performance requirements. However, since most of the coolants evaluated were prediluted, ASTM Prediluted Aqueous Ethylene Glycol (50 volume percent minimum) Base Engine Coolant For Automobiles and Light Duty Service (D 4656) was used for the standard for physical and chemical requirements. It also was followed in preparing the coolant solutions for corrosion tests.

Approximately 300 gal (1336 L) of spent engine coolant was collected by the STG that represented approximately 230 passenger cars of various years, makes, and models. This coolant was collected in a common tank and represented North American, European, and Japanese inhibitor technologies and had a mean service life of seven years. The coolant was then agitated and divided into 5-gal (19-L) containers for processing. Potential suppliers of recycling processes were then invited to recycle 10 gal (38 L) of this spent coolant, balance the freezing point, and re-inhibit such that it would be ready for use at the commercial levels. Furthermore, units having some internal capacity were precharged with the spent coolant solution before the final 10 gal (38 L) were processed so that the coolant tested would be representative of the starting material.

The following is a summary of test data obtained by a leading independent laboratory for

TABLE 8—*GM evaluation: corrosion and performance data.*

			Test Results	
Requirements	ASTM Test Method	GM 1825M	Pail #1	Pail #2
Physical/chemical requirements[a]				
specific gravity, 60/60°F[b]	D 1122	1.065 min	1.079	1.080
freezing point °F	D 1177	−34 min	−34.4	−34.3
boiling point, °F	D 1120	226 min	226	226
effect on automotive finish	D 1882	no effect	none	none
ash content, wt%	D 1119	2.5 max	1.04	1.04
pH	D 1287	7.5 to 11.0	10.2	10.2
Reserve alkalinity, ml	D 1121	report	5.5	5.6
Chlorides, mg/L	D 3634	25 max	<4	<4
R.A., % loss after 1000 hours	D 1121	25% max	NDA	NDA
Performance requirements				
corrosion in glassware	D 1384			
copper		10	0	0
solder		20	−0.3	0
brass		10	−0.3	−0.3
steel		10	0	0
cast iron		10	0	0
aluminum		20	−0.3	+0.3
simulated service test	D 2570			
Copper		10	NDA	NDA
Solder		40	NDA	NDA
Brass		20	NDA	NDA
Steel		20	NDA	NDA
Cast iron		20	NDA	NDA
Aluminum		40	NDA	NDA
heat transfer corrosion	D 4340	1.0	<0.1	0.3
foaming, volume (mL)/break time(s)	D 1881	50/5	47/1	32/1
cavitation erosion	D 2809	8 at 300	NDA	NDA
glycol composition by GC	NA	no req		
Ethylene glycol, wt%		...	49.0	48.8
Diethylene glycol, wt%		...	2.5	2.6
Propylene glycol, wt%		...	<0.5	<0.5

[a] Per D 4656 prediluted specifications.

[b] $t°C = (t°F - 32)/1.8$.

the GM on-site engine coolant recycling evaluation (Tables 7 and 8). The testing was not complete at the completion of this paper so the full data were not available for inclusion, although preliminary results indicate that the finished coolant produced by the MSPP will satisfy the requirements of GM.

D 4656/D 4985 Test Data

Since full performance data were not available from the GM evaluation, test data obtained on testing of the MSPP two-component additives, both light and heavy duty, are presented (Tables 9 and 10). ASTM D 4656 was used for evaluation of the light-duty inhibitor, since a

TABLE 9—*Light-duty performance testing of the MSPP inhibitor in virgin EG.*

Requirements	ASTM D 4656 Specified Test	Specifications	Results
Physical/chemical requirements			
specific gravity, 60/60°F	ASTM D 1122	1.065 min	1.0807
freezing point, 50 vol%	ASTM D 1177	−34° min	−34°F
boiling point	ASTM D 1120	226°F, min	227°F
effect on automotive finish	ASTM D 1882	no effect	. . .[a]
ash content, max wt%	ASTM D 1119	5.0	1.2
pH, 50 vol%	ASTM D 1287	7.5 to 11.0	10.4
reserve alkalinity	ASTM D 1121	report	5.7
General requirements			
color		. . .[b]	. . .
effect on nonmetals		no adverse effect	. . .
storage stability	ASTM draft	1 year min	1½ year min
Performance Requirements			
corrosion in Glassware	ASTM D 1384		
copper		10 mg/coupon, max.	6
solder (30/70)		30	1
brass		10	. . .
steel		10	0
cast iron		10	1
aluminum		30	0
high lead solder		. . .	33
Simulated service test[c]	ASTM D 2570 (79) at 33⅓% antifreeze		
copper		20 mg/coupon	4.8
solder (30/70)		60	. . .
brass		20	7.2
steel		20	0.6
cast iron		20	0.4
aluminum		60	+5.3
high lead solder		. . .	8.3
corrosion of cast aluminum at heat rejecting surfaces	ASTM D 4340	1.0 mg/cm^2/wk, max.	0.2 mg/cm^2/wk
foaming, volume (mL)/ breaktime(s)	ASTM D 1881	150 mL, max./5 s max.	33 mL/1 s
cavitation erosion	ASTM D 2809	8 min at 100 h	10 at 1000 h[d]

NOTE: t°C = (t°F − 32)/1.8.

[a] No adverse effect expected.

[b] Color is entirely up to the manufacturer.

[c] Modified—test run on coolant as received (50/50) and using Ford parts.

[d] Used Ford Test Method BL 3-2, a more stringent test, testing the same factors but under harsher conditions and extended time.

TABLE 10—*Heavy-duty performance testing of the HD MSPP inhibitor in virgin EG.*

Requirements	ASTM D 4985(89) Specified Test	Specifications	Results
Physical/chemical requirements			
specific gravity, 60/60°F	ASTM D 1122	1.110–1.145	1.0807[a]
freezing point, 50 vol%	ASTM D 1177	−34° max	−34°F[b]
boiling point, undiluted	ASTM D 1120	325°F, min	. . .
boiling point, 50 vol%	ASTM D 1120	226°F, min	227°F[c]
effect on automotive finish	ASTM D 1882	none	. . .[d]
ash content, max wt%	ASTM D 1119	5.0	1.6
pH, 50 vol%	ASTM D 1287	7.5 to 11.0	10.4
water, wt%, max	ASTM D 1123	5.0	. . .
chloride, mg/L	ASTM D 3634	25 max	<10
silicon, mg/L	UC	250 max	166
reserve alkalinity, mL	ASTM D 1121	10 min	6.8
General requirements			
color		. . .	. . .
effect on nonmetals		no adverse effect	. . .
storage stability	ASTM draft	1 year min	1½ year min
Performance Requirements			
corrosion in glassware	ASTM D 1384		
copper		10 mg/coupon, max	3.1
solder (30/70)		30	0.7
brass		10	3.5
steel		10	0.3
cast iron		10	0.9
aluminum		30	4.7
simulated service test	ASTM D 2570 (79) at 33⅓% antifreeze		
copper		20 mg/coupon	8.0
solder (30/70)		60	. . .
brass		20	10.1
steel		20	2.5
cast iron		20	0.7
aluminum		60	9.1
high lead solder		. . .	65.4
corrosion of cast aluminum at heat rejecting surfaces	ASTM D 4340	no req	0.4 mg/cm^2/wk
foaming	ASTM D 1881	150 mL, max/5 s max	NR
liner cavitation	UC[g]	mg loss/22 h	49.0

NOTE: t°C = (t°F − 32)/1.8.

[a] Test run on coolant as received (50/50); spec on prediluted AF 1.065 min.

[b] Test run on coolant as received (50/50).

[c] Test run on coolant as received (50/50).

[d] No adverse effect expected.

[e] Color is entirely up to the manufacturer.

[f] Modified—test run on coolant as received (50/50) and using Ford parts.

[g] Test buttons—ASTM G32; Test solution—ASTM standard on corrosion of water + 1/3x 570A/B; amplitude—0.8 mil peak to peak; duty cycle—100 s [80 on/20 off]; temp (initial) 130°F., temp (final) 170°F.

prediluted engine coolant is the finished product from the MSPP. For heavy-duty, D 4985 was used, realizing, of course, that this is an antifreeze concentrate specification.

Hazardous Waste Characterization

As previously mentioned, used antifreeze/coolant or recycling process components, or both, such as filters, are regulated as hazardous waste under 40 CFR 261.24 if certain hazardous or toxic characteristics are present. These characteristics might include corrosivity, reactivity, or toxicity. Toxicity limits can be violated if regulated heavy metals, such as lead, are present in concentrations exceeding the allowable limits.

Lead in used coolant is present as a corrosion metal that is extracted from the soldered joints in the radiator by the coolant while in service. At a pH of 8.5 to 10.0, this lead would primarily be lead hydroxide $Pb(OH)_2$. Typical lead concentration in used coolants is 2 to 30 mg/L with an average of 6 mg/L. As could be expected, this lead is readily filterable using simple mechanical filtration such as that employed in the MSPP as described previously. Table 11 shows data collected by a certified independent environmental test laboratory on a used coolant collected at a service garage involved mainly in over-the-road, heavy-duty engine repair. The data supports that: (1) The used coolant itself was hazardous waste due to lead concentration, (2) The MSPP purified the coolant to acceptable levels, (3) The MSPP filters removed the lead and would be characteristically hazardous, and (4) The ion-exchange regeneration solution did not contain appreciable amounts of lead.

Conclusions

1. Recycling used antifreeze/coolant is becoming a reality in the marketplace and can be cost-effective and show environmental benefit.

2. Data presented show that even average levels of ethylene glycol oxidation products can be corrosive, especially to aluminum, and that these species must be removed in a viable recycling process.

3. The combination of mechanical filtration and dual-bed deionization represents a sound technical process to purify used antifreeze/coolant.

TABLE 11—*Hazardous waste testing of recycling components.*

	Concentration and Units of Samples, mg/kg							
Total Metals	1	2	3	4	5	6	7	Method
Arsenic	...	...	...	...	...	...	...	EPA 7060
Barium	...	...	15	25	...	...	...	EPA 7080
Cadmium	...	...	10	...	1	...	...	EPA 7130
Chromium	...	...	19	4	2	...	...	EPA 7190
Lead	18	...	6 500	53	620	0.67	0.42	EPA 7420
Mercury	...	...	...	...	...	...	...	EPA 7470
Selenium	...	...	...	...	...	...	...	EPA 7740
Silver	...	...	28	...	1	...	...	EPA 7760

NOTE: **Sample 1:** used antifreeze before MSPP; **Sample 2:** used antifreeze after MSPP; **Sample 3:** 25 μm filter; **Sample 4:** activated carbon filter; **Sample 5:** 5 μm filter; **Sample 6:** cation regenerant solution; and **Sample 7:** anion regenerant solution.

4. The removal of a large portion of total dissolved solids (TDS) in a recycling process is key, both to minimize potential water pump failures and to ensure proper additive compatibility and shelf life.

5. Efficient removal of TDS in engine coolant must also be accomplished by a recycling process in order to provide a consistent finished product.

6. Recycled antifreeze/coolant produced by a viable recycling process can meet and exceed current performance standards, such as ASTM D 3306, D 4656, and D 4985.

7. Some portion of all recycled antifreeze/coolant will still require proper disposal, such as filters and distillation bottoms, because of heavy metal concentrations.

Acknowledgments

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[*10*] General Motors Service Technology Group, Wayne Bradly, Senior Project Engineer, Warren, MI.

DISCUSSION

J. A. Lima[1] *(written discussion)*—I am wondering if you have an estimate of total cost to "process" a typical vehicle, not what the charge would be for the actual service, but what the average cost is at the present time to process a car and, in addition, what is the cost of the equipment itself?

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[1] Houghton Chemical Corporation, Allston, MA.

R. C. Richardson (author's response)—Realizing that costs can vary slightly from location to location, an average cost to process a passenger car is approximately $7.50 assuming a 10-qt (9.4 km^3) cooling system capacity. This cost does not include labor and overhead or equipment amortization but does include everything necessary to deliver a fully cleaned, balanced, and reinhibited cooling system. The current cost of the equipment is approximately $8745, which includes a fully equipped MSPP unit with two sets of deionization tanks which gives capacity to process 200 to 300 gal (757 to 1136 L) of used coolant.

P. Woyciesjes[2] *(written discussion)*—What cleaners are recommended for the cooling system? If they are the EDTA type, what effect do they have on your process and on the performance testing of the final product?

R. C. Richardson (author's response)—A citric acid/EDTA based cooling system flush, specifically designed with the MSPP, is recommended. The effect of the flush on the overall process has never been specifically evaluated, although much of the performance data, including the GM-STP evaluation, was done with the flush added to the used coolant before processing. As the final coolant from these evaluations performed well, certainly up to industry standards (D 3306/GM 1825-M), the impact would appear to be minimal. Furthermore, the benefit from chemically cleaning the cooling system has been evaluated and is critical to proper maintenance of a modern automotive cooling system.

A. Gershun[2] *(written discussion)*—Why is the cation exchange column placed before the anion exchange column in your process? What would be the effect of reversing them?

A. C. Richardson (written discussion)—The sequence of the ion-exchange resins is critical, cation exchange followed by anion exchange. Reversing the order would result in the formation of insoluble metal hydroxides in the anion exchange, which would quickly foul the system possibly even resulting in restriction of liquid flow rate.

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[2] First Brands Corporation, Danbury, CT 06810.

Wayne H. Bradley[1]

An Evaluation of Engine Coolant Recycling Processes: Part I

REFERENCE: Bradley, W. H., **"An Evaluation of Engine Coolant Recycling Processes: Part I,"** *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 276–288.

ABSTRACT: The Service Technology Group (STG) is an organization within General Motors (GM) responsible for providing service equipment and information to GM dealerships. STG is charged not just with the responsibility for current GM vehicles, but for the cars and trucks of the future as well. The tools, the procedures and the programs that technicians will use tomorrow must be created and validated today. Various staffs within STG address advanced serviceability readiness, special tool development, service research, and similar themes.

As the awareness of environmental issues has heightened, the disposition of spent engine coolant has begun to affect automotive service. One possible approach to this coolant disposition problem is that of coolant recycling. General Motors Service Technology Group has conducted a study in which the objective was to determine the efficacy of (state of the art) engine coolant recycling. Spent engine coolant was collected from vehicles and combined to form a reference coolant with a mean age of approximately seven years. Various coolant recycling processes were evaluated as they were required to process the reference coolant. Once the recycled samples were obtained, they were sent to an independent test facility. The test criteria was GM 1825M, a virgin coolant corporate specification.

Included in this study was the evaluation of off-site coolant recycling facilities that reformulate engine coolant for reuse.

In advancing its pro-active environmental policy, STG has initiated this study to evaluate the efficacy of engine coolant recycling. It is our belief that the results of this undertaking will be beneficial to our dealers, the environment, and our customers.

KEYWORDS: corrosion, inhibitors, recycling, inhibitors, reference coolant, deionization, filtration, centrifugation, flocculation, coagulation, reverse osmosis, vacuum distillation, coolant extension

Background

Engine Coolant: Its Function and Properties

Practically every passenger vehicle on the road today shares a common ingredient: ethylene glycol used as an integral component in the cooling system. As coolant serves its purpose in protecting the components of the automotive cooling system against corrosive and erosive attack and providing enhanced freeze/boil protection, it begins to take on certain negative characteristics. These characteristics typically manifest themselves by a lowered capacity to protect the cooling system because of the formation of ethylene glycol degraded acids (acetic, glycolic, and formic), accumulated dissolved and suspended solids, principally metal oxides, and salts (these originate from the corrosion of various metals within the cooling system) and make up water contaminants. Cooling system metals are corroded by cavitation corrosion,

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[1] Senior project engineer, General Motors Service Technology Group, 30501 Van Dyke, Warren, MI 48089.

direct chemical attack, or by electrochemical processes, either galvanic when dissimilar metals are electrically coupled, or local cell action between anodes and cathodes on the surface of one metal [*1*].

Sodium (alkali metal) silicate is generally acknowledged to be the most effective inhibitor of aluminum corrosion. For this reason, it is included in almost every (North American) commercial coolant. The silicate, however, can be depleted in customer service, resulting in a loss of aluminum protection [*2*]. Other important corrosion inhibitors included in engine coolants also gradually deplete in service. It is for all of these reasons that General Motors requires specific change intervals for the engine coolant in its vehicles.

Regulating the Disposition of Used Coolant

Until recently, there were few questions asked regarding the disposition of spent coolant. It was either hauled away as waste or disposed of in conventional storm or sewer drains at the rate of an estimated 200 million gallons (757 million litres) per year. As continued emphasis on the environment grew, the disposition of spent coolant took on a different light. Section 313 of Title III of the Federal Superfund Amendments and the Reautherization Act of 1986 classifies ethylene glycol as a toxic waste. The Environmental Protection Agency (EPA) regulatory cutoff for lead (the threshold for allowable lead in any waste) is 5 mg of extractable lead per litre of waste (mg/L), also stated as five parts per million (ppm) of extractable lead. Because the EPA toxicity characteristic is concerned with the likelihood that a hazardous waste will release its heavy metals into ground water and thereby pollute the drinking water system, the EPA extraction procedure defines a waste as hazardous based upon its extractable levels of heavy metals rather than its total concentration.

State and Local Policies

Individual states and local governments (that is, cities and counties) are not preempted by federal law from enacting and enforcing their own environmental laws and regulations regarding the disposal of used coolant which are more stringent than the federal laws and regulations. If a state enacts a more stringent environmental protection provision, then a generator must comply with those higher standards. With regard to ethylene glycol, only California has determined it to be hazardous waste if in sufficient quantities. However, several states have listed it as a "pollutant" or "special," "residual," "industrial," or "commercial" waste, which may not be discharged onto the ground, into waterways or into the local sewage system without special permission of the municipality or local publicly owned treatment works (POTW). Additionally, even in the absence of any such state regulation of ethylene glycol, local POTW discharge ordinances may prohibit or restrict the disposal of ethylene glycol into the local sewer system [*3*].

To provide environmentally responsible engine coolant service alternatives for General Motors (GM) dealers, STG has implemented a coolant recycling program. The objective in conducting this program is to accrue knowledge of engine coolant recycling technology while laying a foundation for future projects designed to further provide beneficial information and data for the promotion of this type of recycling. Obviously, General Motors has a vested interest in the quality of the environment and the performance of the coolants used in its vehicles. It is for these reasons that this engine coolant recycling study was conducted objectively, yet circumspectly. This paper is the first part of a two part series on this engine coolant recycling study and is intended to describe the manner in which the test was conducted. A short discussion is included relative to the results.

Format of the Study

Objective

The objective of this study was to determine whether a commercial engine coolant recycling process, available at the time of this study, was capable of recycling a qualified spent coolant to meet General Motors virgin coolant specification GM 1825M. This is a virgin coolant specification and is the same required for coolant suppliers for initial fill in General Motors vehicles. It parallels ASTM Specification for Ethylene Glycol Base Engine Coolant, for Automobile and Light Duty Service (D 3306) with the exception of some performance requirements (Table 1). Also, an objective was to provide to General Motors dealers the information and the means to choose a recycling process that has been predetermined to be capable of producing an adequate recycled product for GM vehicles. The results of this study will be shared with the public by means of papers such as this and volunteered interaction with outside organizations. This study has been presented to various governmental agencies, and it is believed that it will provide crucial information in shaping and implementing subsequent legislation regarding engine coolant recycling.

Process Selection

The selection process for choosing the various recycling techniques to be evaluated was relatively straight forward. An announcement was made to the ASTM Subcommittee D15.15 on recycled coolants in November of 1990 describing the program and its objective. There were no qualifying factors or requirements that any of the recyclers needed to meet with the exception that their product be ready for release to the public (not in the development stage). Each recycling unit chosen represented a different process. In an attempt to simplify the study, the recycling processes were segregated into two categories: on-site and off-site. The recycling processes that were categorized as on-site were those that would perform the recycling at the dealership. Those that recycled coolant at a facility other than the service outlet where the coolant was acquired were addressed under off-site.

On-Site Coolant Recycling

Coolant Collection Program

In researching any coolant recycling process, it is essential to characterize the coolant that is to be recycled. The spent coolant utilized as the input coolant (designated as the reference coolant) in this program was obtained from General Motors employee vehicles at the Tech Center located in Warren, MI. The selection of the vehicles was accomplished by selecting 200 of the vehicles with the oldest coolant from a total of 600 candidates. The mean age of the coolant from these 200 vehicles was approximately seven years. It is believed that many of these vehicles contained the original factory fill with the exception of occasional overflow tank top off. Individual samples were taken from each vehicle for analysis before mixing with the reference batch. In order to encompass the effects that foreign inhibitor formulations may have on the recycled products, 30 Japanese vehicles were drained, mixed, and added to the reference coolant (unknown age). Although the act of combining all these coolants with varying inhibitor chemistries may not represent a singular inhibitor technology, it is indicative of all coolant recycling practices to varying degrees. Each recycling process, whether it is batch or vehicle oriented, would be expected to encounter mixed coolant chemistries because of the residual coolant in the equipment (direct vehicle recycling equipment) or batch processing.

TABLE 1— *Comparison of coolant specifications, ASTM D 3306 versus GM 1825M.*

Chemical Requirements	ASTM D 3306	GM 1825M
PHYSICAL REQUIREMENTS		
Specific gravity, 60/60-F	1.11 to 1.14	1.11 to 1.14
Freezing point °F, 50% vol.	−34 min	−34 min
Boiling point, °F		
undiluted	300 min	300
50% vol.	226 min	NR
Effect on automotive finish	none	none
Ash content, wt%	5 max	5 max
pH, 50% vol.	7.5 to 11.0	7 to 11
Reserve alkalinity, mL	10 min	10 min
Water, wt%	5.0 max	5.0 max
Chlorides, ppm	NR	NR
RA, % loss after 1000 h	NR	25% max
GENERAL REQUIREMENTS		
Color	dist.	dist. green
Odor	not off.	NR
Storage Stability	NR	6 months
PERFORMANCE REQUIREMENTS		
Corrosion in glassware		
copper	10	10
solder	30	20
brass	10	10
steel	10	10
cast iron	10	10
aluminum	30	20
high lead solder	NR	NR
impingement coupon (C)	NR	NR
impingement coupon (A)	NR	NR
Simulated Service Test		
copper	20	20
solder	60	40
brass	20	20
steel	20	20
cast iron	20	20
aluminum	60	40
high lead solder	NR	NR
Heat transfer corrosion	1.0 mg/cm2/wk	1.0
Foaming	150 mL/5s	50/5 scc
Cavitation erosion	8 min at 100 H	8 at 300
Galvanostatic pitting test	NR	NR
Engine dynamometer	NR	NR
Circulation test	NR	NR
Fleet test	NR	NR

NOTE: NR = Not Required.

Reference Coolant Dispersion

The reference coolant from the 230 vehicles was contained in its entirety in one bulk container. While agitating, the reference coolant was consecutively poured into individual containers for ease of use. Before use, each container was shaken thoroughly to suspend any sediment. It was required of each recycling process to recycle two separate containers of the reference coolant as two separate tests.

Reference Coolant Characterization

A complete characterization of the used coolant used in this study (designated as the "reference" coolant) is shown in Table 2 (two samples were analyzed and labeled 316 and 2). This analysis, conducted at 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). The reference coolant was filtered at 0.45 μm before analysis. Also shown in Table 2 are the results when the reference coolant (unfiltered) was treated with hydrofluoric acid to dissolve all the visible insolubles and colloids. These analyses give a clearer picture of the soluble/insoluble ratio of various constituents, particularly heavy metals.

How the Testing Was Conducted

Each recycling system was tested at the General Motors Service Technology Group Headquarters building located in Warren, MI, before the author. Strict adherence to the manufacturer's operational instructions was followed to ensure that a similar method would be repli-

TABLE 2—*Analysis of reference coolant.*

	Solubles		Acid Treated	
Analyses	#316	#2	#316	#2
pH	8.3	8.3	N/A	N/A
Glycol	59.9	59.9	N/A	N/A
ASTM RA	7.16	7.16	N/A	N/A
TTZ	212	212	N/A	N/A
BZT	23	20	N/A	N/A
MBT	23	20	N/A	N/A
Chloride	50	50	N/A	N/A
Nitrite	19	11	N/A	N/A
Benzoate	2220	2248	N/A	N/A
Nitrate	838	852	N/A	N/A
Sulfate	265	268	N/A	N/A
Sebacate	N/A	N/A	N/A	N/A
2-Et Hexanoic Octanoate	N/A	N/A	N/A	N/A
Boron	458	460	377	400
Aluminum	ND	ND	34	27
Copper	6	5	10	11
Iron	<2	<2	181	138
Lead	<2	<2	28	28
Potassium	1005	970	755	903
Molybdenum	149	147	130	112
Sodium	2512	2469	2088	2184
Phosphorus	641	639	616	597
Silicon	42	41	20	26
Zinc	ND	ND	5	6
Fomate	556	519	N/A	N/A
Glycolate	1387	1347	N/A	N/A

NOTE: ND = not detected. N/A = not analyzed. All data in ppm.

cated in the field. Before testing, each piece of equipment was drained and primed with the reference coolant. This eliminated dilution of the reference coolant with the coolant contained in the equipment. Each system was required to recycle two separate 5-gal (19-L) batches of the reference coolant. This allowed for some measure of consistency while providing a margin of comfort (two test points as opposed to one) in the testing. The recycled product from each process was individually labeled and shipped to an independent test facility experienced in the testing of engine coolants. In accordance with proper testing methods, a blind test was performed at the testing facility where the correlation of the recycled sample and its origin remained unknown. To contribute to the validity of the test procedure, control samples were submitted (also blind to the test facility) in the form of virgin General Motors coolant and the untreated reference coolant. Samples of each recycled product were taken immediately following processing. The corresponding samples were sent to a specialty lab for complete analysis.

Recycling Processes Evaluated

The following list includes the names of the various types of coolant recycling processes evaluated in this study. Some of the processes included mechanical or chemical variations; these are noted. A detailed description (partially or fully derived from each equipment manufacturer) of each process follows:

1. Filtration, simple.
2. Filtration, flocculation/coagulation.
3. Filtration, flocculation/coagulation, oxidation (with and without deionization).
4. Deionization.
5. Reverse Osmosis.
6. Filtration, Centrifugation (with and without deionization).
7. Vacuum Distillation (two units tested).
8. Coolant Life Extension.

Filtration, Simple—This process treated 25-gal (95 L) batches of automobile coolant, which is normally a mixture of approximately 50% ethylene glycol and 50% water. When 25 gal (95 L) have been accumulated in the machine's "dirty coolant" reservoir, the machine is turned on and the solution passes through a 5-μm pre-filter and then through a final filtration, which uses an ultra filtration filter removing impurities as small as ½ μm in size. After the solution has been filtered and is now contained in the clean recycled coolant reservoir, the inhibitor is added to restore the proper balance of additives. The recirculating pump can be run to speed the mixing of the inhibitor with the recycled coolant. Next, the recycled, re-inhibited solution is tested for freeze point, total dissolved solids, and reserve alkalinity.

Filtration, Flocculation, Coagulation—This particular process is conducted on the vehicle via hook up to the cooling system at the radiator and at the heater hose. An alkaline chemical flush is poured into the cooling system, and the vehicle is run at idle for approximately 10 min. With the vehicle shut off, the recycling begins, with coolant directed by ordinary shop air. The coolant is drawn into the holding tank through a coarse filter to catch most suspended solids. While coolant is flowing into the holding tank, special chemicals are added to the holding tank to precipitate out some of the dissolved species. The coolant is then directed back into the vehicle through a fine filter to remove the precipitated solids. This procedure takes about 3 min and is repeated two more times. A proprietary corrosion inhibitor package is then added to the coolant, followed by a stop-leak chemical to replace any filtered stop-leaks that are routinely added to the coolant at the factory on many new cars.

The final steps require addition or removal of antifreeze to restore a 50:50 glycol/water mix for recommended freeze and boil protection and addition of a coolant sealant that replaces any factory stop-leak removed in the filtration process.

Filtration, Flocculation, Coagulation, Air Oxidation (with and without deionization)—This process (directly recycled on vehicle) consists of filtration to remove suspended solids, air oxidation, and hydroxide precipitation to remove dissolved metals with the filters. The pH is set to 9.8 to 10.0 with an antifreeze "extender," and the freeze point is adjusted with 100% pure ethylene glycol. The process can be seen diagrammatically in Fig. 1. This process was evaluated with and without ion-exchange resins.

Deionization—This batch or direct vehicle process was designed to purify used coolant by combining successive stages of suspended solids and dissolved solids removal. Figure 2 is a simplified flow diagram where the graduated shading depicts the successive stages of purification. Filtration begins with a basket strainer (1) removing large particulates such as stop leak materials that are greater than 115 μm in size.

The strainer's main purpose is to protect the system pump (2) and to extend cartridge filter (3,4) life. Next is a cartridge filter (3), which removes suspended solids greater than 25 μm followed by a 5-μm cartridge filter (4) with a core employing granular 20 × 40 mesh activated carbon to absorb organics. This protects the ion-exchange resins from organic fouling, which renders the resins ineffective. Since oil can be a common engine coolant contaminant, this is an important design concept.

After filtration in Stages 1, 2 and 3, the coolant, now free of insoluble particulates and heavy organics, flows into the cation exchange tank (5) through a tube to the bottom of the tank where it flows evenly upward contacting the ion-exchange resin. All positively charged ions (cations) are replaced by hydrogen (H^+) ions during this stage. In Stage 6, all negatively charged ions (anions) are exchanged for hydroxide ions (OH^-). The H^+ and OH^- ions

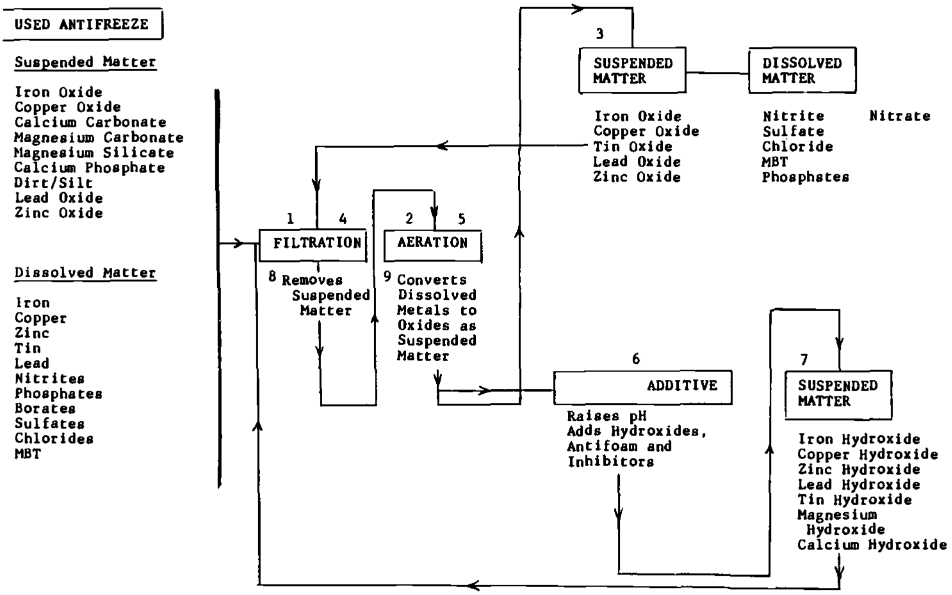

FIG. 1—*Filtration, flocculation, coagulation, and air oxidation process flow chart.*

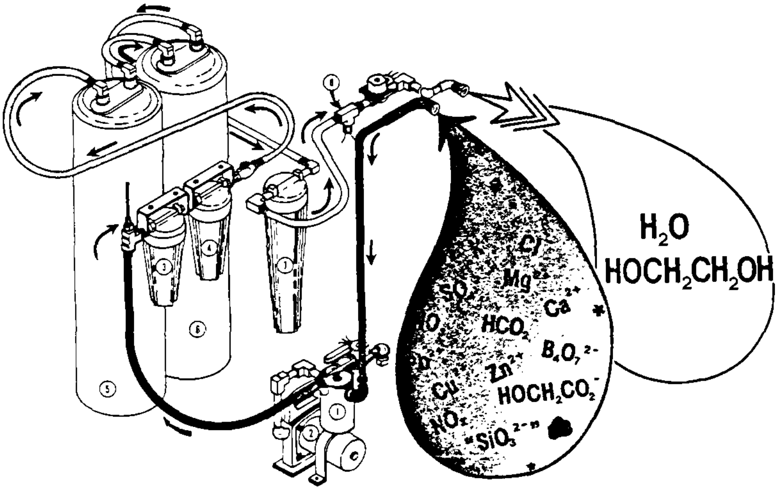

FIG. 2—*Deionization process flow diagram.*

exchanged in Stages 5 and 6 combine to form water (H_2O) in an amount depending on the number of equivalents (moles of charge) of ions removed from the used engine coolant. The resulting purified fluid flows into a final activated carbon filter (7) whose purpose is to remove any entrained gases from the liquid stream.

Finally, the completely purified EG/H_2O mixture passes through an in-line conductivity probe (8), which measures the conductivity of the solution as an indication of the degree of purification by the ion-exchange system in Stages 5 and 6. The probe is designed to show a green light when the conductivity of the solution is below 50 μS/cm. This ensures high-quality effluent and also gives the operator a visual indication that the process is under control and that the ion-exchange beds have not exceeded their capacity. When the ion-exchange resins are exhausted, dissolved solids remain in solution and the conductivity of the effluent rises and quickly exceeds the set point of the probe assembly at 50 μS/cm. This triggers the green light off and the red light on indicating to the operator that the ion-exchange tanks must be removed for regeneration and replaced with a fresh set. At the completion of this process the coolant is re-inhibited and checked for freeze point and reserve alkalinity.

Reverse Osmosis—This batch oriented process is based upon a reverse osmosis membrane. Reverse osmosis uses a membrane to remove dissolved solids from the coolant. Unlike conventional filters, a membrane system separates the feed solution into two streams. The permeate is the fluid that passes through the semipermeable membrane, while the concentrate stream is the part of the feed stream that is used to flush the concentrated solid from the system. One of the most widely known uses of reverse osmosis technology is turning seawater into drinkable water.

Referring to Fig. 3, the pump feeds used coolant to the membrane housings. Coolant (nearly pure ethylene glycol and water) is extracted by the membrane within the housing and leaves the membrane housing in two streams as permeate and concentrate. Permeate is collected at the permeate manifold on systems where more than one membrane housing is used. One permeate line is contained in each membrane housing. The permeate then flows through two flow meters mounted in series and to the outlet point of the machine. External plumbing carries this flow to a permeate storage tank. Concentrate leaves the last membrane and is plumbed to

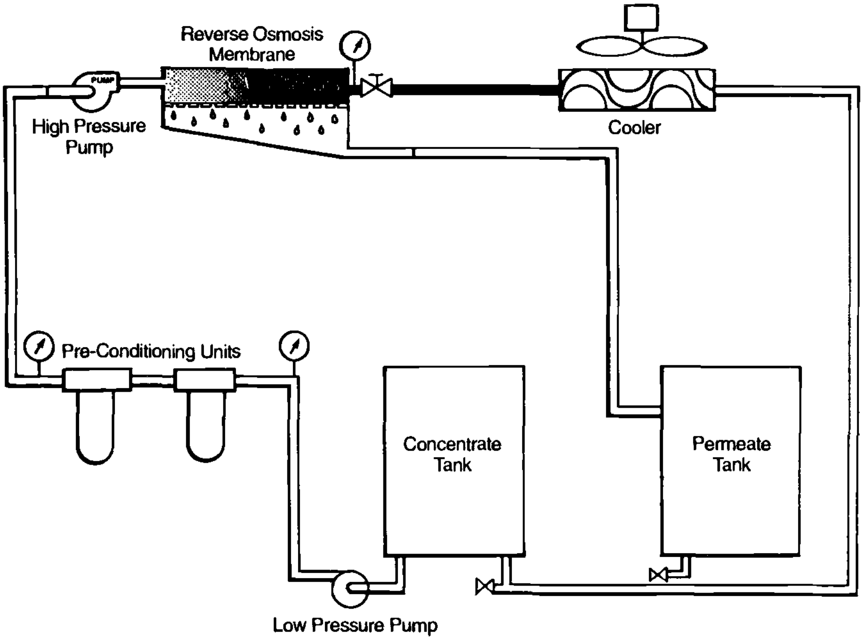

FIG. 3—*Reverse osmosis flow diagram.*

a globe needle valve that controls the pressure within the machine. The concentrate flow continues through a flowmeter and a permeate outlet port. External plumbing carries the concentrate back to the feed tank. The permeate is then adjusted for freeze point and re-inhibited.

Filtration, Centrifugation (with and without deionization)—This process is utilized as a drive-up service to recycle engine coolant on-site. It utilizes the vehicle's engine for the power source and is completely self contained. This process combines a sophisticated series of filters, a thermo-processing operation, a centrifuge system, and a monitored precision additive system that ensures the precise quantities of specially formulated chemical additives are injected.

Referring to Fig. 4, the engine coolant to be processed is evacuated from a storage container containing the coolant designated to be recycled, by a vacuum system in the vehicle. The coolant to be recycled can be stored in any size container, the system can evacuate the coolant from as far away as 100 ft (30.5 m). The engine coolant is drawn through a series of filters reducing the particulates and contaminates. The engine coolant is then heated to reduce its viscosity thereby allowing for a more thorough centrifuge separation of the contaminates from the coolant. After the centrifuge, the coolant is immediately cooled to facilitate handling. The coolant is then injected with the specially formulated additives. As the coolant is processed and flows through the various operations, it is continually monitored, and tests are performed before, during, and after the service.

Vacuum Distillation—Two systems were utilized to evaluate this process. The mechanics of vacuum distillation are straightforward. The coolant to be processed is poured into a boiling chamber. The chamber is then sealed. Heat is then applied to the chamber and, according to basic physical principles, the liquid with the lower boiling point (water) begins to boil out of the chamber first. Exiting the chamber as a vapor, the vapor is directly piped into a heat exchanger where a cooling affect is enacted. The cooling that occurs in the heat exchanger

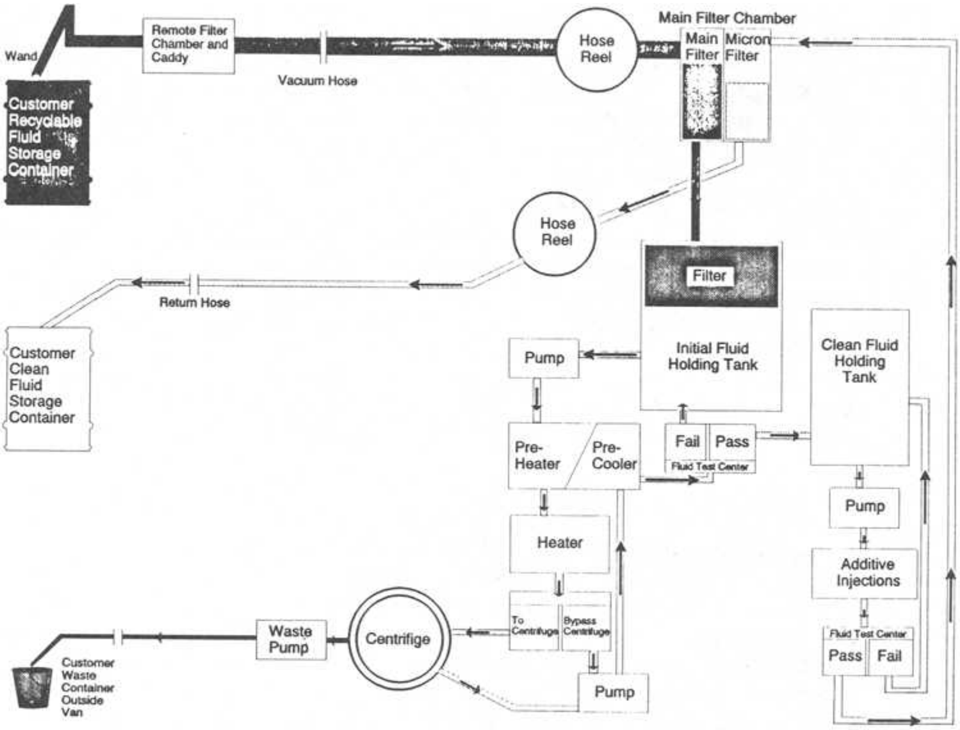

FIG. 4—*Filtration, centrifugation process flow diagram.*

condenses the vapors (lowers the temperature below the boiling point) transforming them back into a liquid. The liquid is then allowed to flow out of the exchanger and into suitable collection vessels to contain either the recovered water or ethylene glycol.

The differences between the two units evaluated consisted of process rates and usability. One system processed coolant at a rate of 5 gal/h (19 L/h) while the other was at a rate of 1 gal/h (4 L/h). One system offered an automatic version, which mixed the water and glycol to a predetermined set point and added the inhibitor package as well.

Coolant Life Extension—This system was developed to extend the useful life of automotive engine coolant. It includes qualification of the coolant by chemical, physical, and visual means; and extension of the coolant life by filtering and the addition of a supplemental coolant additive. Because of the criteria of the qualification tests (mileage $< 65\,000$ km, coolant not to be oily/murky/rusty, glycol level and reserve alkalinity not $<25\%$ or <3, respectively) the reference coolant did not qualify for extension, and therefore this process was not evaluated.

Off-Site Coolant Recycling

There are several facilities in the United States that retrieve spent coolant from service facilities and auto-dealerships for the sole purpose of recycling for reuse as engine coolant. These facilities typically utilize fractional distillation methods although not exclusively. These recycling processes had to be dealt with differently than the smaller on-site systems for reasons such as the significantly larger amounts of coolant needed for processing in each run.

Off-Site Approval Program

In order to determine and maintain the efficacy of off-site coolant recycling, an approval program has been established at General Motors. Letters were distributed to all off-site coolant recycling facilities regardless of the type of process they utilize. The program requires a submitting facility to provide quality control information to ensure a stable process and tradenames of the recycled product along with a list of the outlets where the coolant can be purchased. With this information, finished samples of the recycled product can be acquired by General Motors and sent to a test facility for compliance to GM 1825M, the same criteria used in the on-site tests. Since this approval program is intended to be an ongoing effort, submitting facilities are required to cover the expense of testing. Subsequent retesting will be conducted to ensure continued compliance. Facilities may lose their approved status if they do not continue to meet the program's requirements.

The objective of this program is to provide to General Motors dealers a list of all the facilities capable of providing a recycled coolant that meets or exceeds GM 1825M coolant specifications.

Laboratory Testing of Recycled Coolant

Upon testing the recycled coolants, the ASTM test procedures found within the GM 1825M test specification were conducted in a pre-arranged order. As described in Society of Automotive Engineers (SAE) Report J814, special tests are required to evaluate the performance of coolants with regard to specific forms of corrosive attack. These stepwise procedures are used to avoid the unnecessary expenditure of time and money performing long expensive tests on obviously poor coolants, and to ensure that better coolants will meet service requirements, by the use of more rigorous test conditions. Each of the recycled coolants were tested for compliance of ASTM Method for Corrosion Test for Engine Coolants in Glassware (D 1384), ASTM Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions (D 4340), and chemical/physical tests. If however, the recycled coolant failed to meet the requirements of either D 1384 or D 4340, it was suspended from the test program, and no further testing was performed. Those recycled coolants that met the requirements of both D 1384 and D 4340 were submitted for ASTM Test Method for Caviation Erosion-Corrosion Characteristics of Aluminum Pumps with Engine Coolants (D 2809) and ASTM Method for Simulated Service Corrosion Testing of Engine Coolants (D 2570). For additional information, the radiators and post test coolants were sent for analysis at the conclusion of the simulated service test.

Product Confirmation

In order to assure that the inhibitor formulation used for each recycling process in this test program was identical to that currently utilized in the field, samples of the inhibitor packages were acquired from typical field outlets from each of the processes that had successfully completed D 1384 and D 4340. The acquired inhibitor packages were analyzed and compared to the analysis of the respective recycled coolant inhibitor formulation. The analysis of the inhibitors acquired over the counter had to agree with the inhibitor used in the test program.

To ensure that the performance of each process which meets the pre-described criteria remains unchanged in the field after the completion of this test program, periodic analysis of inhibitor products will be conducted and compared to previous analysis on file. No changes will be allowed in the mechanics of the process or the inhibitor formulation. Furthermore, in order to maintain an approved status, there must not be available alternate inhibitor packages (GM or non-GM facilities).

Conclusions

The purpose of this paper has been to describe the coolant recycling study conducted at STG for the benefit of any who desire to conduct such a test in the future. Also, to provide insight to the results of this study that were incomplete during the writing of this paper. Upon completion, the results will be discussed in the second part of this paper.

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[*2*] Vukasovich, M. S. and Sullivan, F. J., *Inhibitors and Coolant Corrosivity, Engine Coolant Testing, STP 887,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1986, p. 96.

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DISCUSSION

Frank A. Kelly[1] *(written discussion)*—Have you considered providing your dealer organization any economic assessments of the approved recycling processes?

Wayne H. Bradley (author's response)—Some of the recycling equipment that has been approved is in the General Motors dealer equipment program. Those manufacturers that are in the program have made available cost comparison data.

It should be noted however that the actual operating cost is variable and largely dependant upon the equipment's application. The most significant factor being the average condition (that is, total solids content) of the used coolant typically recycled. The more solids involved in the recycling process, the quicker depletion occurs.

Paul Dittmar[2] *(written discussion)*—(1) What recycling processes passed the test? (2) What is your opinion about the capability of the processes that passed for maintaining product quality control on an on going basis?

Wayne H. Bradley (author's response)—1. The following equipment has been endorsed by General Motors for coolant recycling: ACTIV—vacuum distillation, Finish Thompson—vacuum distillation, BG—deionization, and American Fluid Technology—Centrifugation.

2. There are several post-test measurements incorporated into each recycling procedure to assure that the process was successful. Also, variability (in the coolant to be recycled) was accounted for within the diverse composition of the reference coolant used in this evaluation. This, accompanied with an ongoing educational effort, will help ensure a successful recycling program.

Gerry Smith[3] *(written discussion)*—(1) Of the seven types of processes mentioned as being tested, which were found to be effective? (2) Were any methods found to be effective in extending coolant life? If so, what chemistry and/or processes worked?

Wayne H. Bradley (author's response)—1. The following processes were endorsed by General Motors for engine coolant recycling: ACTIV—vacuum distillation, Finish Thompson—vacuum distillation, BG—deionization, and American Fluid Technology—centrifugation.

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[1] Caterpillar, Inc., Technical Center Building E, P.O. Box 1875, Peoria, IL 61656-1875.

[2] Safety-Keen Corp, 12555 W. Old Higgins Rd., Elk Grove Village, IL 60007.

[3] Gold Eagle Company, 4400 S. Kildare, Chicago, IL 60632.

2. The concept of coolant life extension was included in this evaluation. However, because of their coolant qualifications criteria and the characteristics of the reference coolant used in the study, coolant life extension was not evaluated.

Joseph A. Lima[4] *(written discussion)*—With the plethora of on-site systems, the attendant problems of maintenance and additive control and the apparent success of on-board recycling on heavy duty equipment, I am wondering why the automobile manufacturers are not installing on-board filtration systems and including coolant system evaluations at their programmed maintenance intervals, such as 30 000, 60 000, and 90 000 miles (48 279, 96 558, and 144 837 km).

If I may comment, it would seem to me that this would offer the consumer a more effective and supervised alternative to present on-site capability.

Beyond this, there will be eventual need to recycle extended coolant, and I am wondering what evaluations have been made of central off-site recovery systems, where large batch sizes would allow for economically justifiable testing to ensure that the quality desired is met before the material being offered for re-use in vehicles.

Wayne H. Bradley (author's response)—On-board coolant treatment similar to heavy duty applications has been considered for use in automotive applications. The difficulty in implementing this approach in automotive applications is the difference in maintenance techniques from those practiced in heavy duty fleets. Regular additions of SCAs and coolant change out can, and is, controlled in heavy duty fleet applications. In automotive applications however coolant service is not controlled to this degree, and therefore this concept is not feasible.

To address off-site coolant recycling facilities, General Motors has established an approval program. Within this program, coolant recycling facilities may submit pertinent information about their process (that is, quality control data) as well as the names of outlets where their recycled product can be purchased. GM personnel will acquire samples of the product and submit them for test at the submitters expense. Providing both the performance and process requirements are met, the facility will be endorsed. Periodic retesting will occur to ensure product quality.

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[4] Houghton Chemical Corporation, Allston, MA.

F. A. Kelley[1]

Heavy Duty Diesel Engine Coolants: Technology Update

REFERENCE: Kelley, F. A., **"Heavy Duty Diesel Engine Coolants: Technology Update,"** *Engine Coolant Testing: Third Volume, ASTM STP 1192,* R. E. Beal, Ed., American Society for Testing and Materials, Philadelphia, 1993, pp. 289–296.

ABSTRACT: A summary of current heavy duty engine coolant technology is provided which includes a description of heavy duty engines and applications, current problems and concerns which face the industry, industry standard specifications and test methods which are under development to address the concerns, and future directions for the technology. The special needs of heavy duty engines dictate that engine coolant formulations be developed and made available that are tailored to these engines. Efforts to improve fuel economy and durability while reducing emissions and noise will have an important impact on the application of engine coolant technology to heavy duty diesel engines in the future.

KEYWORDS: heavy duty engine coolants, liner pitting, cavitation corrosion, coolant recycling, water pump seals, supplemental coolant additives, coolant maintenance, coolant test methods, water quality

Heavy duty diesel engines have been the work horse of industry for more than 60 years. Through those years, technology has been developed continually to meet demands for durable, cost-effective power systems. Current demands of diesel engine technology are somewhat different than they may have been in the past, however. Today's manufacturers continue to work on engines that provide better fuel economy, better durability, and better reliability, but much more emphasis is placed on improving the environmental impact of diesel engines with significant efforts under way to reduce emissions and reduce noise. Cooling systems of heavy duty diesel engines, and the coolants used in them, are increasingly becoming critical components whose importance cannot be overlooked if all of the demands facing the industry are to be met.

Traditionally, engine coolants developed primarily to suit the needs of automotive engines have been used in heavy duty diesel engine applications. However, for many years now, it has been recognized that significant differences exist between the two types of engine technology, requiring somewhat different treatment for satisfactory results.

Some facets of heavy duty diesel engine technology will be characterized, specific engine coolant-related problems and concerns that face the industry will be discussed, efforts within the ASTM D-15 Engine Coolants Committee to establish suitable standards to address the specific needs of the industry will be highlighted, and some comments about future trends in the technology will be provided in this article.

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[1] Project Manager, Advanced Materials Technology Div., Research Dept., Caterpillar Inc., Peoria, IL.

Heavy Duty Engine Applications

Heavy duty diesel engines are used in a number of demanding applications (Table 1). The popularity of diesel engines for these applications is due to a reputation for excellent fuel economy, high reliability, long service life, and high sustained torque when operating at low speeds. These advantages generally far outweigh the disadvantages of higher initial cost, somewhat heavier weight, and operational roughness. Diesel engines come in many shapes and sizes. They can deliver anywhere from a few kilowatts to more than 15 000 kw (20 000 horsepower) in large marine engines. Since the overwhelming majority of diesel engines produced in the United States are used in the on-highway truck, construction equipment, and farm machinery applications, most of this discussion will relate to the use of diesel engines in these applications. The typical heavy duty diesel engine used in on-highway truck, construction, and farm machinery applications is in the 110 to 330 kw (150 to 450 horsepower) range. Cooling system sizes typically range from 20 to 80 L (5 to 20 gallons).

A characteristic that is common to many of these engines is the use of a wet sleeve cylinder liner in the design. This, coupled with the high pressures that are characteristic of the diesel combustion process and the strong tendency for severe piston impact on the liner, leads to the occurrence of liner pitting. This problem will be discussed in more detail in the next section.

Several characteristics of diesel engine applications are important to consider that have an effect on the type of engine coolant formulation and maintenance strategy that is best suited for use. Today's typical diesel engines are primarily cast iron systems with copper and brass used in radiators and oil coolers. This contrasts with the extensive use of aluminum in many automotive engines. Heavy duty diesel engines are expected to operate for better than 800 000 km (500 000 miles) before requiring a major overhaul. It is possible, with the use of good quality engine coolant and oil formulations and adherence to recommended maintenance practices, to reach 1 600 000 km (1 000 000 miles).

Heavy duty diesel engines are often operated with high load factors and with high rates of use in comparison to automotive engines. It is not uncommon for a heavy duty on-highway truck to log more than 240 000 km (150 000 miles) in a year. Many heavy duty trucks travel routes that stretch from coast to coast and include both flat and mountainous terrain. Construction equipment in some mining applications is operated nearly continuously over three shifts. In most applications, downtime is not appreciated since this amounts to a loss in revenue for the equipment owner.

The environments in which heavy duty diesel engines must operate have an impact on cooling systems. They must be able to function in cold, arctic climates as well as hot, tropical locations. Care must be taken not to overconcentrate the cooling system with glycol in obtaining the necessary freeze protection for arctic applications as this will lead to problems with additive drop-out. A 60 vol.% concentration of ethylene glycol concentrate is considered to be the high-

TABLE 1—*Heavy duty engine applications.*

- On-Highway Truck
- Construction Equipment
- Farm Machinery
- Railroad
- Marine
- Electric Power Generation
- Industrial

est practical level for use as this level will provide the maximum practical freeze protection for ethylene glycol-water mixtures. In warm climates, it is still common for water with an appropriate concentration of supplemental coolant additive (SCA) to be used in heavy duty engine cooling systems. This practice will probably become less acceptable as engine operating temperatures increase and aluminum components find their way into applications in heavy duty diesels in the future.

Current engine coolant technology requires the use of SCAs in combination with a good quality automotive engine coolant that is low in silicates to achieve optimum results. SCA formulations provide liner pitting protection, and some improved capability to control scaling of heat transfer surfaces. True heavy duty engine coolants are beginning to appear in the marketplace, eliminating the need for the addition of an SCA at initial fill, but still require maintenance dosages of SCA at regular intervals. These maintenance dosages are applied through the addition of specified quantities of liquid SCA or through filter changes containing SCA in solid form.

The need to regularly replenish inhibitors in heavy duty engine applications can be attributed to high use rates resulting in depletion of key inhibitors in engine coolant formulations prior to the exhaustion of the ethylene glycol itself. It would not be economical to replace the inhibitors by draining the engine coolant and filling with a fresh charge of coolant. The accumulation of spent inhibitors and regular additions of SCA eventually leads to the need to replace the entire coolant in the system due to the increase in total dissolved solids that results. Typical heavy duty engine change interval recommendations are in the range from 160 000 to 320 000 km (100 000 to 200 000 miles) or 1 to 2 years of service.

Current Problems and Concerns

Liner Pitting

Perhaps, the most significant coolant-related engine problem experienced by heavy duty engine manufacturers is liner pitting. Liner pitting has been known to occur for many years in diesel engines [*1*]. It is the result of cavitation and erosion processes that occur on the water side of diesel engine cylinder liners. Cylinder liners vibrate from the motion of the piston within the cylinder. This vibration creates pressure variations in certain regions of the fluid causing vapor bubbles to form and collapse in concert with the vibrating surface of the liner. This produces a cavitation effect where collapsing bubbles violently impinge on the liner surface, eroding away material. Cavitation-erosion produces increased corrosion of the cast iron by removing protective films that leave the exposed surface susceptible to a rapid, localized corrosion attack.

This corrosion can be arrested by the presence of very rapid film forming agents in the engine coolant. Initially, additions of relatively high concentrations of sodium dichromate corrosion inhibitor to the cooling system were found to be effective in reducing or eliminating the damage. Chromates are no longer used and today's formulations for the protection of heavy duty engines from liner pitting contain sufficient levels of sodium nitrite, or combinations of sodium nitrite with sodium molybdate, to control the problem. These film formers are not normally present in most automotive technology engine coolants.

Silicate Drop-out

Another problem of heavy duty diesel engines is that of silicate drop-out. Silicates have become very popular in automotive engine coolant formulations because of their effectiveness in controlling aluminum corrosion in high heat transfer areas of automobiles [*2*]. Silicates can be relatively unstable in solution and are prone to precipitate in some situations, such as when the total dissolved solids level is high, high hardness water is added to the mixture, or glycol concentration is high. This problem is further complicated by the need to use an SCA for heavy duty engine applications because this adds more solids to the system and, usually, more silicates as well. The tendency for silicate drop-out to occur has led to recommendations in the heavy duty engine industry to use engine coolant formulations containing low levels of silicate corrosion inhibitor to produce minimal interference with SCA additions.

Water Pump Seal Leakage

Water pump seal leakage is a common problem in heavy duty applications. The seals used in heavy duty engine water pumps are generally similar in design to those used in automotive applications. However, they are plagued more often by problems caused by silicate drop-out and high levels of total dissolved solids in heavy duty engine systems. Water pump seal leakage problems are usually difficult to resolve because there are so many contributing variables. In order to minimize the likelihood of water pump seal failure in heavy duty engines, it is necessary to avoid high levels of silicate in the engine coolant, maintain low total dissolved solids levels, and to keep glycol concentrations below 70%.

Solder Bloom/Solder Corrosion

Radiators and oil coolers on heavy duty engines must withstand higher levels of stress, shock, and vibration than their automotive counterparts. For this reason, corrosion of solder can be a bigger problem in heavy duty engine applications. There are two types of solder corrosion problems. Solder bloom is a solder corrosion product that forms as a highly voluminous deposit. The make-up of the deposit is generally low in lead but contains high levels of other materials that have been codeposited with the lead from the engine coolant. The solder bloom process is not thought to produce weakened solder joints in most cases, but does often lead to overheating problems by closing off the ends of the tubes to restrict coolant flow. The potential for solder bloom to occur is reduced by assuring that solder fluxes are thoroughly cleaned from any new or rebuilt system and that only good quality engine coolant and water is added to the cooling system. Other forms of solder corrosion more directly attack the solder joint, leading to failure of the joint and leakage. One aggravator to solder corrosion is the nitrite corrosion inhibitor used to protect against liner pitting. If the cooling system is overdosed with SCA, the resulting high nitrite levels can lead to increased solder corrosion. For this reason, it is necessary to maintain SCA levels within the operating range specified by the engine manufacturer and SCA supplier.

Scaling

Scaling of high heat transfer surfaces is particularly troublesome in heavy duty engines. Coolant loss is more common in heavy duty engine applications. This leads to frequent additions of water to the cooling system. If high hardness water is added to the system, the potential for producing scale deposits on the liners is increased. Scale deposits on the coolant side insulate the liners and affect the heat transfer from the cylinder. This can lead to higher operating temperatures in the ring belt zone and an increase in piston deposits which, in turn, can cause premature wear-out on the oil side of the cylinder kit. To minimize the problem it is recommended that good quality water be used. Most SCA formulations provide some additives designed to counteract the effects of scaling.

Recycling

Environmental concerns have produced more awareness for the need to recycle used engine coolants. A significant number of approaches to engine coolant recycling have surfaced in recent years. Many of the approaches being marketed are not suitable for the purpose of recycling engine coolant to be used in heavy duty engines because they do not remove the dissolved solids from the system. The primary reason for draining engine coolant from a heavy duty engine is to remove contaminants that have accumulated in the system during use. These contaminants include corrosion products, spent inhibitors, oxidized glycol, hard water salts, oil, etc. Many of these contaminants are soluble in the coolant and are not removed by filtration or simple ion exchange. It is absolutely imperative that recycled coolant for heavy duty engine usage have these contaminants removed prior to reinstallation in the system. One process that has been evaluated and has been found to be acceptable for the purpose of recycling used engine coolant for heavy duty engine usage is distillation. It is very important to follow the engine manufacturer's recommendation for recycled coolants as improper practices will lead to premature engine failure.

Maintenance

As evidenced, proper maintenance is critical for the successful operation of heavy duty engines. Either a low silicate engine coolant formulation with the appropriate amount of SCA or a true heavy duty engine coolant formulation incorporating the initial dosage of liner pitting and scaling protection should be used. Maintenance dosages of SCA should be added at recommended intervals to replenish depleted inhibitors. And good quality water should be used. Suggested limits for water appropriate for use in heavy duty engine cooling systems have been developed (Table 2).

Standards Under Development

Most automotive engine coolant formulations fall short of providing adequate performance in the typical heavy duty diesel engine. The ASTM D-15 Engine Coolants Committee has been very active in seeking to develop new standards, test methods, and specifications to support the needs of the heavy duty engine industry. One heavy duty engine specification has been introduced and several other specifications and test methods are under development.

The one specification that is now in place is ASTM D 4985-89 Standard Specification for Low Silicate Ethylene Glycol Base Engine Coolant for Heavy Duty Engines Requiring an Initial Charge of Supplemental Coolant Additive (SCA). It is intended to provide the heavy duty

TABLE 2—*Recommended water quality limits.*[a]

Property	Specific Values	ASTM Test Method
Total Solids, ppm	340 max.	D 1888
Total Hardness, ppm	170 max.	D 1126
Chlorides, ppm	40 max.	D 512, D 4327
Sulfates, ppm	100 max.	D 516, D 4327
pH	5.5–9.0	D 1293

[a] Recommended by Engine Manufacturers' Association coolants subcommittee based on a survey of service recommendations of North American heavy duty diesel engine manufacturers.

industry with a standard engine coolant that minimizes the problem of silicate overconcentration and drop-out that began to cause significant difficulties in the early to middle 1980s.

Heading the list of new heavy duty engine coolant specifications under development is the supplemental coolant additive specification. The heavy duty engine industry has relied on the use of SCAs. The new specification under development will provide an industry approved standard for those existing products which conform to the informal standard that has developed over the years and provide engine manufacturers with a better means for describing to their customers those products that meet the necessary requirements.

To address the difficulties of obtaining suitable water meeting suggested quality limits, a specification will be developed for prediluted engine coolants, which are blended with an appropriate quantity of ethylene glycol for freeze protection and water meeting very stringent quality standards. The initial version for heavy duty engines will be based on the existing ASTM D 4985 low silicate engine coolant specification.

The current movement toward increased recycling of used engine coolant will not be effective until appropriate specifications are developed defining what is expected of the recycled product. As mentioned previously, it will be very important for recycled coolants intended for use in heavy duty engines to have sufficient amounts of contaminants removed such that the resulting product does not interfere with SCA additions or water pump seal performance. Corrosion performance capability will be required to match that of products based on virgin materials.

There is a need for a specification that is based on formulations tailored specifically to the needs of heavy duty engines. A "true" heavy duty engine coolant formulation simplifies the installation of new engine coolant by not requiring the addition of an SCA at initial fill. This avoids the inefficiency of combining two separate inhibitor systems during the initial fill and compatibility problems that can result. It provides an engine coolant mixture that has a reduced total dissolved solids level at initial fill. These formulations currently still require the addition of maintenance dosages of SCAs at periodic intervals after the initial fill.

It will be important to develop appropriate bench tests for inclusion in each of the specifications that are under development. Currently, acceptable performance in the critical problem areas discussed previously is mainly established through full-scale engine testing. Specifications based on full-scale engine tests would tend to reduce the participation of many potential suppliers who would have difficulty justifying the cost of demonstrating conformance for their engine coolant or SCA products. Formulation specifications that define some or all of the composition of the conforming products provide only a partial solution because they may preclude some products that otherwise may be proven acceptable through proper engine dynamometer or field testing.

Four bench test procedures have been proposed for development within the ASTM D-15.11 Subcommittee on Heavy Duty Engine Coolants to provide the necessary performance definitions desired for heavy duty engine applications. A vibratory cavitation bench test based on the use of an ultrasonic horn has been chosen as the method for demonstrating acceptable liner pitting protection. Methods based on this approach have been shown to discriminate between formulations that perform acceptably in field experience to provide adequate liner pitting protection and those which perform unacceptably in this regard [*3*]. An industry standard test for evaluating the tendency of engine coolant formulations or SCAs to produce water pump seal leakage problems is also under development [*4*]. The third bench test under development addresses the issue of scaling of heat transfer surfaces and is expected to determine the scaling protection provided by formulations intended for heavy duty engine applications. In this test, the test fluid composition containing hard water salts is flowed past a heated iron surface which is then weighed to determine the extent of scaling. Lastly, a test that demonstrates acceptable compatibility between engine coolant and SCA products is being developed. In this case, the combined mixture is centrifuged and any precipitated material that collects is measured.

Future Directions

In the coming years, diesel engine technology will experience significant changes as engine manufacturers work to develop engines that meet new regulations for exhaust emissions and noise, while seeking improvements in fuel economy, service life, and ease of maintenance. Many of the approaches to future heavy duty engine technology will result in higher operating temperatures. It will be a major challenge to achieve these goals, and engine cooling systems will play a key role in determining ultimate success.

Future emphasis on improved fuel economy and reduced costs will most likely bring more usage of aluminum into the picture. However, increased aluminum usage in heavy duty engine cooling systems will occur only if cooling system designs and engine coolant formulations that demonstrate acceptable reliability and durability can be devised. Aluminum radiator technology will have to demonstrate significantly improved durability and serviceability in order to be of use in heavy duty engine cooling systems. Engineers will need to be certain that the application of any aluminum component in a heavy duty engine cooling system is compatible with expected maintenance practices and available engine coolant technology for the engine.

Solder corrosion problems have led engineers to search for alternative methods of improving the robustness of heavy duty radiator systems. Also, manufacturers are looking for ways to reduce the usage of lead in their products for environmental considerations. The two approaches that are receiving significant attention are the development of joint designs that greatly reduce the exposure of the solder to the engine coolant and development of alternative solders. Zinc based solder development is an example of the latter approach.

Alternative engine coolant fluids have received a significant amount of scrutiny. Most significantly, propylene glycol-based engine coolants have received much attention. Although propylene glycol has been used for many years during periods of short ethylene glycol supply, only recently has significant interest been placed on the prospects for taking advantage of the specific properties of propylene glycol as an engine coolant fluid of choice. The advantages most often cited include reduced toxicity in comparison to ethylene glycol and improved corrosion performance, particularly in the case of aluminum. Some investigators have reported that propylene glycol-based engine coolant formulations can provide improved protection against liner pitting [5] compared to their ethylene glycol counterparts. The effect of the propylene glycol is thought to be primarily physical in that the intensity of the bubble collapse might be reduced.

Although most of the emphasis on propylene glycol is on traditional aqueous-based systems, much interest has been generated for the development of anhydrous propylene glycol based systems [6]. This approach takes advantage of the wide fluid temperature range of −60 to 187°C (−76 to 369°F) that propylene glycol offers. This allows fluid systems to be designed requiring no water for freeze protection and no pressure for boiling point elevation. Interest in heavy duty engines comes primarily from the ability to operate at higher temperatures or the possibility for reducing radiator frontal area for streamlining vehicles in on-highway truck applications.

The prospect that coolant formulations can be developed for heavy duty engine applications that have extended protection capability without the need to rely on SCA additions at initial fill or for inhibitor replenishment has begun to garner a significant amount of attention. Long-life engine coolant formulations based on organic acid inhibitor chemistry are representative of one approach to this type of technology [7]. Anhydrous fluid technology, such as the previously mentioned propylene glycol-based technology or oil-based technology, are other possible ways of achieving this desirable goal. A true heavy duty engine coolant with long-life capability would have significant value to the user of heavy duty engine technology.

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