CLEANING STAINLESS STEEL

STP 538

AMERICAN SOCIETY FOR TESTING AND MATERIALS

CLEANING STAINLESS STEEL

A symposium
presented by Committee A-1
on Steel, Stainless Steel and
Related Alloys, and Committee D-12
on Soaps and Other Detergents,
AMERICAN SOCIETY FOR
TESTING AND MATERIALS
Cleveland, Ohio, 17-19 Oct. 1972

ASTM SPECIAL TECHNICAL PUBLICATION 538

E. S. Kopecki, symposium chairman

List price $18.00

04-538000-02

AMERICAN SOCIETY FOR TESTING AND MATERIALS
1916 Race Street, Philadelphia, Pa. 19103

Library of Congress Catalog Card Number: 73-80188

**Printed in Tallahassee, Fla.
October 1973**

Foreword

The symposium on Cleaning Stainless Steel was presented 17-19 October 1972, in Cleveland, Ohio, and was sponsored by Committee A-1 on Steel, Stainless Steel and Related Alloys, and Committee D-12 on Soaps and Other Detergents. E. S. Kopecki, Committee of Stainless Steel Producers of the American Iron and Steel Institute, presided as the symposium chairman.

Related
ASTM Publications

Stainless Steel for Architectural Use, STP 454 (1969), $9.75, 04-454000-02

Contents

Introduction

Cleanliness and stainless steel are so closely interrelated and interdependent, that in many applications one is not possible without the other. In the dairy industry, on one hand, stainless steel provides the degree of cleanliness that is required of equipment in contact with the dairy product. On the other hand, the very nature of stainless steel is such that it best serves the widespread purposes for which it is utilized, if it is kept clean and in a passive state. Precautions must be observed to avoid conditions which can destroy or disturb the passive state. Because these precautions involve equipment design, control of the operations used in fabrication, as well as subsequent use and maintenance of the equipment, the complexity of the subject is apparent. Particularly so, when taking into account the multitude of corrodents to which stainless steels are exposed, the variety of soils which are encountered, and the numerous cleaning methods and media which are offered to meet these challenges.

Committee A-1 on Steel, Stainless Steel and Related Alloys, and Committee D-12 on Soaps and Other Detergents, cooperated in sponsoring a symposium on cleaning stainless steel, in an effort to assemble data on the "state-of-the-art" for as many pertinent aspects of the subject as possible and to focus attention on new developments.

This symposium represents a comprehensive coverage devoted exclusively to cleaning stainless steel. The information contained in the 23 papers will be useful to manufacturers of stainless steel products or equipment; to those designing such equipment; to those already using stainless steel equipment or contemplating its use because of new corrosion conditions being encountered; and to those who produce chemicals or devices used in cleaning this equipment.

Practical, up-to-date information on the well-established methods such as alkaline, acid, and solvent cleaning, is presented. New developments are also discussed, such as those which permit automation of vibratory cleaning techniques.

Several papers explore the cleaning requirements faced by nuclear power plants, which utilize stainless steel extensively. Information is also presented on cleaning agent actions on stainless steel components for sodium heat transport systems, which are designed to operate at up to 1200°F.

Another facet of power plants—both nuclear and fossil-fueled—where cleaning of stainless steel is of importance, pertains to condenser tubing. In this service, which requires cleaning to maintain heat transfer efficiency of the tubing, the cleaning has the added benefit of improving the performance of stainless steel. The role of chemical and in-service mechanical cleaning techniques and their influence on power plant operations and costs, are described.

Cleanliness requirements in the chemical industry, and in the food industry—where cleaning-in-place procedures are employed—are also emphasized.

E. S. Kopecki

Committee of Stainless Steel Producers
American Iron and Steel Institute
New York, N. Y.
symposium chairman

STP538-EB/Oct. 1973

Designation: A 380 - 72

American National Standard G 81.16
American National Standards Institute

Standard Recommended Practice for
CLEANING AND DESCALING STAINLESS STEEL PARTS, EQUIPMENT, AND SYSTEMS[1]

This Standard is issued under the fixed designation A 380; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This standard covers recommendations and precautions for cleaning and descaling of new stainless steel parts, assemblies, equipment, and installed systems. These recommendations are not intended to be mandatory, but rather are presented as procedures for guidance when it is recognized that for a particular service it is desired to remove surface contaminants that may impair the normal corrosion resistance of the particular stainless grade or may cause product contamination. Although they apply primarily to materials in the composition ranges of the austenitic, ferritic, and martensitic stainless steels, the practices described may also be useful for cleaning other metals if due consideration is given to corrosion and possible metallurgical effects.

1.2 The standard does not cover decontamination or cleaning of equipment or systems that have been in service, nor does it cover descaling and cleaning of materials at the mill. On the other hand, some of the practices may be applicable for these purposes. While the standard provides recommendations and information concerning the use of acids and other cleaning and descaling agents, it cannot encompass detailed cleaning procedures for specific types of equipment or installations. It therefore in no way precludes the necessity for careful planning and judgment in the selection and implementation of such procedures.

1.3 These practices may be applied when free iron, oxide scale, rust, grease, oil, carbonaceous or other residual chemical films, soil, particles, metal chips, dirt, or other nonvolatile deposits might adversely affect the metallurgical or sanitary condition or stability of a surface, the mechanical operation of a part, component, or system, or contaminate a process fluid. The degree of cleanness required on a surface depends on the application. In some cases, no more than degreasing or removal of gross contamination is necessary. Others, such as food-handling, pharmaceutical, aerospace, and certain nuclear applications, may require extremely high levels of cleanness, including removal of all detectable residual chemical films and contaminants that are invisible to ordinary inspection methods.

1.4 Attainment of surfaces that are free of iron, metallic deposits, and other contamination depends on a combination of proper design, fabrication methods, cleaning and descaling, and protection to prevent recontamination of cleaned surfaces. Meaningful tests to establish the degree of cleanness of a surface are few, and those are often difficult to administer and to evaluate objectively. Visual inspection is suitable for the detection of gross contamination, scale, rust, and particulates, but may not reveal the presence of thin films of oil or residual chemical films. In addition, visual inspection of internal surfaces is often impossible because of the configuration of the item. Methods are described for the detection of free iron and transparent chemical and oily

---

[1] This recommended practice is under the jurisdiction of ASTM Committee A-1 on Steel, Stainless Steel and Related Alloys and is the direct responsibility of Subcommittee A01.14 on Methods of Corrosion Testing.

Current edition approved March 3, 1972. Published May 1972. Originally published as A 380 – 54 T. Last previous edition A 380 – 57.

deposits.

2. Applicable Documents

2.1 *ASTM Standards:*

F 21, Test for Hydrophobic Surface Films by the Atomizer Test.[2]

F 22, Test for Hydrophobic Surface Films by the Water-Break Test.[2]

2.2 *Other Documents:*

209a, Federal Standard for Clean Room and Work Station Requiring Controlled Environments.

3. Design

3.1 Consideration should be given in the design of parts, equipment, and systems that will require cleaning to minimize the presence of crevices, pockets, blind holes, undrainable cavities, and other areas in which dirt, cleaning solutions, or sludge might lodge or become trapped, and to provide for effective circulation and removal of cleaning solutions. In equipment and systems that will be cleaned in place or that cannot be immersed in the cleaning solution, it is advisable to slope lines for drainage; to provide vents at high points and drains at low points of the item or system; to arrange for removal or isolation of parts that might be damaged by the cleaning solution or fumes from the cleaning solutions; to provide means for attaching temporary fill and circulation lines; and to provide for inspection of cleaned surfaces.

3.2 In a complex piping system it may be difficult to determine how effective a cleaning operation has been. One method of designing inspectability into the system is to provide a short flanged length of pipe (that is, a spool piece) at a location where the cleaning is likely to be least effective; the spool piece can then be removed for inspection upon completion of cleaning.

4. Precleaning

4.1 Precleaning is the removal of grease, oil, paint, soil, grit, and other gross contamination preparatory to a fabrication process or final cleaning. Precleaning is not as critical and is generally not as thorough as subsequent cleaning operations. Materials should be precleaned before hot-forming, annealing, or other high-temperature operation, before any descaling operation, and before any finish-cleaning operation where the parts will be immersed or where the cleaning solutions will be reused. Items that are subject to several redraws or a series of hot-forming operations, with intermediate anneals, must be cleaned after each forming operation, prior to annealing. Precleaning may be accomplished by vapor degreasing; immersion in, spraying, or swabbing with alkaline or emulsion cleaners, steam, or high-pressure water-jet (see 6.2).

5. Descaling

5.1 *General*—Descaling is the removal of heavy, tightly adherent oxide films resulting from hot-forming, heat-treatment, welding, and other high-temperature operations. Because mill products are usually supplied in the descaled condition, descaling (except removal of localized scale resulting from welding) is generally not necessary during fabrication of equipment or erection of systems (see 6.3). When necessary, scale may be removed by one of the chemical methods listed below, by mechanical methods (for example, abrasive blasting, sanding, grinding, power brushing), or by a combination of these.

5.2 *Chemical Descaling (Pickling)*—Chemical descaling agents include aqueous solutions of sulfuric, nitric, and hydrofluoric acid as described in Appendix A1, molten alkali or salt baths, and various proprietary formulations.

5.2.1 *Acid Pickling*—Nitric-hydrofluoric acid solution is most widely used by fabricators of stainless steel equipment and removes both metallic contamination and welding and heat-treating scales. Nitric-hydrofluoric acid must be used with caution on sensitized austenitic stainless steels and hardened martensitic stainless steels. Solutions of nitric acid alone are usually not effective for removing heavy-oxide scale.

5.2.2 Surfaces to be descaled are usually precleaned prior to chemical treatment. When size and shape of product permit, total immersion in the pickling solution is preferred. Where immersion is impractical, descaling may be accomplished by (*1*) wetting the surfaces by swabbing or spraying; or (*2*) by par-

---

[2] *Annual Book of ASTM Standards, Part 8.*

tially filling the item with pickling solution and rotating or rocking to slosh the solution so that all surfaces receive the required chemical treatment. The surface should be kept in contact with agitated solution for about 15 to 30 min or until inspection shows that complete scale removal has been accomplished. Without agitation, additional exposure time may be required. If rocking or rotation are impracticable, pickling solution may be circulated through the item or system until inspection shows that descaling has been accomplished.

5.2.3 Over-pickling must be avoided. Uniform removal of scale with acid pickling depends on the acid used, acid concentration, solution temperature, and contact time (see Appendix A1). Continuous exposure to pickling solutions for more than 30 min is not recommended. The item should be drained and rinsed after 30 min and examined to check the effectiveness of the treatment. Additional treatment may be required. Most pickling solutions will loosen weld and heat-treating scale but may not remove them completely. Intermittent scrubbing with a stainless steel brush or fiber-bristle brush, in conjunction with pickling or the initial rinse, may facilitate the removal of scale particles and products of chemical reaction (that is, pickling *smut*).

5.2.4 After chemical descaling, surfaces must be thoroughly rinsed to remove residual chemicals; a neutralization step is sometimes necessary before final rinsing. Chemical descaling methods, factors in their selection, and precautions in their use are described in the *Metals Handbook*.[3] When chemical descaling is necessary, it should be done while the part is in its simplest possible geometry, before subsequent fabrication or installation steps create internal crevices or undrainable spaces that may trap descaling agents, sludge, particles, or contaminated rinse water that might either result in eventual corrosion or adversely affect operation of the item after it is placed in service.

5.3 *Mechanical Descaling*—Mechanical descaling methods include abrasive blasting, power brushing, sanding, grinding, and chipping. Procedural requirements and precautions for some of these methods are given in the *Metals Handbook*.[3] Mechanical descaling methods have the advantage that they do not produce such physical or chemical conditions as intergranular attack, pitting, hydrogen embrittlement, cracks, or smut deposits. For some materials, in particular the austenitic stainless steels when in the sensitized condition and the martensitic stainless steels when in the hardened condition, mechanical descaling may be the only suitable method. Grinding is usually the most effective means of removing localized scale such as that which results from welding. Disadvantages of mechanical descaling are cost, as compared to chemical descaling, and the fact that surface defects (for example, laps, pits, slivers) may be obscured, making them difficult to detect.

5.3.1 Surfaces to be descaled may have to be precleaned. Particular care must be taken to avoid damage by mechanical methods when descaling thin sections, polished surfaces, and close-tolerance parts. After mechanical descaling, surfaces should be cleaned by scrubbing with hot water and fiber brushes, followed by rinsing with clean, hot water.

5.3.2 Grinding wheels and sanding materials should not contain iron, iron oxide, zinc, or other undesirable materials. Grinding wheels, sanding materials, and wire brushes previously used on other metals should not be used on stainless steel. Wire brushes should be of a stainless steel which is equal in corrosion resistance to the material being worked on.

5.3.3 Clean, previously unused glass beads or iron-free silica or alumina sand are recommended for abrasive blasting. Steel shot or grit is generally not recommended because of the possibility of embedding iron particles. The use of stainless steel shot or grit reduces the danger of rusting and iron contamination, but cannot completely eliminate the possibility of embedding residues of iron-oxide scale. If a totally iron and scale free surface is required, abrasive blasting may be followed by a brief acid dip (see Appendix A2).

6. Cleaning

6.1 *General*—Cleaning includes all opera-

---

[3] "Heat Treating, Cleaning, and Finishing", *Metals Handbook*, American Society for Metals, 8th ed., Vol 2, 1964.

tions necessary for the removal of surface contaminants from metals to ensure (*1*) maximum corrosion resistance of the metal; (*2*) prevention of product contamination; and (*3*) achievement of desired appearance. Cleanness is a perishable condition. Careful planning is necessary to achieve and maintain clean surfaces, especially where a high degree of cleanness is required. Selection of cleaning processes is influenced mainly by the type of contaminant to be removed, the required degree of cleanness, and cost. If careful control of fabrication processes, sequencing of cleaning and fabrication operations, and measures to prevent recontamination of cleaned surfaces are exercised, very little special cleaning of the finished item or system may be necessary to attain the desired level of cleanness. If there is a question concerning the effectiveness of cleaning agents or procedures, or the possible adverse effects of some cleaning agents or procedures on the materials to be cleaned, trial runs, using test specimens and sensitive inspection techniques may be desirable. Descriptions, processes, and precautions to be observed in cleaning are given in the *Metals Handbook*.[3] Proprietary cleaners may contain harmful ingredients, such as chlorides or sulfur, which could adversely affect the performance of a part, equipment, or system under service conditions. It is recommended that the manufacturer of the cleaner be consulted if there is reason for concern.

NOTE 1—Instances are known where stainless steel vessels have stress cracked before start-up due to steaming out or boiling out with a chloride-containing detergent.

6.2 *Cleaning Methods*—Degreasing and general cleaning may be accomplished by immersion in, swabbing with, or spraying with alkaline, emulsion, solvent, or detergent cleaners or a combination of these; by vapor degreasing; by ultrasonics using various cleaners; by steam, with or without a cleaner; or by high-pressure water-jetting. The cleaning method available at any given time during the fabrication or installation of a component or system is a function of the geometric complexity of the item, the type of contamination present, the degree of cleanliness required, and cost. Methods commonly used for removing deposited contaminants (as opposed to scale) are described briefly below and in greater detail (including factors to be considered in their selection and use) in the *Metals Handbook*[3] and the *SSPC Steel Structures Painting Handbook*.[4] The safety precautions of 8.6 must be observed in the use of these methods. Particular care must be exercised when cleaning closed systems and items with crevices or internal voids to prevent retention of cleaning solutions and residues.

6.2.1 *Alkaline Cleaning* is used for the removal of oily, semisolid, and solid contaminants from metals. To a great extent the solutions used depend on their detergent qualities for cleaning action and effectiveness. Agitation and temperature of the solution are important.

6.2.2 *Emulsion Cleaning* is a process for removing oily deposits and other common contaminants from metals by the use of common organic solvents dispersed in an aqueous solution with the aid of a soap or other emulsifying agent (an emulsifying agent is one which increases the stability of a dispersion of one liquid in another). It is effective for removing a wide variety of contaminants including pigmented and unpigmented drawing compounds and lubricants, cutting fluids, and residues resulting from liquid penetrant inspection. Emulsion cleaning is used when rapid, superficial cleaning is required and when a light residual film of oil is not objectionable.

6.2.3 *Solvent Cleaning* is a process for removing contaminants from metal surfaces by immersion or by spraying or swabbing with common organic solvents such as the aliphatic petroleums, chlorinated hydrocarbons, or blends of these two classes of solvents. Cleaning is usually performed at or slightly above room temperature. Except for parts with extremely heavy contamination or with hard-to-reach areas, or both, good agitation will usually eliminate the need for prolonged soaking. Virtually all metal can be cleaned with the commonly used solvents unless the solvent has become contaminated with acid, alkali, oil, or other foreign material. Chlorinated solvents are not recommended for degreasing of closed systems or

---

[4] *Good Painting Practices*, Steel Structures Painting Council, Vol 1, 1954, Chapters 2 and 3.

items with crevices or internal voids.

6.2.4 *Vapor Degreasing* is a generic term applied to a cleaning process that employs hot vapors of a volatile chlorinated solvent to remove contaminants, and is particularly effective against oils, waxes, and greases. The cleanness and chemical stability of the degreasing solvent are critical factors in the efficiency of the vapor and possible chemical attack of the metal. Water in the degreasing tank or on the item being cleaned may react with the solvent to form hydrochloric acid, which may be harmful to the metal. No water should be present in the degreasing tank or on the item being cleaned. Acids, oxidizing agents, and cyanides must be prevented from contaminating the solvent. Materials such as silicones cause foaming at the liquid-vapor interface and may result in recontamination of the workpiece as it is removed from the degreaser. Vapor degreasing with chlorinated solvents is not recommended for closed systems or items with internal voids or crevices.

6.2.5 *Ultrasonic Cleaning* is often used in conjunction with certain solvent and detergent cleaners to loosen and remove contaminants from deep recesses and other difficult to reach areas, particularly in small work-pieces. Cavitation in the liquid produced by the high frequency sound causes micro agitation of the solvent in even tiny recesses of the workpiece, making the method especially desirable for cleaning parts or assemblies having an intricate configuration. For extremely high levels of surface cleanness, high-purity solvents (1 ppm total nonvolatile residue) are required.

6.2.6 *Synthetic Detergents* are extensively used as surface-active agents because they are freer rinsing than soaps, aid in soils dispersion, and prevent recontamination. They are effective for softening hard water and in lowering the surface and interfacial tensions of the solutions. Synthetic detergents, in particular, should be checked for the presence of harmful ingredients as noted in 6.1.

6.2.7 *Chelate Cleaning*—Chelates are chemicals that form soluble, complex molecules with certain metal ions, inactivating the ions in solution so they cannot normally react with another element or ions to produce precipitates or scale. They enhance the solubility of scales and certain other contaminants, do not precipitate different scales when the cleaning solution becomes spent, and can be used on some scales and contaminants that even mineral acids will not attack. When properly used (chelating agents must be continuously circulated and must be maintained within carefully controlled temperature limits), intergranular attack, pitting, and other harmful effects are minimal. Chelating agents are particularly useful for cleaning installed equipment and systems.

6.2.8 *Mechanical Cleaning* (also see 5.3). Very light abrasive blasting, vapor blasting using a fine abrasive suspended in water, grinding, or wire brushing are often desirable for removing surface contaminants and rust. Cleanliness of abrasives and cleaning equipment is extremely important to prevent recontamination of the surfaces being cleaned. Although surfaces may appear visually clean following such procedures, residual films which could prevent the formation of an optimum passive condition may still be present. Subsequent treatment such as acid cleaning or passivation, or both, may therefore be required for some alloys.

6.2.9 *Steam Cleaning* is used mostly for cleaning bulky objects that are too large for soak tanks or spray-washing equipment. It may be used with cleaning agents such as emulsions, solvents, alkalis, and detergents. Steam lances are frequently used for cleaning piping assemblies. Steam pressures from 50 to 75 psi are usually adequate (see 6.1).

6.2.10 *Water-Jetting* at water pressures of up to 10,000 psi is effective for removing grease, oils, chemical deposits (except adsorbed chemicals), dirt, loose and moderately adherent scale, and other contaminants that are not actually bonded to the metal. The method is particularly applicable for cleaning piping assemblies which can withstand the high pressures involved; self-propelled nozzles or "moles" are generally used for this purpose.

6.2.11 *Acid Cleaning* (passivation) is a process in which a solution of a mineral or organic acid in water, sometimes in combination with a wetting agent or detergent or both, is employed to remove iron and other metallic contamination, light oxide films, shop soil, and similar contaminants. Suggested solutions, contact times, and solution temperatures for various alloys are given in Appendix

A2. Acid cleaning is not generally effective for removal of oils, greases, and waxes. Surfaces should be precleaned to remove oils and greases before acid cleaning. Common techniques for acid cleaning are immersion, swabbing, and spraying. Maximum surface quality is best achieved by using a minimum cleaning time at a given acid concentration and temperature. After acid cleaning the surfaces must be thoroughly rinsed several times with clean water to remove all traces of the acid. A neutralizing treatmpnt may be required under some conditions; if used, neutralization must be followed by repeated water rinsing to remove all trace of the neutralizing agent. Acid cleaning is not recommended where mechanical cleaning or other chemical methods will suffice; if not carefully controlled, acid cleaning may damage the surface being cleaned and may even results in further contamination of the surface being cleaned.

NOTE 2—The term passivation is used to indicate a chemically inactive surface condition of stainless steels. It was at one time considered that an oxidizing treatment such as a nitric acid dip was essential to establish a passive film. However, it has more recently been found that mere contact with air or other oxygen-containing environment is usually sufficient to establish a *passive* film. A passivation treatment following acid or mechanical cleaning or descaling is not necessary provided that thorough cleaning has been accomplished and there is subsequent exposure to air or other oxygen-containing environment.

6.3 *Cleaning of Welds and Weld-Joint Areas*—The joint area and surrounding metal for several inches back from the joint preparation, on both faces of the weld, should be cleaned immediately before starting to weld. Cleaning may be accomplished by brushing with a clean, stainless steel brush or scrubbing with a clean, lint-free cloth moistened with solvent, or both. When the joint has cooled after welding, remove all accessible weld spatter, welding flux, scale, arc strikes, etc., by grinding. According to the application, some scale or heat temper may be permissible on the nonprocess side of a weld, but should be removed from the process side if possible. If chemical cleaning of the process side of the weld is deemed necessary, the precautions of this standard must be observed. Austenitic stainless steels in the sensitized condition should generally not be descaled with nitric-hydrofluoric acid solutions. Welds may also be cleaned as described in Table A2, Part III, Treatment *P* or *Q* (also see 5.2.3 and 5.2.4).

6.4 *Final Cleaning*—If proper care has been taken in earlier fabrication and cleaning, final cleaning may consist of little more than scrubbing with hot water or hot water and detergent (such as trisodium phosphate, TSP), using fiber brushes. Detergent washing must be followed by a hot-water rinse to remove residual chemicals. Spot cleaning to remove localized contamination may be accomplished by wiping with a clean, solvent-moistened cloth.

6.5 *Precision Cleaning*—Certain nuclear, space, and other especially critical applications may require that only very high purity alcohols, acetone, ketones, trichlorotrifluoroethane, or other *precision cleaning agents* be used for final cleaning or recleaning of critical surfaces after fabrication advances to the point that internal crevices, undrainable spaces, blind holes, or surfaces that are not accessible for thorough scrubbing, rinsing, and inspection are formed. Such items are often assembled under clean-room conditions (see 8.5.5) and require approval, by the purchaser, of carefully prepared cleaning procedures before the start of fabrication.

6.6 *Cleaning of Installed Systems*—There are two approaches to cleaning installed systems. In the first, which is probably adequate for most applications, cleaning solutions are circulated through the completed system after erection, taking care to remove or protect items that could be damaged during the cleaning operation. In the second approach, which may be required for gaseous or liquid oxygen, liquid metal, or other reactive-process solutions, piping and components are installed in a manner to avoid or minimize contamination of process-solution surfaces during erection so that little additional cleaning is necessary after erection; post-erection flushing, if necessary, is done with the process fluid. If process surfaces are coated with an appreciable amount of iron oxide, a chelating treatment or high-pressure water-jetting treatment should be considered in place of acid treatment (see 6.2.7 and 6.2.10).

6.6.1 *Post-Erection Cleaning*—Circulate hot water to which a detergent has been added, for at least 4 to 8 h. A water temperature of at least 140 to 160 F (60 to 71 C) is recommended. (See 6.1). Rinse by circulating clean-hot water until the effluent is clear. If excessive particulate matter is present, the cleaning cycle may be preceded with a high-pressure steam blow, repeating as necessary until a polished-aluminum target on the outlet of the system is no longer dulled and scratched by particulates loosened by the high-velocity steam. Valves and similar items must be protected from damage during a steam blow.

6.6.2 If metallic iron is indicated by one of the methods suggested in Section 7, it can be removed by circulating one of the acid-cleaning solutions suggested in Appendix A2 at room temperature until laboratory determination for iron, made on samples of the solution taken hourly, indicate no further increase in iron content, after which circulation may be stopped and the system drained. After this treatment, circulate clean hot water (that is, without detergent) through the system for 4 h to remove all traces of acid and corrosion product resulting from the acid treatment, or until the pH of the rinse water returns to neutral.

6.6.3 In critical systems where post-erection cleaning is not desirable (for example, liquid oxygen or nuclear reactor primary coolant systems), on-site erection may be conducted under clean-room conditions. Erection instructions may require that wrapping and seals of incoming materials and equipment be kept intact until the item is inside the clean area, and that careful surveillance be exercised to prevent foreign materials (for example, cleaning swabs or tools) from being dropped or left in the system. Where contamination does occur, the cleaning procedure usually is developed through consultation between the erector and the purchaser (or his site representative). Frequently, post-erection flushing is accomplished by circulating the process fluid through the system until contamination is reduced to tolerable levels.

6.6.4 When cleaning critical installed systems, do not permit the process surfaces to dry between successive cleaning and rinsing steps, or between the final rinse and filling with the layup solution.

7. Inspection After Cleaning

7.1 *General*—Inspection techniques should represent careful, considered review of end-use requirements of parts, equipment, and systems. There is no substitute for good, uniform, cleaning practices which yield a metallurgically sound and smooth surface, followed by adequate protection to preserve that condition. Establishment of the most reliable tests and test standards for cleanness are helpful in attaining the desired performance of parts, equipment, and systems. Testing should be sufficiently extensive to ensure the cleanness of all surfaces exposed to process fluids when in service. The following represent some tests which have been successfully applied to stainless steels.

7.2 *Gross Inspection*

7.2.1 *Visual*—Items cleaned in accordance with this standard should be free of paint, oil, grease, welding flux, slag, heat-treating and hot-forming scale (tightly adherent scale resulting from welding may be permissible on some surfaces), dirt, trash, metal and abrasive particles and chips, and other gross contamination. Some deposited atmospheric dust will normally be present on exterior surfaces but should not be present on interior surfaces. Visual inspection should be carried out under a lighting level, including both general and supplementary lighting, of at least 100 footcandles (1076 lx), and preferably 250 footcandles (2690 lx) on the surfaces being inspected. Visual inspection should be supplemented with borescopes, mirrors, and other aids, as necessary, to properly examine inaccessible or difficult-to-see surfaces. Lights should be positioned to prevent glare on the surfaces being inspected.

7.2.2 *Wipe Tests*—Rubbing of a surface with a clean, lint-free, white cotton cloth or filter paper moistened (but not saturated) with high-purity solvent (see 6.5), may be used for evaluating the cleanness of surfaces not accessible for direct visual inspection. Wipe tests of small diameter tubing are made by blowing a clean white felt plug, slightly larger in diameter than the inside diameter of the tube, through the tube with clean, dry, filtered compressed air. Cleanness in wipe tests is evaluated by the type of contamination rubbed off on the swab or plug. The presence of a smudge on the cloth is evidence of contamination. In cases of dispute concerning the harmful nature of the contamination, a sample of the smudge may be transferred to a clean quartz microscope slide for infrared analysis. The wipe test is sometimes supplemented by repeating the test with a black cloth to disclose contaminants that would be invisible on a white cloth.

7.2.3 *Residual Pattern*—Dry the cleaned surface after finish-cleaning at 120 F (49 C) for 20 min. The presence of stains or water spots on the dried surfaces indicates the presence of residual soil and incomplete cleaning. The test is rapid but not very sensitive.

7.2.4 *Water-Break Test* is a test for the presence of hydrophobic contaminants on a cleaned surface. It is applicable only for items that can be dipped in water and should be made with high-purity water. The test procedure and interpretation of results are described in Method F 22. The test is moderately sensitive.

7.2.5 *Test for Free Iron; Gross Indication*—Metallic iron or iron oxide remaining on a stainless steel surface after pickling, acid cleaning, or passivation, followed by water rinse, will usually be apparent within 24 h by the presence of *tell-tale* rust stains. Formation of these stains may be accelerated by exposing the surface to intermittent wetting and drying during the 24-h period.

7.3 *Precision Inspection*

7.3.1 *Solvent-Ring Test* is a test to reveal the presence of tightly adherent transparent films that may not be revealed by visual inspection or wipe tests. A comparison standard is prepared by placing on a clean quartz microscope slide a single drop of high-purity solvent and allowing it to evaporate. Next place another drop on the surface to be evaluated, stir briefly, and transfer, using a clean capillary or glass rod, to a clean quartz microscope slide and allow the drop to evaporate. Make as many test slides as necessary to give a reasonable sample of the surface being examined. If foreign material has been dissolved by the solvent, a distinct ring will be formed on the outer edge of the drop as it evaporates. The nature of the contaminant can be determined by infra-red analysis, comparing the infrared analysis with that of the standard.

7.3.2 *Black Light Inspection* is a test suitable for the detection of certain oil films and other transparent films that are not detectable under white light. In an area that is blacked out to white light, inspect all visible accessible surfaces with the aid of a new, flood-type, ultraviolet lamp. For inaccessible areas, use a wipe test as described in 7.2.2 and subject the used cloth or plug to ultraviolet lamp inspection in a blacked-out area. Fluorescence of the surface, cloth, or plug indicates the presence of contaminants. The nature of the contamination can be determined by subjecting a sample of the contaminant, that has been transferred to a clean quartz microscope slide, to infrared analysis. The test will not detect straight-chain hydrocarbons such as mineral oils.

7.3.3 *Atomizer Test* is a test for the presence of hydrophobic films. It is applicable to both small and large surfaces that are accessible for direct visual examination, and is about 100 times more sensitive than the water-break test. The test procedure and interpretation of results are described in Method F 21. High-purity water should be used for the test.

7.3.4 *Ferroxyl Test for Free Iron* is a highly sensitive test and should be used only when even traces of free iron or iron oxide might be objectionable. It should be made only by personnel familiar with its limitations. The test can be used on stainless steel to detect iron contamination, including iron-tool marks, residual-iron salts from pickling solutions, iron dust, iron deposits in welds, embedded iron or iron oxide, etc.

The test solution is prepared by first adding nitric acid to distilled water and then adding potassium ferricyanide, in the following proportions:

Distilled water	94 mass percent	1000 cm³	1 gal
Nitric acid (60–67 percent)	3 mass percent	20 cm³	⅕ pt
Potassium ferricyanide	3 mass percent	30 g	4 oz

Apply solution with an aluminum, plastic, glass, or rubber atomizer having no iron or steel parts, or by swabbing (atomizer spray is preferred).

7.3.4.1 The appearance of a blue stain (within 15 s of application) is evidence of surface iron contamination (several minutes may be required for detection of oxide scale). The solution should be removed from the surface as quickly as possible after testing using water or, if necessary, white vinegar or a solution of 5 to 20 mass, percent acetic acid and scrubbing with a fiber brush. Flush the surface with water several times after use of vinegar or acetic acid.[5]

NOTE 3—Potassium ferricyanide is not a dangerous poison as are the simple cyanides. However, when heated to decomposition or in contact with concentrated acid, it emits highly toxic cyanide fumes.

NOTE 4—Rubber gloves, clothing, and face shields should be worn when applying the test solution, and inhalation of the atomized spray should be avoided.

NOTE 5—The test is not recommended for process-surfaces of equipment that will be used for processing food, beverages, pharmaceuticals, or other products for human consumption unless all traces of the test solution can be thoroughly removed.

NOTE 6—The test solution will change color on standing and must be mixed fresh prior to each use.

8. Precautions

8.1 *Minimizing Iron Contamination*—Iron contamination on stainless steel parts, components, and systems is almost always confined to the surface. If reasonable care is taken in fabrication, simple inexpensive cleaning procedures may suffice for its removal, and very little special cleaning should be required. Fabrication should be confined to an area where only the one grade of material is being worked. Powder cutting should be minimized or prohibited. Handling equipment such as slings, hooks, and lift-truck forks should be protected with clean wood, cloth, or plastic buffers to reduce contact with the iron surfaces. Walking on corrosion-resistant alloy surfaces should be avoided; where unavoidable, personnel should wear clean shoe covers each time they enter. Kraft paper, blotting paper, paperboard, flannel, vinyl-backed adhesive tape or paper, or other protective material should be laid over areas where personnel are required to walk. Shearing tables, press brakes, layout stands, and other carbon-steel work surfaces should be covered with clean kraft paper, cardboard, or blotting paper to reduce the amount of contact with the carbon steel. Hand tools, brushes, molding tools, and other tools and supplies required for fabrication should be segregated from similar items used in the fabrication of carbon steel equipment, and should be restricted to use on the one material; tools and supplies used with other materials should not be brought into the fabrication area. Tools and fixtures should be made of hardened tool steel or chrome-plated steel. Wire brushes should be stainless steel, or of an alloy composition similar to the steel being cleaned, and should not have been previously used on other materials. Only new, washed sand, free of iron particles, and stainless steel chills and chaplets should be used for casting.

8.2 *Reuse of Cleaning and Pickling Solutions*—Cleaning and pickling agents are weakened and contaminated by materials and soil being removed from surfaces as they are cleaned. Solutions may become spent or depleted in concentration after extended use, and it is necessary to check concentrations and to replace or replenish solutions when cleaning or pickling action slows. It may be impractical or uneconomical to discard solutions after a single use, even in precision cleaning operations (that is, finish-cleaning using very high-purity solvents and carried out under clean-room and rigidly controlled environmental conditions). When solutions are re-used, care must be taken to prevent the accumulation of sludge in the bottom of cleaning tanks; the formation of oil, scums, and undissolved matter on liquid surfaces; and high concentrations of emulsified oil, metal or chemical ions, and suspended solids in the liquids. Periodic cleaning of vats and degreasing tanks, decanting, periodic bottom-drain, agitation of solutions, and similar provisions are essential to maintain the effectiveness of solutions. Care must be taken to prevent water contamination of trichloroethylene and other halogenated solvents, both while in storage and in use. Redistillation and filtering of solvents and vapor-degreasing agents are necessary before reuse. Makeup is often required to maintain concentrations and pH of cleaning solutions at effective levels. Do not overuse chemical cleaners, particularly acids and vapor-degreasing solvents; if light films or oily residues remain on the metal surfaces after use of such agents, additional scrubbing with hot water and detergent, followed by repeated rinsing with large quantities of hot water, may be necessary.

---

[5] For further information see *Journal of Materials*, Am. Soc. Testing Mats. Vol 3, No. 4, December 1968, pp. 983–995.

8.3 *Rinse Water*—Ordinary industrial or potable waters are usually suitable for most metal-cleaning applications. Biologically tested potable water should be used for final rinsing of food-handling, pharmaceutical, dairy, potable-water, and other sanitary equipment and systems. Rinsing and flushing of critical components and systems after finish-cleaning often requires high-purity deionized water, having strict controls on halide content, pH, resistivity, turbidity, and nonvolatile residues. Analytical methods that may be used for establishing the purity of rinse water should be demonstrated to have the sensitivity necessary to detect specified impurity levels; the analytical methods given in the *Annual Book of ASTM Standards*, Part 23 are recommended for referee purposes in case of dispute. To minimize the use of costly high-purity water, preliminary rinses can often be made with somewhat lesser quality water, followed by final rinsing with the high-purity water. It is also possible in many cases to use effluent or overflow from the final rinse operation for preliminary rinsing of other items.

8.4 *Circulation of Cleaning Solutions and Rinse Water*—For restricted internal surfaces (for example, small diameter piping systems or the shell or tube side of a heat exchanger), high-velocity, turbulent flow of cleaning solutions and rinse water may be necessary to provide the scrubbing action needed for effective cleaning and rinsing. The velocity required is a function of the degree of cleanness required and the size of particles which are permissible in the system after the start of operation. If particles between 500 and 1000 μm are permissible, a mean flushing velocity of 1 to 2 ft/s (0.3 to 0.6 m/s) may be sufficient for pipe diameters of 2 in. and smaller; to remove 100 to 200-μm particles, a mean flushing velocity of 3 to 4 ft/s (0.9 to 1.2 m/s) may be required.

8.5 *Protection of Cleaned Surfaces*—Measures to protect cleaned surfaces should be taken as soon as final cleaning is completed, and should be maintained during all subsequent fabrication, shipping, inspection, storage, and installation.

8.5.1 Do not remove wrappings and seals from incoming materials and components until they are at the use site, ready to be used or installed. If wrappings and seals must be disturbed for receiving inspection, do not damage them, remove no more than necessary to carry out the inspection, and rewrap and reseal as soon as the inspection is complete. For critical items that were cleaned by the supplier, and that will not be given further cleaning at the use site or after installation, the condition of seals and wrappings should be inspected regularly and at fairly short intervals while the item is in storage.

8.5.2 Finish-cleaned materials and components should not be stored directly on the ground or floor, and should not be permitted, insofar as practicable, to come in contact with galvanized or carbon steel, mercury, zinc, lead, brass, low-melting point metals, or alloys or compounds of such materials. Acid cleaning of surfaces that have been in contact with such materials may be necessary to prevent failure of the item when subsequently heated. The use of carbon or galvanized steel wire for bundling and galvanized steel identification tags should be avoided.

8.5.3 Store materials and equipment, when in process, on wood skids or pallets or on metal surfaces that have been protected to prevent direct contact with stainless steel surfaces. Keep openings of hollow items (pipe, tubing, valves, tanks, pumps, pressure vessels, etc.,) capped or sealed at all times except when they must be open to do work on the item, using polyethylene, nylon, TFE-fluorocarbon plastic, stainless steel, or wood caps, plugs, or seals. Where cleanness of exterior surfaces is important, keep the item wrapped with clear polyethylene or TFE-fluorocarbon plastic sheet at all times except when it is actually being worked on. Canvas, adhesive paper or plastics such as poly(vinyl chloride) may decompose in time to form corrosive substances; for example, when exposed to sunlight or ultraviolet light. The reuse of caps, plugs, or packaging materials should be avoided unless they have been cleaned prior to reuse.

8.5.4 Clean stainless steel wire brushes and hand tools before reuse on corrosion-resistant materials; if they have not been cleaned and if they could have been used on electrolytically different materials, the surfaces contacted by the tools should be acid-cleaned. The use of soft-face hammers or terne (lead) coated, galvanized, or unprotected carbon steel tables, jigs, racks, slings, or fixtures should be avoided (see 8.5.2).

8.5.5 If close control of particulate contamination is required, particularly of internal surfaces, the latter stages of assembly and fabrication may have to be carried out in a clean room. For most large items an air cleanliness class (see Federal Standard 209a) at the work surface of Class 50,000 to 100,000 (that is, a maximum of from 50,000 to 100,000 particles 0.5 μm or larger suspended in the air) is probably sufficient.

NOTE 7—A clean room is a specially constructed enclosure in which intake air is filtered so that the air at a work station contains no more than a specified number of particles of a specified size; special personnel and housekeeping procedures are required to maintain cleanness levels in a clean room (See Federal Standard 209a).

8.5.6 Workmen handling finish-cleaned surfaces of critical items should wear clean cotton or synthetic-fiber gloves. Rubber or plastic gloves are suitable during precleaning operations or cleaning of non-critical surfaces.

8.5.7 Installed piping systems are often *laid up wet;* that is, they are filled with water (or process fluid) after in-place cleaning until ready to be placed in service. Storage water should be of the same quality as the makeup water for the system, and should be introduced in a manner that it directly replaces the final flush water without permitting the internal surfaces of the system to dry.

8.5.8 Equipment and assemblies for critical applications may be stored and shipped with pressurized, dry, filtered, oil-free nitrogen to prevent corrosion until they are ready to be installed. Means must be provided for maintaining and monitoring the gas pressure during shipping and storage. If the item is to be shipped to or through mountains or other areas where the altitude varies greatly from that where it was pressurized, consideration must be given to the effect of that change in altitude on the pressure inside the item, and possible rupture or loss of seals.

8.5.9 Pressure-sensitive tape is often used for sealing or protective covers, seals, caps, plugs, and wrappings. If possible, the gummed surface of the tape should not come in contact with stainless steel surfaces. If tape has come in contact with the metal, clean it with solvent or hot water, and vigorous scrubbing.

8.5.10 Protective adhesive papers or plastics are often used to protect the finish of sheet stock and parts. These materials may harden or deteriorate when subjected to pressure or sunlight, and damage the surface.

8.6 *Safety*—Cleaning operations often present numerous hazards to both personnel and facilities. Data sheets of the Manufacturing Chemists Association should be consulted to determine the hazards of handling specific chemicals.

8.6.1 Precautions must be taken to protect personnel, equipment, and facilities. This includes provisions for venting of explosive or toxic reaction-product gases, safe disposal of used solutions, provision of barriers and warning signs, provisions for safe transfer of dangerous chemicals, and maintenance of constant vigilance for hazards and leaks during the cleaning operation.

8.6.2 The physical capability of the item or system to be cleaned, together with its foundations, to withstand the loads produced by the additional weight of fluids used in the cleaning operation, must be established before the start of cleaning operations.

8.6.3 Insofar as possible, chemicals having explosive, toxic, or obnoxious fumes should be handled out of doors.

8.6.4 The area in which the cleaning operation is being conducted should be kept clean and free of debris at all times, and should be cleaned upon completion of the operation.

8.7 *Disposal of Used Solutions and Water*—Federal, state, and local safety and water pollution control regulations should be consulted, particularly when large volumes of chemical solutions must be disposed of. Controlled release of large volumes of rinse water may be necessary to avoid damaging sewers or stream beds.

APPENDIXES

TABLE A1 **Acid Descaling (Pickling) of Stainless Steel**

Alloy	Condition	Treatment			
		Code	Solution, Volume, percent[a]	Temperature, deg F	Time, Minutes
200, 300, and 400 Series, precipitation hardening, and maraging alloys (except free-machining alloys).	fully annealed only	A	H_2SO_4, 8–11 percent[b] Follow by treatment D or F, Appendix A2, as appropriate	150–180	5-45 max[c]
200 and 300 Series; 400 Series containing Cr 16 percent or more; precipitation-hardening alloys (except free-machining alloys)	fully annealed only	B	HNO_3, 15–25 percent plus HF, 1–4 percent	70–140 max	5–30[c]
All free-machining alloys and 400 Series containing less than Cr 16 percent.	fully annealed only	C	HNO_3, 10–15 percent plus HF, ½–1½ percent	70 (up to 140 with caution)	5–30[c]

[a] Solution prepared from reagents of following mass percent: H_2SO_4, 98; HNO_3, 67; HF, 70.

[b] Tight scale may be removed by a dip in this solution for a few minutes followed by water rinse and nitric-hydrofluoric acid treatment as noted.

[c] Minimum contact times necessary to obtain the desired surface should be used in order to prevent over-pickling. Tests should be made to establish correct procedures for specific applications.

A1. Recommendations and Precautions

A1.1 Where size and shape permit, immersion in the acid solution is preferred; when immersion is not practicable, one of the following room-temperature methods may be used:

A1.1.1 For interior surfaces, partially fill item with solution and rock, rotate, or circulate so that all inside surfaces are thoroughly wetted. Keep surfaces in contact with acid solution until inspection shows that scale is completely removed. Additional exposure without agitation may be needed. Treat exterior surfaces in accordance with A1.1.2.

A1.1.2 Surfaces that cannot be pickled by filling the item may be descaled by swabbing or spraying with acid solution for about 30 min, or until inspection shows that scale is completely removed.

A1.2 Severe pitting may result from prolonged exposure to certain acid solutions if the solution becomes depleted or if the concentration of metallic salts becomes too high as a result of prolonged use of the solution; take care to prevent over-pickling.

A1.3 Nitric-hydrofluoric acid solutions may intergranularly corrode certain alloys that have been sensitized by improper heat treatment or by welding. Crevices resulting from intergranular attack can collect and concentrate halogens under service conditions or during cleaning or processing with certain chemicals; these halogens can cause stress-corrosion cracking. These alloys should generally not be acid-pickled while in the sensitized condition. Consideration should be given to stabilized or low-carbon grades if acid pickling after welding is unavoidable.

A1.4 Some latitude is permissible in adjusting acid concentrations, temperatures, and contact times. In general, lower values in this table apply to lower alloys, and higher values to higher alloys. Close control over these variables is necessary once proper values are established in order to preserve desired finishes or close dimensional tolerances, or both.

A1.5 Materials must be degreased before acid pickling and must be vigorously brushed with hot water and a bristle brush or with high-pressure water jet on completion of pickling; pH of final rinse water should be between 6 and 8 for most applications, or 6.5 to 7.5 for critical applications.

A1.6 Hardenable 400 Series alloys, maraging alloys, and precipitation-hardening alloys in the hardened condition are subject to hydrogen embrittlement or intergranular attack by acids. Descaling by mechanical methods is recommended where possible. If acid pickling is unavoidable, parts should be heated at 250 to 300 F (121 to 149 C) for 24 h immediately following acid treatment to drive off the hydrogen and reduce the susceptibility to embrittlement.

A1.7 Proper personnel protection, including face shields, rubber gloves, and rubber protective clothing, must be provided when handling acids and other corrosive chemicals. Adequate ventilation and strict personnel-access controls must be maintained in areas where such chemicals are being used.

TABLE A2 **Acid Cleaning of Stainless Steel**

Alloy	Condition	Treatment			
		Code	Solution, Volume, percent[a]	Temperature, deg F	Time, Minutes
PART I—Cleaning with Nitric-Hydrofluoric Acid					
Purpose—For use after descaling by mechanical or other chemical methods as a further treatment to remove residual particles of scale or products of chemical action (that is, smut), and to produce a uniform "white pickled" finish.					
200 and 300 Series, 400 Series containing Cr 16 percent or more, and precipitation-hardening alloys (except free-machining alloys).	fully annealed only	D	HNO_3, 6 15 percent plus HF, ½ to 1½ percent	70 140	10
Free-machining alloys, maraging alloys, and 400 Series containing less than Cr 16 percent.	fully annealed only	E	HNO_3, 10 percent plus HF, ½ to 1½ percent	70 (up to 140 with caution)	1 2
PART II—Cleaning with Nitric Acid Solution					
Purpose—For removal of soluble salts, corrosion products, and free iron and other metallic contamination resulting from handling, fabrication, or exposure to contaminated atmospheres (see 6.2.11)					
200 and 300 Series, 400 Series, precipitation hardening and maraging alloys containing Cr 16 percent or more (except free-machining alloys)	annealed, cold-rolled, or work-hardened, with dull or nonreflective surfaces	F	HNO_3, 20 40 percent	120 160 70 100	20 30 60
Same	annealed, cold-rolled, or work-hardened with bright-machined or polished surfaces	G	HNO_3, 20 40 percent plus $Na_2Cr_2O_7 \cdot 2H_2O$, 2 6 mass, percent	110 130 70 100	20 30 60
400 Series, maraging and precipitation-hardening alloys containing less than Cr 16 percent high-carbon-straight Cr alloys (except free-machining alloys).	annealed or hardened with dull or nonreflective surfaces	H	HNO_3, 20 50 percent	110 130 70 100	20 30 60
Same	annealed or hardened with bright machined or polished surfaces	I[b]	HNO_3, 20 50 percent plus $Na_2Cr_2O_7 \cdot 2H_2O$, 2 6 mass, percent	110 130 70 100	20 30 60
200, 300, and 400 Series free-machining alloys	annealed or hardened, with bright-machined or polished surfaces	J[b]	HNO_3, 20 50 percent plus $Na_2Cr_2O_7 \cdot 2H_2O$, 2 6 mass, percent	110 130 70 100	20 30 60
Same	same	K[b]	HNO_3, 1 2 percent plus $Na_2Cr_2O_7 \cdot 2H_2O$, 1 5 mass, percent	120 140	10
Same	same	L[b]	HNO_3, 12 percent plus $CuSO_4 \cdot 5H_2O$, 4 mass percent	120 140	10
Special free-machining 400 Series alloys with more than Mn 1.25 percent or more than S 0.40 percent.	annealed or hardened with bright-machined or polished surfaces	M[b]	HNO_3, 40 60 percent plus $Na_2Cr_2O_7 \cdot 2H_2O$, 2 6 mass, percent	120 160	20 30
PART III—Cleaning with Other Chemical Solutions					
Purpose—General cleaning.					
200, 300, and 400 Series (except free-machining alloys), precipitation hardening and maraging alloys	fully annealed only	N	citric acid, 1 mass percent plus $NaNO_3$, 1 mass percent	70	60
Same	same	O	ammonium citrate, 5 10 mass percent	120 160	10 60

TABLE A2 *Continued*

PART III—Cleaning with Other Chemical Solutions *Continued*

Alloy	Condition	Treatment			
		Code	Solution, Volume, percent[a]	Temperature, deg F	Time, Minutes
Assemblies of stainless and carbon steel (eg., heat exchanger with stainless steel tubes and carbon steel shell)	sensitized	P	inhibited solution of hydroxyacetic acid, 2 mass percent and formic acid, 1 mass percent	200	6 h
Same	same	Q	inhibited ammonia-neutralized solution of EDTA (ethylene-diamene-tetraacetic acid) followed by hot-water rinse and dip in solution of 10 ppm ammonium hydroxide plus 100 ppm hydrazine	up to 250	6 h

[a] Solution prepared from reagents of folowing mass percent: HNO_3, 67; HF, 70.
[b] See A2.2.

A2. Recommendations and Precautions

A2.1 Treatments shown are generally adequate for removal of contamination without seriously changing surface appearance of parts. For specific requirements for items to be used in corrosive service or where surface appearance is critical, trials should be conducted to establish satisfactory procedures.

A2.2 The high-carbon and free-machining alloys may be subject to etching or discoloration in nitric acid. This tendency can be minimized by the use of high acid concentrations with inhibitors. Avoid acid cleaning when possible; use mechanical cleaning followed by scrubbing with hot water and detergent.

A2.3 Inhibitors may not always be required to maintain bright finishes on 200 and 300 Series, maraging, and precipitation-hardening alloys.

A2.4 Hardenable 400 Series, maraging, and precipitation-hardening alloys in the hardened condition are subject to hydrogen embrittlement or intergranular attack when exposed to acids. Cleaning by mechanical methods or other chemical methods is recommended. If acid treatment in unavoidable, parts should be heated at 250 to 300 F for 24 h immediately following acid cleaning to drive off hydrogen and reduce susceptibility to embrittlement.

A2.5 Nitric-hydrofluoric acid solutions may intergranularly corrode certain alloys that have been sensitized by improper heat treatment or by welding. Crevices resulting from intergranular attack can collect and concentrate halogens under service conditions or during cleaning or subsequent processing; these halogens can cause stress-corrosion cracking. Such alloys should not be cleaned with nitric-hydrofluoric acid solutions while in the sensitized condition. Consideration should be given to use of stabilized or low-carbon alloys if this kind of cleaning after welding is unavoidable.

A2.6 Severe pitting may result from prolonged exposure to certain acids if the solution becomes depleted or if the concentration of metallic salts becomes too high as a result of prolonged use of the solution; take care to prevent over-exposure.

A2.7 Nitric acid solutions are effective for removing free iron and other metallic contamination, but are not effective against scale, heavy deposits of corrosion products, temper films, or greasy or oily contaminants. Refer to Appendix A1 for recommended practices where scale, heavy deposits of corrosion products, or heat-temper discoloration must be removed. Use conventional degreasing methods for removal of greasy or oily contaminants before any acid treatment.

A2.8 The citric acid-sodium nitrate treatment is the least hazardous for removal of free iron and other metallic contamination and light surface contamination. Spraying of the solution, as compared to immersion, tends to reduce cleaning time.

A2.9 Some latitude is permissible in adjusting acid concentrations, temperatures, and contact times; close control over these variables is essential once proper values have been established. Care must be taken to prevent acid depletion and buildup of metallic salt concentrations with prolonged use of solutions.

A2.10 Materials must be degreased before acid treatment, and must be vigorously scrubbed with hot water and bristle brushes or with high-pressure water-jet immediately after completion of acid treatment; pH of final rinse water should be between 6 and 8 for most applications, or 6.5 to 7.5 for critical applications.

A2.11 Proper personnel protection, including face shields, rubber gloves, and rubber protective clothing, must be provided when handling acids and other corrosive chemicals. Adequate ventilation and strict personnel access controls must be maintained where such chemicals are being used.

By publication of this standard no position is taken with respect to the validity of any patent rights in connection therewith, and the American Society for Testing and Materials does not undertake to insure anyone utilizing the standard against liability for infringement of any Letters Patent nor assume any such liability.

R. A. Rauscher[1]

Alkaline Cleaning of Stainless Steel: An Overview

REFERENCE: Rauscher, R. A., "**Alkaline Cleaning of Stainless Steel: An Overview,**" *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 17–22.

ABSTRACT: An overall view of alkaline cleaning of stainless steel is presented by this paper. It deals with the advantages of alkaline chemical cleaning and the requirements that must be met by properly compounded alkaline solutions.

The importance of proper rinsing and water management is included for the interest of metal manufacturers and fabricators. A brief discussion on waste treatment is also included.

A study of the relationship between cleaning costs and profits as they affect the production manager is explained in detail with a formula presented for determining unit cost.

KEY WORDS: stainless steels, cleaning, detergents, alkalies

Among chemical cleaners, the alkaline base cleaners have been and continue to be the most widely used type of formulated cleaners. When formulated with synthetic agents they create an effective detergent cleaning action.

Alkaline cleaners can remove a wide range of soils including heat-treating salts; inorganic soldering, brazing and welding fluxes; lubricants and coolants; and polishing and buffing compounds. They can be applied by just about any method of application known—by soak or tank cleaning, by spray, in electrocleaning or barrel tumbling.

The most commonly used alkali bases are carbonates (such as sodium carbonate or soda ash), phosphates (such as trisodium phosphate or TSP), silicates (such as sodium orthosilicate or metasilicate), and hydroxides (such as sodium hydroxide). Another common alkali base is the borates.

Applications of Alkali Bases

Each alkali base serves a specific purpose. The carbonates, for example, serve as buffers, as low-cost alkalinity sources, and as water softeners.

The phosphates serve primarily as water softeners. In hard water areas, that is, where there are relatively large proportions of calcium and magnesium ions in the water, these ions will combine with ingredients in the cleaning solution to form insoluble materials. This formation of insoluble materials can be combatted

[1] Manager, Metal Industries Division, Oakite Products, Inc., Berkeley Heights, N. J. 07922.

by a sequestering agent in the formulated cleaner which, in effect, ties up the calcium and magnesium ions. And the phosphates are effective sequestering agents. They also impart alkalinity, rinsability, some buffer action, and are fair emulsifiers.

The silicates are excellent emulsifiers, good buffers (where pH is over 9), will hold soils in suspension, and provide active alkalinity. Hydroxides supply the necessary alkalinity, increase electrical conductivity of the solutions, and improve saponification.

Deficiencies

However, pure raw alkalies have serious deficiencies as far as cleaners are concerned–for example, they can form insoluble residues with hard water salts, and will not rinse freely; they can corrode or pit metal; they can be dangerous to personnel–and these deficiencies must be overcome. To this end, the alkali bases are mixed with surface active agents, which, in essence, utilize the desirable features of the alkalies even as they tone down the undesirable features. At the same time, the surface active agents or surfactants add certain benefits of their own.

Composition of Cleaners

Cleaners can be formulated from a variety of alkalies and as many as three surfactants.

Though most surfactants are usually identified as "wetting agents," "emulsifiers," "deflocculants," etc., these reactions are gross effects rather than specific properties. It is true that, in any surfactant, one effect will dominate. A surfactant may be known, for example, as an excellent emulsifier; however, there will also be present in the surfactant a wetting and deflocculating action.

No surfactant possesses any single property to the exclusion of all others.

The primary purpose of wetting agents is to break the common boundary which forms anywhere soil and surfaces meet. This boundary is created and maintained by interfacial adhesional forces, electrostatic forces, and a purely mechanical juxtaposition. These forces, in turn, are affected by the physical and chemical interrelations of both soil and surface characteristics, such as soil particle size, viscosity, possible chemical reactions with the surface and the surface porosity, hardness, and so forth.

However, once the combination of soaps, alkalies, and surfactants has broken this boundary, the soils must be prevented from redepositing on the surface.

To accomplish this, an efficient alkaline cleaner will disperse soil throughout the solution once the soil has been removed from the work surface. If it does not, the solution in the surrounding area would become highly contaminated and would be more apt to resoil the work surface when it is removed from the cleaning solution.

The redepositing of the soil can be prevented. It is most often accomplished by the effect of emulsification (the suspension of oils in solution) or deflocculation (the suspension of soil particles in solution) or both.

pH Levels

Another feature of properly designed alkaline cleaners is adequate buffering ability. This is the ability to maintain the optimum pH for the surfactants incorporated into the cleaner despite contamination of the cleaning solution.

Alkaline cleaners must also provide active as well as available alkalinity because most soaps and synthetic detergents are more efficient where pH values are between 7 and 13.

This alkalinity level is continually being changed or lowered through such chemical reactions as saponification and neutralization, and by such physical reactions as drag-out. Buffers tend to preserve the original pH of a solution against these chemical and physical changes. The buffering action and the available alkalinity give long life to a cleaner at a constant pH, a very important consideration.

pH is a measure of the intensity of acidity or alkalinity of any given solution. Its importance here lies in the fact that soap and other surface-active agents have optimum pH ranges at which they exhibit maximum detergency. Forced above or below this range (by soils, for example) cleaning action decreases; the effectiveness of detergent is reduced. The buffering salts help maintain the proper pH range.

Of special importance on stainless steel is an inhibitor, which enables the solution to remove specific soils without disturbing the passive oxide film. The inhibitor deposits on the surface a thin protective film that resists any attack by the highly alkaline constituents of the cleaning solution. The inhibitor has dimension and must be removed to activate the surface for subsequent electroplating, or similar operations.

The end result of all this activity, this selection, compilation, and mixing of ingredients is an alkaline cleaner which will offer several desirable characteristics.

It should wet out and emulsify or deflocculate soils and soften water, either by sequestering or chelation. It should buffer the solution to enable long cleaning life, and where necessary, it should inhibit the cleaning solution to provide safety to metals. It should offer ease of application and storage.

And the purpose of this scientifically designed and formulated solution is to reduce or break the interfacial surface–which is the common boundary between soil and surface–to hold soils in suspension for easy rinsing, with safety to personnel and metal. The goal is to provide fast, efficient cleaning with least effort at lowest cost.

Rinsing

Cleaning does not stop with the application of a detergent. A vital part of the success of any cleaning operation is rinsing. Unfortunately, rinsing is one of the most neglected aspects of any cleaning/finishing process. Proper rinsing is absolutely essential to success and it is easily obtained. The difference in cost between good and poor rinsing is so minimal as to be nonexistent.

Rinsing serves two essential purposes. First, it removes undesirable residues which could either affect the surface (by actual chemical alteration) or interfere with subsequent finishing operations. In addition, it tends to extend solution life of cleaning and finishing solutions by minimizing carry-over from one phase of the process to another. By so doing it reduces contamination and results in a more controllable operation. Rinsing efficiency is a function of the flow rate of incoming solution from previous stages due to drag-out and the flow rate of incoming fresh water. Rate of dilution (which can be practically instantaneous or slow, depending on the degree of agitation) is another factor which can affect rinsing efficiency.

Improvements in rinsing efficiency can be expected with a better understanding of the fundamentals. There are essentially two types of rinsing. The simplest and probably the most commonly used is a simple rinse where one or more ranks or recirculating rinses are in sequence. In most cases fresh water is introduced into each stage and then discarded. This procedure will result in good rinsing but it can hardly be considered either efficient or inexpensive.

Much more efficient is counter-flow rinsing. In this, two or more tanks are aligned in sequence. Fresh water is introduced into only one tank or rinse (the final one) and then is transferred, generally by some form of overflow, to each preceding stage of the rinse line.

Another aspect of efficiency/economy under consideration in many operations, especially in recent times, is the use of reconditioned water for rinsing operations. Such use has several obvious advantages. Depending on the quality, it can completely eliminate the use of fresh rinse water. It could increase, in many instances, rinse water quality, and it could aid in alleviating disposal problems.

Disposal Problems

Disposal problems, have been with us for some time now. And there is no letup in sight. In addition to restrictions on sludge, solid refuse, floating solids, oil, grease, and scum, metal manufacturers and finishers could be faced with restrictions on the dissolved oxygen content, the temperature of the solution discharged, the color and turbidity, coliform bacteria count, taste, odor, pH, and other pollutants that affect the composition of bottom fauna, affect the physical or chemical nature of the bottom and interfere with the propagation of fish.

The first place to start is not in treatment, but in cutting down whenever possible, the necessity for treatment. This involves the use of phosphate-free and biodegradable cleaning materials and by collecting soils such as oil and grease before they get into discharge solutions.

If the waste cannot be eliminated, but must be treated, the decision must be made whether to reclaim the water and recycle it for reuse, or provide the necessary waste treatment on-site prior to discharge, or a combination of the two.

Recycling

Where there is a cost for the water used, and if substantial volume is required, recycling is certainly to be investigated. Recycling may be very simple—such as a tank where particles are settled out and the (generally) soapy water is reused as is—or it may be very complex, with chemical additives, cartridges or similar filter media, and may be automatic or operated by an attendant.

The cost may vary considerably depending on the degree of recycling and the equipment necessary to obtain the desired degree, which in turn is influenced by the volume of water to be handled, quality of water desired, and services performed.

Where water recycling is not feasible, or for one reason or another, not desirable, it is possible that the water might have to be treated on site prior to discharge. If such is the case, three basic operations are involved; clarification, oil separation (or split), and neutralization.

Clarification

Clarification of waste water is the process of removing turbidity (a clouding of the water due to sediment dispersed throughout it), sediment, and floating material. It is usually the first step in any water treatment program, and in some cases may be the only one necessary.

Clarifiers are mechanical methods of treatment. They are based on settling rate (or area) and detention time. The amount of water overflow varies from 250 to 1800 gal per ft^2 per day, with detention time in ranges of 1 to 4 h.

Clarifiers involve another treatment, coagulation, which speeds up the settling of suspended matter into larger particles, and makes it possible to remove small solids not touched by conventional sedimentation. It does this by creating a jelly-like spongy mass called floc. The enormous surface area of this mass traps and absorbs particles of sediment, organic matter, and bacteria. This is obviously a chemical reaction; removal of the floc itself, however, is a mechanical one.

Oil Separations

Oil separations or "splits" are necessary where oils and other petroleum products are mixed with water. These products generally have a lower specific gravity than water and will rise rather than settle.

Free oil will separate from water by gravity alone and can be removed by mechanical means such as skimmers. However, when both free and emulsified oil are present, a combination of mechanical and chemical means must be used. The most economical solution is to first remove as much oil as possible mechanically and then use chemical coagulation to break the remaining emulsion.

Neutralization

The third process, neutralization, is simply adjusting waste solutions until they are neither acidic nor alkaline, by adding acidic solution to alkaline waste, or adding alkaline solutions to acidic waste. The purpose is to keep pH in the range of 6.0 to 8.0 required by most water quality criteria.

Cost Factors

The cost of cleaning is the ultimate evaluation of the success of the cleaning operation. The cost is a production cost and must be subjected to the same intense analysis as any phase of production operation. Furthermore, it is essential that the exact nature of cleaning/conditioning costs be understood. They are not merely a compilation of the costs of materials and labor, etc., but instead, represent a unit cost which can be determined by the formula:

$$F + S \div (P - R) = C$$

Here F represents the factors, other than the cost of the cleaning materials, which enter into the costs of a cleaning operation. These include the rated cost of the space occupied by the equipment used for cleaning or conditioning or both, capital costs, amortization, and maintenance of the equipment. Also included are utilities such as water, heat, and power required to maintain the operation, as well as all labor costs such as labor to make up the original solutions and needed additions, daily labor costs, and the labor costs of laboratory controls, where used. Also, treatment costs for disposal of spent solutions are becoming increasingly important. Although these costs will differ from operation to operation, or even production run to production run, strict accounting of each is necessary.

S is the cost of cleaning material necessary to charge the tank originally, plus the cost of daily upkeep additions needed until the solution is discarded.

P is the number of parts or total number of square feet of work processed.

R is the number of rejects expressed as either unit of work or in square feet.

Thus, the sum of F plus S divided by the sum of P minus R will equal C, the unit cost.

Stripping or any other operation involved in preparing rejected or newly received parts for reprocessing is an additional factor to be considered or evaluated.

Conclusions

Cleaning is essential during fabrication of stainless steel, not only to prevent corrosion and maintain the appearance of the metal, but also to ensure the quality of welded or soldered joints. Any interference with the formation of the protective oxide coating on stainless steel will tend to reduce corrosion resistance. When foreign matter interferes with the proper formation of chromium oxide formed during the initial oxidation of the stainless steel then prompt action to assure exposure of the surface to air is beneficial. Thus, the way to keep stainless steel truly stainless is to clean it whenever and wherever necessary—during fabrication or working or in service.

R. K. Brandt[1] *and M. J. Bach*[1]

Cleaning Stainless Steel with Alkaline Solutions

REFERENCE: Brandt, R. K. and Bach, M. J., "Cleaning Stainless Steel with Alkaline Solutions," *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 23–32.

ABSTRACT: Cleaning stainless steel in alkaline solutions begins with consideration of the soil, the alloy, the nature, size and value of the part to be cleaned, the amount of work to be processed, economics, the types of cleaning equipment available, the degree of cleanliness required as dictated by subsequent use of the part, environmental prohibitions, and disposal requirements.

The paper lists the classes of soil found on stainless steel with the cleaning mechanism they require. The classes of alkaline chemicals used in cleaners and the cleaning function they perform are also given. Cross referencing the two lists leads to an understanding of complex cleaner compositions.

Methods of cleaning including soak tank, spray systems, and electrolytic processes are discussed. Laboratory testing of cleaners and control methods for in-use solutions are well covered for practical purposes. These tests include pH, total alkalinity, chelate content, and soil load.

The importance of water quality is stressed. Rinsing is vital to any cleaning operation and should be done properly to avoid pollution and high costs, while producing a residue-free surface.

The paper ends with a brief discussion of safety in handling alkalies and methods of disposal for spent solutions.

KEY WORDS: stainless steels, cleaning, alkalies, finishing

Designing an alkaline cleaning system for stainless steel begins with a study of the soil to be removed. The surface finish of the stainless steel is produced by the metalworking operation and cannot be altered appreciably in an alkaline cleaning system. An alkaline cleaner composition is often a complex mixture of materials which act by a combination of chemical and physical processes to remove soils from the metal and to prevent its redeposition. Cleaner effectiveness is increased by supplementing the standard soak-tank process with mechanical or electrolytic energy input.

Laboratory cleaning tests correlate well with production performance. Having selected the best cleaner and operating conditions in this way, one must run suitable control tests during use to maintain the system at peak efficiency.

Serious consideration should be given to water hardness and to water conservation by use of multistage rinsing techniques to reduce pollution and disposal costs. Cleaners containing biodegradable surfactants and little or no

---

[1] Director of research and chemist, respectively, Apex Alkali Products Co., Philadelphia, Pa. 19127.

phosphate are now available, as are suitable disposal methods.

Soils

This paper covers those cleaning problems normally found in the metalworking industry. It will deal mostly with soil found on wire, tubing, and formed parts after drawing, stamping, or cutting operations.

Table 1 lists the most commonly found soils on stainless steels, their usual source, and the normal cleaning mechanism involved in their removal. Commonly, one or several of these soils in combination present the predominant cleaning problem.

Cleaning should be scheduled as soon as possible, preferably immediately following the metalworking operation. Difficulty of removal increases with time between finishing and cleaning. Some organic materials solidify on the surface as solvents or water evaporate and the temperature drops. Chemical changes may occur such as oxidative polymerization or reactions of fatty acids with the metal surface or soil components to form metallic salts. Water evaporation may also convert an emulsion from oil-in-water to the water-in-oil form, which is far more difficult to remove.

Cleaners

Cleaners are formulated in such a way that these multicomponent soils which are unique and specific to a given operation are removed most efficiently. A consideration of the various types of ingredients is of interest to a discussion of alkaline cleaning processes. Table 2 shows the classes of ingredients used in alkaline products and their principle functions.

Compositions may include one or all of these classes of ingredients. In each class, in addition to the example, there are numerous other related chemicals of slightly different activity. The compounder must strive to formulate the optimum synergistic combination which will do the best job with the plant equipment available.

The most common cleaning system consists of a heated soak tank. Normal soak tank systems are operated at concentrations of 4 to 12 oz per gal and temperatures of 180 to 200°F. Soak times vary widely but are usually 10 to 15 min. The maintenance of proper concentration and temperature is very important in a soak tank operation.

There are as many different types of plants and equipment as there are cleaning processes. However, there are several important considerations in the design of a soak tank. A surface skimmer should be provided to remove floating soil and debris as it forms. The heating system must be adequate for coldest weather operation and placed so that soil buildup will not occur to block heat transfer. Incidentally, it is well to keep the tank hot during idle periods to prevent thickening due to soaps, or separation of active ingredients due to cold water insolubility at operating concentrations. A sludge conveyor to remove sediments from the bottom of the tank automatically would be of considerable

TABLE 1–*Stainless steel metalworking soils, their source and primary removal mechanism.*

Type	Source	Primary Removal Mechanism
Specialty Coatings		
Oxalate	pretreatment of metal for improved lubrication in the metal working process	solubilized by alkali
Lime		solubilized by chelation
Borax		dissolved in water
Lubricants		
Chlorinated oils	specialty lubricants used for various metal working operations	detergency and emulsification
Mineral oils		detergency and emulsification
Soap powders		
Soluble		dissolve in water
Insoluble		convert to soluble, chelation
Polymer resins		detergency and emulsification (may require prior degreasing)
Buffing compounds	polishing operations	saponification, emulsification, suspension, (may require precleaning in emulsifiable solvent)
Fats and fatty acids	lubricant	detergency, emulsification and saponification
Miscellaneous		
Quench oil	heat treating quench	emulsification
Rust	atmospheric corrosion	chelation
Oxides	heat treating, atmospheric corrosion	chelation
Smut (metal carbides and amorphous carbon)	annealing, heat treating, welding	oxidation of carbon and chelation
Iron sulfides & chlorides	lubricant e.p. residues, acid residue	chelation and alkali solubilized
Pigments	lubricants	disperse and suspend
Debris (metal particles and dirt)	metal surface, environment	detergency and suspension

value.

Any cleaning process will be improved by mechanical assistance. Mechanical action consists of thermal currents and movement in and out of the solution by the part. Input of energy such as by ultrasonics, a motor stirrer, air agitation if foaming permits, or a circulating pump in the tank serves to improve thoroughness and speed of cleaning. Brushing of strip steel and barrel tumbling of small parts are other examples of mechanical energy input.

Spray cleaning is an exceptionally effective mechanical adjunct to alkaline cleaning. Chemical action is accelerated by agitation, so that the improvement is due to greater reactivity as well as the physical lifting and sweeping work which penetrates and dislodges the soil. Cleaning times are far shorter than those required for soak cleaning of the same material. The extreme agitation and aeration produced by spraying necessitates careful formulation of the cleaner to controlled foam levels. The wetting and penetrating surfactants, used at relatively high levels in soak tank cleaners, are normally high foamers. Small

TABLE 2–*Alkaline cleaner ingredients and their function.*

Ingredient	Example	Primary Function
Alkali	sodium hydroxide sodium carbonate	saponification, acid soil neutralization, solubilizes fatty soils. Increase electrical conductivity
Silicates	sodium metasilicate	deflocculate solid dirt, suspends loosened dirt, prevents redeposition, inhibits attack of sensitive metals, buffer alkalinity.
Phosphates	tetrasodium pyrophosphates	water softening, emulsifying, soil dispersant, sequestrant, buffer.
Organic chelators	ethylene diamine tetracetic acid, alkali salt	sequestrant for heavy metals.
Synthetic detergent-emulsifiers	soap, ethylene oxide condensates, alkyl aryl sulfonates	wetting, penetration, emulsification, rinse aids, coupling.
Corrosion inhibitors	sodium nitrite	prevent metal oxidation and chemical reaction.
Solvents	kerosine	lower the viscosity of greasy soils.
Water		liquify the product for ease of handling.

amounts of special low foam surfactants must be used in spray cleaners. Odd shaped parts may cause trouble in spray equipment if the spray does not reach all areas of the part. These cleaners are used at concentrations of 1/2 to 2 oz per gal, at temperatures around 180°F.

The speed and efficiency of a cleaner can be greatly enhanced by electrolytic action through application of low voltage d-c current at densities of 10 to 150 A per ft^2. The part to be cleaned may be made either anodic or cathodic or alternately one then the other, termed periodic reversal cleaning. To further clarify terminology, when the part is anodic (positive) the process is called reverse current cleaning. When the part is cathodic (negative) it is termed direct current cleaning. Oxygen gas is generated at the anode and hydrogen gas at the cathode. The volume of hydrogen gas is two times the volume of oxygen gas produced and, therefore, a greater mechanical scrubbing action is found at the cathode. However, the hydrogen atoms may penetrate the metal and form molecules which are trapped as a gas which reduces the strength of the metal. Since medium chrome steels are especially sensitive to hydrogen embrittlement, direct current cleaning will rarely be used with stainless steel.

In reverse current cleaning with the stainless steel as the anode, where oxygen is produced on the metal surface, other advantages are also seen. The metal surface is actually being dissolved as well as mechanically cleaned by the gas scrubbing. This plating-off action tends to remove metallic smuts and prevents deposition of undesirable metal ions and suspended soil material.

Electrolytic cleaning can produce scrupulously clean active metal surfaces and is the normal process where these are required. Heavily soiled metal will quickly contaminate a tank so that precleaning is recommended. This may be a vapor degreasing operation, an emulsifiable solvent pre-dip, a heavy-duty alkaline spray or soak tank or a second electrolytic system. The electrolytic method provides for greatest speeds with cleaning times in the area of 1/2 to 2 min being sufficient for most operations. Electrocleaners are normally run at 4 to 12 oz per gal and 160 to 200°F temperatures.

Proper foam levels are important in electrolytic cleaning. It is advantageous to maintain a level of foam sufficient to trap the alkaline spray, yet it must be low enough so that it will not hold large volumes of hydrogen gas, which can explode. The cleaner composition must be carefully balanced to provide this action. In addition, a vital characteristic of an electrolytic cleaner is the ability to conduct high electrical current at a given voltage. Ingredients of the formulation must be selected so as to impart high conductivity to the water solution while providing the other properties which are required of a good cleaner.

Laboratory Testing

Laboratory cleaning tests correlate well with production performance so that it is relatively easy to select the optimum cleaner for a given set of conditions. Since a series of possible cleaners will be available for a given metal-soil-process combination, it is incumbent upon the supplier to conduct tests to ensure that the best cleaner at the lowest cost, is recommended. To do this properly a sufficient number of pieces from the production line, which carry the lubricant or soil to be removed, should be supplied to the laboratory. A study of available production equipment and the processing variations possible must be conducted. Utilizing these limiting parameters, reasonably accurate concentrations, temperature, current densities, and other variables can be determined experimentally for the best cleaner.

Control Methods

In order to obtain the best results and the longest use of a cleaning solution, it is strongly recommended that in-plant control tests be run periodically. Many suppliers provide simple test kits for this purpose. However, more exact and definitive data can be obtained by using standard, relatively simple laboratory apparatus. The frequency of testing is dependent upon the amount of work processed and should be determined empirically so that relatively small concentration adjustments are made often, rather than making large infrequent additions. This tends to ensure uniform performance.

A group of three or four tests will provide adequate information to evaluate the condition of the solution. These are pH, active alkalinity, chelating power, and total solids content. The pH should be determined with a good, accurately standardized pH meter. Test papers may be useful but frequently are inaccurate for used solutions. A pH test shows the strength of the alkaline ingredients but does not indicate the amount present. A significant drop in pH may indicate carry-in of acid contaminants.

The amount of active alkaline ingredients in the solution must be determined by titration with standardized acid solution to a pH of 8.3 which is the end point for phenolphthalein indicator. The specific procedure is outlined in the Appendix. This normally gives the amount of effective alkaline cleaner in the solution.

Chelating power is determined by titrating a filtered sample of the solution with a standard calcium chloride solution using a specific indicator. The end point is shown by development of turbidity in the sample. Again, this test method is outlined in the Appendix. This test measures the quantities of available chelators or sequestrants such as certain phosphates or special organic acid products. These materials bind and solubilize polyvalent metal salts which might otherwise form insoluble sludges similar to bathtub ring. They are also effective as softeners where hard water is used. These materials frequently provide detergency action which appears to be independent of their chelating ability. This test is not applicable to all solutions since many cleaners do not contain chelating agents.

Total solids is determined by simply evaporating a given weight of solution to dryness and weighing the residue. It measures the total cleaner content plus soil loading of the solution. When studied in relation to the active ingredient level, it serves as a useful guide to the condition of the cleaner solution.

Experience gained with these tests will not only provide optimum performance parameters but will allow plant operators to discard and renew cleaning solutions before rejects are processed. They are used to maintain conditions which produce suitably clean metal. Thoroughness of cleaning can normally be determined by general appearance, a water break test, and white cloth wipe test.

A water-break-free surface is one on which a continuous water film remains after rinsing which shows no formation of water droplets due to oil spots remaining on the metal. This is the most widely used single test for determination of satisfactory cleaning. A white cloth may be utilized in several ways to further define degrees of cleanliness. Oily dirt films show readily on white cloth after wiping. Wiping a surface when wet will often show the presence of residual dirt on the metal which is not visibly apparent. It shows as a black mark on the cloth. It is an excellent way to detect smut which is usually a combination of amorphous carbon and iron carbide. This is especially useful on materials such as small wire where the water break test is useless. On large surfaces, a wipe with a solvent wetted cloth will reveal thin films of soil which may have been water wettable. A difference in cleanliness between the wiped and unwiped areas is apparent upon visual inspection.

Water

Excessively hard water can seriously affect a cleaning solution by reaction with and deactivation of ingredients such as surfactants and chelators. It can form insoluble material by reaction of the magnesium and calcium salts with fatty portions of the residual soils. While most cleaners are designed to handle these contaminants, there is a point, dependent upon the relationship of degree of hardness to cleaner concentration, beyond which water softening or deionizing is economically beneficial.

If water spotting of the finished product is a problem, then serious consideration must be given to deionizing at least the final rinse water.

Rinsing

Proper rinsing techniques are important to any cleaning operation. Numerous factors influence the choice of methods. Desirable goals are clean metal with low water consumption, no stream pollution, and low disposal costs.

Warm water gives superior rinsing to that with cold water. Cold water tends to solidify fatty materials and inorganic salts are less soluble in cold water. Agitated water rinses faster and more thoroughly than still water. Air or mechanical stirring costs little but provides much benefit.

Pollution problems and disposal costs are demanding reduced water usage for rinsing purposes. Fortunately, dramatic reduction in rinse water consumption can be achieved by using multiple rinse tanks. Cascade or countercurrent rinsing permits a reduction of water flow of about 90 percent for each tank in the countercurrent sequence. This is especially true if the tanks are connected so that water flows from the final rinse to the first rinse tank. If the flow for good rinsing with one tank is 100 gal per min (gpm) this can be cut to about 10 gpm with two tanks and to 1 gpm with three.[2] When the water flow rate is reduced in this way, mechanical agitation must be provided in the rinse tanks.

In order to avoid excessive loss of cleaner by drag out, a slow withdrawal rate and a drain-off delay over the wash tank are recommended. Where high temperatures are involved, drying of the parts may be encountered. This is undesirable since the residual film will be harder to dissolve if dry. A solenoid controlled fog spray of water onto the draining metal may be used to prevent this. It must be operated only during the drain period to avoid excessive dilution of the cleaning solution. The ideal situation would be one where the fog spray flow was equal to the evaporative losses from the hot solution.

Handling and Safety

Alkaline compounds in contact with the skin will cause severe chemical burns unless promptly washed off and treated. Normal safety precautions are often ignored by the uninformed. Workers in areas where these materials are used should be fully instructed concerning protective equipment use and first aid methods. First aid and medical care procedures for alkali burns are well covered in the literature. Eye wash and safety shower stations should be nearby. Goggles and protective clothing should be worn.

Many highly alkaline compounds are exothermic when mixed with water. The compound should always be added to water, never water to the compound. It should be added cautiously, especially if the water is hot, to avoid violent boiling

---

[2] Ceresa, M. and Lancy, L.E., *Metal Finishing Guidebook and Directory 1972*, p. 761.

action. Some users are switching to prediluted liquid concentrates, which can be pumped, to avoid this problem and the danger involved with handling of powders. Adequate ventilation systems are recommended to prevent breathing of alkali laden mists.

Disposal

Water and stream pollution has become a very important matter, forcing the development of suitable disposal procedures for waste cleaning solutions. In addition, cleaner formulations have been modified to reduce the problem. Biodegradable surfactants are now almost universally used so that any which passes through a disposal system is utilized by bacteria for food to ultimately convert them to carbon dioxide and water.

The phosphates used in cleaners support green algae growth which results in eutrophication of waterways. Many areas have regulations on phosphate use in laundry detergents and these restrictions are affecting industrial users in some cases. Sewage authorities are becoming more restrictive on the materials entering city sewage disposal systems. Local laws vary considerably so that the specific limitations should be made known to the supplier before introduction of a new cleaner. Many low and nonphosphated cleaners are now available which often do a better job than the phosphated materials they replace.

Disposal methods are being developed to handle industrial wastes of this type. The literature abounds with reports and numerous patents are being issued in this area. It appears to us that neutralization, alum and polyelectrolyte flocculation, followed by filtration, will lead the chemical methods. Evaporative concentration may be an economical process. Contract hauling and disposal companies are available in some areas which eliminate on-site problems. A low cost method where one is able to obtain full cooperation of the city sewage people is to install a holding tank from which the waste is discharged to the sewer on a low volume continuous basis. The relatively small volumes involved would not be expected to seriously affect the normal sewage plant operations.

Summary

The selection of a cleaner is based on the many factors involved in a given set of operating conditions. These include the soil, the metal, the nature, size and value of the part, the amount of work to be processed, economics, the cleaning equipment available, the degree of cleanliness dictated by subsequent use of the part, environmental prohibitions, and disposal requirements.

APPENDIX

Titration Control for Active Alkalinity

Several solutions of known concentration should be made covering the range expected to be used in the system. Each gram of alkaline cleaner, dissolved in distilled water and diluted to 100 ml in a volumetric flask, is equal to 1.335 oz per gal. These solutions should then be titrated for active alkalinity using the following procedure. Prepare a reference graph showing milliliters of standardized acid versus concentration of cleaner in ounces per gallon. This graph can then be used when titrating used solutions by simply reading the concentration from the graph.

Equipment and Chemicals Needed

One 50 ml calibrated burette graduated in 1/10 ml
One 10 ml calibrated transfer pipette
One 250 ml Erlenmeyer flask
Phenolphthalein
Isopropyl alcohol, 99 percent
0.1000 Normal hydrochloric acid

Procedure

1. Pipette 10 ml of room temperature cleaning solution into a 250 ml Erlenmeyer flask and dilute with 75 to 100 ml of distilled water.
2. Add two drops of indicator solution (1 percent phenolphthalein in isopropyl alcohol).
3. Titrate with 0.1000 Normal acid to the phenolphthalein end point.
4. Refer to the graph prepared as outlined above for the concentration in ounces per gallon of active ingredients.

Titration Control for Chelating Activity

Several solutions of known concentration should be made covering the range expected to be used in the system. Each gram of alkaline cleaner, dissolved in distilled water and diluted to 100 ml in a volumetric flask, is equal to 1.335 oz per gal. These solutions should then be titrated for chelating activity using the following procedure. Prepare a reference graph showing milliliters of calcium chloride solution versus concentration of cleaner in ounces per gallon. This graph can then be used when titrating used solutions by simply reading the concentration from this graph.

Equipment and Chemicals Needed

Whatman No. 40, 9.0 cm filter paper or equivalent
One glass funnel, short stem, 60 mm diameter, 60 deg angle
One pyrex beaker, 250 ml
One 25 ml calibrated transfer pipette
One 250 ml Erlenmeyer flask
One 50 ml calibrated burette graduated in 1/10 ml
One 5 ml graduated cylinder
Ammonium oxalate, reagent grade
Calcium chloride, reagent grade

Procedure

1. Withdraw a sample of cleaner solution and filter to obtain a clear filtrate. The solution must be free of turbidity.
2. Pipette 25 ml of the filtrate into a 250 ml Erlenmeyer flask and add 25 to 30 ml of distilled water.
3. Add 5 ml of indicator solution (4 g ammonium oxalate in 100 ml of distilled water).

4. Titrate with 0.5 percent calcium chloride (5.00 g anhydrous reagent grade calcium chloride in water and made up to 1000 ml in a volumetric flask), solution, in 0.5 ml increments, shaking after each addition until a faint but definite turbidity persists for at least 45 s. This is the end point.

5. Refer to the graph prepared as outlined above for the concentration of active chelating ingredients expressed in ounces per gallon of cleaner.

M. Z. Poliakoff[1]

Solvent Cleaners – Where and How to Use Them

REFERENCE: Poliakoff, M. Z., "Solvent Cleaners–Where and How to Use Them," *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 33–42.

ABSTRACT: This paper provides a practical, user-oriented understanding of the nature of non-aqueous cleaning solvents, and their uses in industry. While much of the information applies to industry in general, emphasis is on the use of these materials for cleaning stainless steel. Subjects covered include: chemical composition of solvent cleaners, including basic solvents as well as proprietary compositions; kinds of soils removable by non-aqueous cleaning solvents; methods of cleaning; hazards associated with use of solvent cleaners, such as flammability, toxicity; and safe handling procedures. A discussion of ASTM Committee D-26 on Halogenated Organic Solvents activity is included.

KEY WORDS: cleaning, stainless steels, solvents

The intent of this paper is to provide a practical, user-oriented exposition on solvent cleaners for the stainless steel industry, as the title states, ". . . where and how to use them." I propose to describe solvent cleaners, what they are, what kinds of cleaning jobs they can do, their advantages as well as limitations, and some recommended practices in using them as well as in protecting personnel and plant from their hazards. This paper will exclude consideration of solvent cleaners in ultrasonic and vapor degreasing applications, since these subjects are covered elsewhere in this symposium. The term "solvent cleaner," as it is used here, refers to organic solvents which are substantially free of water or nonvolatile materials, and which do not mix with water.

What Is the Composition of Solvent Cleaners?

A knowledge of the properties of solvent cleaners and the chemicals used to formulate them is helpful in assessing their usefulness in a particular application, their hazards, and their limitations. The following groups of chemicals account for more than 90 percent of commercially used solvent cleaners. (As these chemicals are discussed, it will be useful to refer to Tables 1 and 2, which exhibit many of their specific properties.)

---

[1] Vice president and technical director, DIACHEM of B. C., Ltd., Burnaby, B. C., Canada.

TABLE 1–*Properties of halogenated solvents used in cold cleaning*.[a]

Solvent	Boiling Point, deg F	Vapor Pressure, mm Hg at 25°C	Evaporation Rate, CCl_4 = 100	Flash Point Tag. C.C. deg F	Flammable Limits; % Volume in air, lower–upper	Density, lb per gal	Threshold Limit Value (1967), ppm/air
Methylene chloride	104	420	147	none	none	11.1	500
Trichlorotrifluoroethane	118	320	170	none	none	13.2	1000
Chloroform	142	200	118	none	none	12.4	50
Methyl chloroform	165	130	100	none	[b]	11.1	350
Carbon tetrachloride	171	114	100	none	none	13.3	10
Ethylene dichloride	181	78	79	70	6.2–15.9	10.5	100
Trichloroethylene	188	70	84	none	[b]	12.2	100
Perchloroethylene	250	23	39	none	none	13.6	100

[a] Sources: Ref *2* and American Mutual Insurance Alliance, Chicago I. Mellan, *Industrial Solvents*, 2nd ed, Reinhold Publishing Co.

[b] These solvents have a definite flammable range. Commercially available products vary as to inhibitor content. Values should be requested from suppliers.

TABLE 2–*Properties of non-halogenated solvents used in cold cleaning.*[a]

Solvent	Boiling Point, deg F	Vapor Pressure, mm Hg at 20°C	Evaporation Rate, Ether = 1	Flash Point Tag. C.C. deg F	Flammable Limits; % Volume in air, lower–upper	Density, lbs per gal	Threshold Limit Value (1967), ppm/air
Acetone	133.7	186	2.8	0	2.2–13.0	6.6	1000
Methyl alcohol	147.4	98	5.4	52	6.0–36.5	6.6	200
Ethyl alcohol	173.3	44	14	55	3.3–19.0	6.5	1000
Methyl ethyl ketone	175.3	71	5.8	24	1.8–11.5	6.7	200
Benzene	176.2	76	5.2	12	1.4– 8.0	7.3	25
Isopropyl alcohol	180.0	31.6	14	53	2.0–12	6.5	400
Toluene	231.1	22	13.7	40	1.3– 7.0	7.2	200
Mineral spirits	300 to 400	7	25	105	0.8– 6.0	6.4	500
Turpentine	310 to 340	4	55	95	0.8	7.2	100

[a] Sources: Ref *2* and American Mutual Insurance Alliance, Chicago I. Mellan, *Industrial Solvents,* 2nd ed, Reinhold Publishing Co.

Halogenated Hydrocarbons—These are a group of chemicals containing various quantities of the halogens chlorine or fluorine in the molecule. Generally speaking, the chlorinated solvents are more toxic and less costly than the fluorinated compounds. The most widely used chlorinated chemicals include trichloroethylene, perchloroethylene, methyl chloroform or 1,1,1-trichloroethane, ethylene dichloride. Carbon tetrachloride, once the most widely used chlorinated solvent, has been almost completely phased out of use in cleaning applications because of its toxicity, but we include it here for comparison purposes. Toxicity varies widely in this group, and the most common industrial problems include depressent effects on the central nervous system, dermatitis, and liver damage.

The fluorinated hydrocarbons are characterized by excellent chemical stability, a low level of toxicity, nonflammability, low solvent power, and high cost. They are more familiar as aerosol propellents, but the less volatile members of the group are widely used in specialized cleaning situations which can tolerate their relatively high initial cost.

Aliphatic Hydrocarbons—Also known as paraffinic hydrocarbons, these are the main constituents of petroleum distillates such as mineral spirits, Stoddard solvent, kerosine, and v, m, and p naptha. They are low in solvent power and have a low order of toxicity, being generally inert biochemically. From the toxicity standpoint their primary problem is dermatitis, since all of these materials will generally defat the skin. All are flammable and the degree of flammability depends on their boiling range. Low boiling fractions like gasoline are extremely flammable and the higher boiling stoddard solvents and kerosines have flash points above 100°F. Possessing low solvent power, they will readily dissolve oils and some asphaltic materials but are not active solvents for resins and plastics. Aliphatic hydrocarbons are very widely used industrially by themselves and blended with chlorinated hydrocarbons.

Aromatic Hydrocarbons—(Also known as benzeneoid hydrocarbons because their molecular structure contains the benzene ring.) Typical among these are benzene, xylene, and toluene. These chemicals are generally local irritants and can cause severe pulmonary and vascular injury when absorbed in sufficient quantities. They are potent narcotics. Dermatitis and effects on the central nervous system are the primary toxicity hazards of the aromatics. Their air pollution potential is significant and existing legislation limits quantities which may evaporate into the environment. Benzene is the worst of the group and usually is totally excluded in cleaning solvent compositions. All are flammable. All possess excellent solvent power and are often included in formulations requiring rapid penetration of tarry asphaltic and resinous soils.

Other Additives—Less frequently used in cleaning solvent formulations are alcohols, glycol-ethers, ketones, and esters. Typical examples include acetone, methyl ethyl ketone, ethylene glycol monoethylether, ethylene glycol monobutylether, and the alcohols—methanol, ethanol, and isopropanol. In this group, methanol stands out as having been responsible for a number of industrial fatalities. Each of these materials can provide specialized properties to a solvent cleaning formulation. Alcohols and glycol-ethers, for example, will help remove traces of moisture from a surface. Ketones and esters will often help dissolve and remove lacquer and protective coatings.

Many of the chemicals described in the above paragraphs are widely used by themselves as cleaning solvents. Indeed the U. S. Government as well as the American Society for Testing and Materials (ASTM) have promulgated specifications covering such materials for cleaning purposes. In addition, literally thousands of blended or compounded solvent cleaners are available in the trade under a wide variety of names, most of which provide no clue concerning their composition. The U. S. Government also has a number of specifications covering these blended cleaning solvents, for example: "C-C-00434 (GSA-FSS), Cleaning Compound, Solvent (cold operations)" describes the properties of the product desired but does not specify composition; "MIL-C-181718b" describes a specific composition containing methylene chloride, perchloroethylene, and mineral spirits; and "MIL-C-8638" used for aircraft oxygen system cleaning describes a compound of trichlorotrifluoroethane, tetrachlorodifluoroethane, and isopropyl alcohol.

Where Are Solvent Cleaners Used?

Because of the large number of raw materials available, cleaning compositions with an extremely wide range of properties can be formulated to produce cleaners suitable for specific needs, for example;

1. extremely rapid to extremely slow drying cleaners;
2. low residue high purity cleaners—for aerospace and guidance applications;
3. low solvency products where solvent may come in contact with sensitive plastics and rubber-like materials;
4. high solvency products where removal of resins, plastics, paints are essential; and
5. low cost, where low flash point or higher toxicity is tolerable because proper precautions can be engineered into the system.

Applications and methods of using solvent cleaners on stainless steel surfaces is really no different from their general industrial use. In cleaning stainless steel we encounter fewer corrosion problems, since usually the contact time between cleaner and surface is relatively short.

Typical applications for solvent cleaners include:

1. where the use of water is undesirable—as on live electrical and electronic devices, or where humidity caused by the presence of water might corrode neighboring equipment;
2. where soils consist of grease, tar, rosin, oils;
3. where fast evaporation is desirable; and
4. during production and assembly of equipment to flush away shop soils, cutting oils, protective oils and lubricants.

In the manufacturing industries, solvent cleaners are used:

1. to wipe down new and stored sheet to remove shop soils;
2. for dip cleaning components, prior to and after assembly (business ma-

chines, electronic devices, etc.);

3. for flushing fuel and gas handling systems (missile);
4. to clean process equipment–food, pharmaceutical, chemical; and
5. in printed circuit production, to remove resin-based fluxes, photo resists, and ink.

In the maintenance and repair field, cleaning solvents are often used for "cleaning in place" where equipment cannot be removed–such as fuel lines, pressure systems, instruments, electronic and electrical devices, and packaging machinery.

Solvent cleaners will soften, dissolve, and remove soils composed of oils, tars, asphaltics, and resins. Materials like salt, sugar, lint, dried garden variety of dirt are not dissolved by solvent cleaners. Sometimes these dry inorganic soils are held to the surface by an oily or greasy film, and in these cases they may often be removed along with the oil or grease by a solvent cleaner. If mechanical force such as high pressure spray, hand wiping or brushing, or ultrasonic energy is applied, inorganic soils can be scrubbed away from the surface by the applied energy. However, in the absence of these mechanical aids, solvent cleaners are not effective for removal of inorganic or most water soluble soils.

The degree of cleanliness desired in a particular application also governs the choice of cleaning solvent. A quick wipe or brush with solvent is highly effective for removing gross quantities of oil and grease. Parts dry rapidly leaving the slight sheen of a residual oily film. If film free cleaning is essential, such parts must be rinsed in fresh uncontaminated solvent. Once used as a rinse, such solvent becomes contaminated and is no longer capable of leaving a film-free surface. Where complete film-free solvent cleaning is required, simple "dip, wipe, and flush" is often uneconomical, because repeated rinsing with clean solvent is necessary. Vapor degreasing is the economical answer to this requirement.

Solvent cleaners will remove and dissolve petroleum and vegetable oils, and most will soften and even gradually remove tars and resin. Dry and oxidized oils, however, are another matter. These require a different degree of solvency. Removal of such soils as oil based paint films, varnish, baked-on cooking oils and fats would probably require inclusion of methylene chloride, ketones, or aromatics in the formulation.

Sometimes the presence of these highly active solvents are a hindrance to effective cleaning. Removal of residues from adhesive and masking tapes and protective papers on highly polished surfaces calls for very specific formulation. Wipe cleaning with high solvency cleaners will cause complete dissolution of the resinous components of the adhesive, producing a liquid adhesive on the surface. The wipe procedure spreads the adhesive around rather than lifting it off. The most useful solvent cleaner for such a problem is one which only swells the resin slightly and wets the substrate, allowing the resin to ball up and adhere to the wiping cloth.

Soldering and braising fluxes vary widely. Where the flux is an inorganic salt such as zinc chloride or a borate, it is pointless to use solvent cleaners. On the other hand, the solvent cleaner will be effective where the flux is resin-based, as is frequently the case in printed circuit manufacture.

Rapid evaporation rate is sometimes essential in production line operations. However, it is a mixed blessing. Extremely rapid drying as would be achievable with methylene chloride or trichlorotrifluoroethane can cause rapid cooling, with resultant condensation of moisture on the surface. If, as often happens, small amounts of inorganic soils remain behind on the surface, these will dissolve in the condensed moisture, leaving a smutty deposit spread over the surface. Condensed moisture could also be harmful where live electrical equipment is involved.

While not normally a problem in cleaning stainless steel surfaces, corrosion can occur to surrounding equipment, where halogenated solvents are in use. When subjected to high temperatures, halogenated solvents will decompose, often resulting in formation of hydrochloric acid and other corrosive compounds. This is often observed around gas-fired space heaters subjected to the vapors of halogenated solvents. Frequent need for replacement of burners can be corrected by installation of adequate vapor handling equipment.

How Are Cleaning Solvents Used?

Since ultrasonic and vapor degreasing are discussed elsewhere, we will touch breifly on the other usual methods, which include wipe or brush, dip, flush or spray, and circulation. These are only a few key points, since most suppliers provide ample instructions geared to the specific application.

Wipe or Brush Cleaning—Wipe or brush cleaning is very efficient for gross soil removal, since it combines tremendous surface agitation with the action of the solvent. A note of caution here involves the choice of bristles used in brush cleaning. Some synthetic bristles will dissolve in the more active solvent cleaners. Nylon and polyolefins are usually sufficiently inert for this purpose.

Dip Cleaning—In dip cleaning, which can involve simple immersion in a bucket or sophisticated mechanically agitated tanks, agitation of the part or of the solvent cleaner is essential for rapid effective cleaning. Injection of air to achieve agitation should be avoided, since it causes excessive solvent vaporization and loss.

Spray Cleaning and Flush Cleaning—Spray cleaning involves atomization of the solvent cleaner into droplets which impinge on the soil surface, whereas flush cleaning involves bathing the surface with a solid stream of cleaner. In spray applications, the atomization should be achieved by mechanical break-up at the nozzle, and not through injection of air and solvent, and inefficient cleaning. Spray pattern has much to do with effective cleaning as well as ventilation requirements.

Circulation Cleaning—Circulation cleaning is employed primarily for flushing the interior of pipelines, tanks, cylinders as might be involved in fuel systems, oxygen systems, and chemical and food handling systems. After circulation cleaning, care must be exerted to ensure that all solvent is purged from the system before it is put back in use.

How Can Solvent Cleaners Be Used Safely?

The term "safety solvent" has often been applied to solvent cleaners. This is unfortunate terminology, since to some it may mean safety to the surface being cleaned, whereas to others it may mean free from hazard. All solvent cleaners are hazardous to some extent, but as long as proper precautions are taken to ensure safety to personnel and plant, they can be used safely [*1*].[2]

Many of the useful properties of cleaning solvents depend on rapid evaporation. The speed or rate of evaporation varies with the chemical nature of the solvent, temperature, barometric pressure, surface tension, and the rate at which air passes over the surface of the solvent. Through evaporation there results, especially in confined areas, a high concentration of solvent vapors in the air immediately above the liquid surface. This high concentration of solvent vapors in the atmosphere presents a toxicity hazard to persons in the area, and may also present a fire hazard.

Flammability

It is a mistake to assume that flash and fire point values provide a complete picture of the flammability of a cleaning solvent, especially where such solvents are composed of more than one ingredient. Some components of the blend may evaporate faster than others, thus causing a change in the composition of the material and a likely change in flash point. For example, a blend containing fast evaporating methylene chloride and slow evaporating mineral spirits may initially have no flash point. On standing in an open bucket or while spraying, the methylene chloride which masks the flash point will evaporate off quickly, leaving behind a higher proportion of mineral spirits with its flash point of 105°F. Federal Specification 0-C-00434, mentioned earlier, takes this fact into consideration by requiring a minimum initial Cleveland Open Cup flash point of 180°F and a miniflash point after 50 percent evaporation of 120°F.

It is unfortunate that there is no universally accepted method of expressing flammability. The City of New York Fire Department has its own standards; Underwriters Laboratories' classification of hazardous liquids uses its own numerical scale; and Interstate Commerce Commission specifies a red label on products with a flash point below 80°F. The American Society for Testing and Materials in Committee D-26 on Halogenated Organic Solvents has been struggling with methods of evaluating fire hazard of halogenated solvents with admixtures thereof, since it recognizes the limitation of the existing flash point tests.

Generally speaking, the halogenated hydrocarbons (with the exception of ethylene dichloride) do not present significant fire hazards. Even though methyl chloroform and trichloro-ethylene do have flammable limits, normal industrial cleaning conditions allow their use without significant fire hazard. The use of the non-halogenated solvents, either alone or in blends with halogenated solvents, calls for care in evaluating flammability potential.

---

[2] The italic numbers in brackets refer to the list of references appended to this paper.

Toxicity [2]

As we have noted, both fire hazard and health hazard are related to concentration of vapors in air. If the concentration of vapors of solvent in air are low enough for safety toxicologically, the potential for fire or explosion will also be negligible. The American Conference of Governmental Industrial Hygienists has established threshold limit values (TLV) for many of the commonly used solvents. These values are published periodically by the ACGIH and copies may be obtained from them in Cincinnati. To quote their statement: "These values should be used as guides in the control of health hazards and should not be regarded as fine lines between safe and dangerous concentrations. They represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect."

Unfortunately, no such TLV's have been established for blended solvents. One ordinarily uses as a guideline the TLV of the most toxic ingredient of a blend. Some progress is being made toward determination of threshold limit values of blended solvents through the efforts of ASTM Committee D-26. By cooperation with the Public Health Service, a grant has been obtained for vapor inhalation studies of several blended solvents, and some interesting data should be available soon.

Adequate ventilation is an essential in any process utilizing cleaning solvents. Such ventilation should always carry the vapors away from the face of personnel into the exhaust ducts. The subject of ventilation and exhaust systems is well covered in "Industrial Ventilation Manual" prepared by the Committee on Industrial Ventilation, American Conference of Governmental Industrial Hygienists [*3*].

While the major toxicity hazard of cleaning solvents involves inhalation of vapors, skin contact and resultant dermatitis is also very prevalent. Dermatitis is a leading industrial disease, and solvents are second only to cutting oils and lubricants in causing this. Cleaning solvents can cause dermatitis in a number of ways. First of all, they will dissolve and remove natural oils from the skin, causing drying and cracking. In addition, chlorinated solvents can actually dissolve the superficial keratin layer of the skin on prolonged contact. Red blotches and blistering of the skin are often caused by wearing solvent soaked clothing which rubs and abraids the skin. An example of this is the use of improper protective gloves which allow penetration of the solvent through the glove and hold the solvent in continuous contact with the hand [*4*].

I know of no protective glove which is completely resistant to all solvents used in solvent cleaning. Neoprene protects against aliphatic hydrocarbons, but is not satisfactory against the aromatics or the halogenated hydrocarbons. Butyl rubber can not completely resist the high solvency of methylene chloride. Polyvinyl alcohol plastic is resistant to most of the solvents in cleaning formulations, yet it dissolves readily in water and acetone, so that the glove becomes useless unless these materials can be kept away from it. Polyolefins are promising materials if they can be fabricated into heavy duty work gloves. Where gloves are used, more than one pair should be available so that they can be cleaned and aired out in order to remove absorbed solvent after each couple of hours of use.

Barrier hand protective creams provide limited protection.

Conclusions

In evaluating a solvent cleaning process, one must seek that composition which does the cleaning job most efficiently under conditions of minimum hazard to personnel and equipment at minimum cost. I hope these comments will aid in such choices.

Those interested in further study in this area are referred to membership in ASTM Committee D-26 on Halogenated Organic Solvents. Subcommittee D-26.03 covers the subject of Cold Cleaning and has published a manual on cold cleaning with halogenated solvents [*5*].

References

[*1*] "Hygieneic Guide Series," American Industrial Hygiene Association, Detroit, Mich.

[*2*] Patty, F. A., Facett, D. W., and Irish, D. D., *Industrial Hygiene and Toxicology,* Interscience Publishers, New York.

[*3*] *Industrial Ventilation Manual,* American Conference of Governmental Industrial Hygienists, Lansing, Mich.

[*4*] McFee, D. R., Journal, American Society of Safety Engineers, May 1964.

[*5*] *Cold Cleaning with Halogenated Solvents,* American Society for Testing and Materials, 1966.

W. J. Blume[1]

Role of Organic Acids in Cleaning Stainless Steels

REFERENCE: Blume, W. J., "Role of Organic Acids in Cleaning Stainless Steels," *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 43–53.

ABSTRACT: The author discusses the various uses of organic acids in the preparation and maintenance of stainless steels. Included is a review of the fundamental properties of organic acids, and a discussion of the methods of use in acid and alkaline cleaning, electropolishing, and the application of oxalate coatings. Emphasis is placed on providing a state-of-the-art survey of these current and potential uses of organic acids.

KEY WORDS: cleaning, stainless steels, chelating agents, finishing, acidity, buffering

Organic acid chelating agents have received wide attention by the metal cleaning and finishing industry in recent years because of their mild acidity, safety and ease of handling, low order of toxicity, and generally rapid biodegradability. This paper discusses the underlying properties and chemistry of these chelating agents and their application to the preparation and maintenance of stainless steels.

Properties

The functional attractiveness of these organic acids may be attributed to their combined ability to serve as acids, buffers, and sequesterants. As background for the following discussion of their applications to stainless steels, I would like to briefly review these properties.

Acidity

These chemicals are acids in the sense that, in solution, they release one or more hydronium ions. As Table 1 shows, many of the commonly used organic acids are di- or tri-basic; that is, they have two or three available hydrogen ions and, accordingly, multiple acid dissociation constants, one for each successive stage of ionization.

Typical of these acids is citric acid, which exhibits the following steps in dissociation.

---

[1] Technical service representative, TEKCHEM Technical Service Dept., Pfizer Chemicals Division, Brooklyn, N. Y. 11206.

$$H_3Cit + H_2O \rightleftharpoons H_2Cit^- + H_3O^+ + K_1$$
$$H_2Cit^- + H_2O \rightleftharpoons HCit^= + H_3O^+ + K_2$$
$$HCit^= + H_2O \rightleftharpoons Cit^{-3} + H_3O^+ + K_3$$

$$H_3Cit + 3H_2O \rightleftharpoons Cit^{-3} + 3H_3O^+ + K_a = K_1 \cdot K_2 \cdot K_3$$

Also of interest, when comparing various acids, is their neutralization equivalent. The equivalent weight (neutralization equivalent) relates the weight of acid required to produce a 1.0N acid solution or, performing calculations incorporating dissociation constant, the amount of acid required to produce a desired solution pH. The appropriate molecular and equivalent weights for these acids are also tabulated for reference in Table 1.

Buffering

Buffering capacity is of interest whenever the process under consideration must be run over a narrow pH range. The pH range in which an acid forms useful buffers is determined by the ionization constant (K_a) of the acid.

In general, an acid will buffer within ±1 pH unit of its pK_a value. As examples, gluconic acid, with pK = 3.56 will buffer between pH 2.5 to 4.6 (3.56 ± 1). Tribasic citric acid, on the other hand, will effectively buffer at any pH between about 2.1 and 6.4 (3.06 ± 1, 4.74 ± 1, and 5.4 ± 1).

Sequesterants

If a molecule contains two or more complexing sites, which are capable of coordinating around a metal ion, this compound is called a "chelating agent." A chelating agent which forms a water-soluble complex with a metal ion is also a "sequesterant." These two terms are now used interchangeably, but the important property to keep in mind is the formation of a water-soluble complex.

Most of the organic acids under consideration in this paper are sequesterants. The chelate stability constant, stated as log K, shows the ratio of the chelated metal ion to the free metal ion in solution. The higher the value of K for a particular metal ion-sequesterant system, the more effectively will that compound complex the metal ion. Table 2 lists the log K values for some common metal ion-organic acid sequesterant systems.

While they are generally acids by nature, there are sequesterants available for cleaning and metal ion contamination control at any pH. Thus, derusting and descaling formulations can be constructed, using organic acids, to function at any pH from strongly acidic to high levels of free caustic.

Applications

Organic acids have found wide usage in the cleaning and finishing of ferrous metals, including stainless steel, and hold promise for even broader utilization of their diverse properties. Included among the current uses are acid cleaning and

TABLE 1–*p*K *Values of organic acids.*

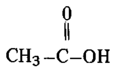
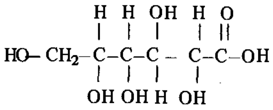
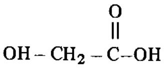
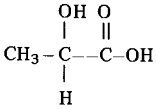
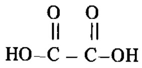
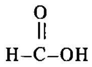
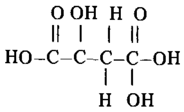
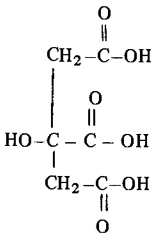
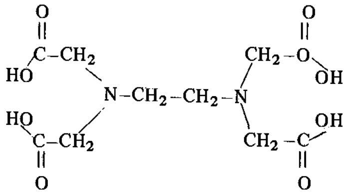
Organic Acid	Formula	pK	Molecular Weight	Equivalent Weight
Acetic	 $CH_3-\overset{\overset{O}{\parallel}}{C}-OH$	4.75	60.05	60.05
Gluconic	 $HO-CH_2-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{\overset{O}{\parallel}}{C}-OH$	3.56	196.16	196.16
Glycolic	 $OH-CH_2-\overset{\overset{O}{\parallel}}{C}-OH$	3.87	76.05	76.05
Lactic	 $CH_3-\overset{OH}{\underset{H}{C}}-\overset{\overset{O}{\parallel}}{C}-OH$	3.8	90.08	90.08
Oxalic	 $HO-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-OH$	1.19 pK_1 4.21 pK_2	126.07	63.04
Formic	 $H-\overset{\overset{O}{\parallel}}{C}-OH$	3.75	46.02	46.02
Sulfuric	H_2SO_4	0.40 pK_1 1.92 pK_2	98.08	49.04
Tartaric	 $HO-\overset{\overset{O}{\parallel}}{C}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{\overset{O}{\parallel}}{C}-OH$	2.88 pK_1 3.94 pK_2	150.09	75.05
Citric	 $HO-\overset{CH_2-\overset{\overset{O}{\parallel}}{C}-OH}{\underset{CH_2-\underset{\underset{O}{\parallel}}{C}-OH}{C}}-\overset{\overset{O}{\parallel}}{C}-OH$	3.1 pK_1 4.7 pK_2 6.4 pK_3	192.12	64.04
EDTA		1.99 pK_1 2.67 pK_2 6.16 pK_3 10.26 pK_4	292	73

TABLE 2–*Metal ion stability constants*[a] *of organic acids.*

Organic Acid	Logarithms of Stability Constants[b]							
	Al^{+++}	Ca^{++}	Mg^{++}	Fe^{+++}	Fe^{++}	Ni^{++}	Cu^{++}	Zn^{++}
Acetic	. . .	0.53	0.51	. . .	. . .	0.71	. . .	1.03
Gluconic	. . .	1.22	0.70	37.2	1.0	. . .	18.29	1.70
Glycolic	. . .	1.59	1.33 0.92	4.7	. . .	. . .	.81	1.92
Oxalic	$13\beta_2$ $16.3\beta_3$	3	2.55	9.4 $6.8K_2$ $4.0K_3$	$9.57\beta_2$	$6.51\beta_2$ $14\beta_2$	$8.5\beta_2$	$7.36\beta_2$
Tartaric	. . .	$2.80(K_1)$ $1.80(K_1)$ $1.73(K_1)$	1.36	18.06	$4.85(K_2)$	. . .	$3.20(K_1)$ $1.91(K_2)$ $0.34(K_3)$ $1.73(K_4)$	$2.68(K)$
Citric	7.0	3.2^c	3.2	11.85^c	3.08^c	4.4	18.0	4.5
Ethylenediamine Tetraacetic	16.13	10.7	8.69	25.1	14.33	18.6	18.8	16.5

[a] Adapted from Bjerram, J., Schwarzenback, G., and Sillen, L.G., "Stability Constants of Metal Ion Complexes, with Solubility Products of Inorganic Substances," Part I, *Organic Ligands*, The Chemical Society, London, 1957.

[b] All values are K_1 values unless stated. If more than one mole of a ligand reacts with a metal ion, the second equilibrium reaction is characterized by a second K value (K_2) or a third K value (K_3). If an equilibrium reaction between a metal ion M and a ligand L proceeds in stepwise fashion, the cumulative stability constant, $Beta_{11}$, is the product of the K values.

[c] At pH 7.2 to 7.3.

descaling, process equipment cleaning, alkaline descaling, electrolytic pickling and polishing, oxalate coatings, and so forth.

Acid Cleaning–General

Organic acids, particularly citric acid and diammonium citrate, are frequently used to remove rust and mill scale from newly fabricated stainless steel stock. The ability of these chemicals to produce an oxide-free metal surface is particularly valuable when stainless steel is used for storage and manufacture of foodstuffs, fine chemicals, or other materials whose purity is important. In addition to their safety, ease of handling and disposal, and noncorrosiveness, they also eliminate the chance of chloride stress cracking and hydrogen or caustic embrittlement in applications where these considerations are important.

Fabricators of stainless steel use solutions of dibasic ammonium citrate to remove embedded iron and scale from the surface of the alloy. Such contamination usually originates from various machining and handling operations. After treatment with ammonium citrate dibasic, the familiar ferroxyl test (potassium ferricyanide-nitric acid test) for the detection of metallic iron gives a negative reaction.

Stainless steels are substantially corrosion resistant. However, without thorough removal of surface iron contamination, which does not have stainless steel properties, the steel assumes an undesirable appearance when oxidation takes place. In addition, the corrosion resistance of the steel is considerably lowered; for instance, the corrosive action of moist salt air is accelerated. Once the embedded iron has been removed from the surface, the intrinsic corrosion resistance of the stainless steel is restored. The following chart lists the various conditions found efficient for the removal of iron contamination from the surface of stainless steel when using dibasic ammonium citrate solutions.

Dibasic Ammonium Citrate,%	Temperature,°C	Time, min	Anionic or Nonionic Wetting Agent,%	Agitation
5	80	10	0.1	No
3	80	15	0.1	No
2	80	20	0.1	No
1	80	10	0.1	Yes

In cases where mild acidity is required, and particularly when ferric oxide deposits are involved, the use of ammoniated citric acid solutions is preferable. Generally, a 3 to 5 percent citric acid solution is prepared and the pH adjusted to between 3 and 4 with ammonium hydroxide. Bright, silvery metal surfaces result.

In cleaning tanks for storage of whiskey, for example, the presence of even small traces of ferrous ions can lead to discoloration of the whiskey. Cleaning with nitric or hydrochloric acid dissolves iron deposits, but either because of incomplete scale removal or redeposition of oxides during rinsing, or because of after-rust from corrosion pitting, unsatisfactory results are frequently obtained. Tests in the laboratory and in the field have shown that citric acid, dibasic ammonium citrate or ammoniated citric acid effectively renews the corrosion resistant stainless surface, and whiskey storage is therefore safe in equipment so treated.

Equipment Cleaning—Large quantities of citric acid and, to a lesser extent, EDTA, glycolic and formic acids are used each year for the pre-service and post-operational cleaning of utility and industrial steam generating units [*1-3*].[2] This application developed specifically to overcome the problems of hydrogen embrittlement, chloride stress cracking, and corrosion pitting inherent in using hydrochloric-acid for post-operational cleaning the austenitic stainless steels used in supercritical boilers.

The advantage of using these acids for such jobs is that they form stable, water-soluble chelates with metal ions such as iron, nickel, and copper, and prevent the formation of insoluble oxides and hydroxides during the cleaning and rinsing operations. The iron ammonium citrate complex is soluble over a very wide pH range (actually up to about pH 10), thus enabling both iron and copper oxides to be removed by the same solution by making a simple pH adjustment [*4*].

The excellent cleaning power of ammoniated citric acid, coupled with its low corrosion rates and nontoxicity, have resulted in its wide usage for other types of equipment cleaning as well. An application finding increasing use is the cleaning and decontamination of stainless steel heat exchange surfaces of nuclear reactors [*5,6*]. The procedure generally calls for three-step cleaning as follows:

Step 1—Circulate a hot alkaline permanganate solution composed of 10 percent potassium permanganate plus 3 to 5 percent caustic soda.

Step 2—Fresh water rinse.

Step 3—Circulate a hot organic acid descaling solution, typical of which are the following:

(*a*)	Oxalic acid	2 to 3%
	Dibasic ammonium citrate	4 to 6%
	Ferric sulfate or nitrate	1.7 to 2.4%
	Diethyl thiourea	0.8 to 1.2%
(*b*)	Citric acid	2.0%
	Dibasic ammonium citrate	5.0%
	Disodium EDTA	0.5%

Compounds for cleaning of stainless steel food and pharmaceutical processing equipment frequently employ nontoxic organic acids such as citric and gluconic. Ammoniated citric acid has also been employed for pre-service cleaning of

---

[2] The italic numbers in brackets refer to the list of references appended to this paper.

fabricated stainless steel equipment, including tanks, machinery, trucks, and railroad cars. For large-sized applications such as these, in which size prohibits soak cleaning, steam cleaning has been found to be effective.

In steam cleaning, an ammoniated citric acid concentrate is sucked into a high pressure jet of steam at such a rate as to give a concentration of between 1 to 5 percent in the superheated water. This technique is particularly useful for the removal of "tramp" iron from stainless steel. The addition of a low foaming nonionic wetting agent to the ammoniated citric acid injection will normally assist in the removal of general soil and grease. In order to remove all traces of cleaning chemicals this is normally followed by a straight steam (hot water) rinse.

Pickling—During acid or electrolytic pickling with sulfuric acid, insoluble iron sulfates accumulate which are detrimental to the bath so that frequent regeneration or dumping is required. The addition of citric or gluconic acid accelerates the pickling rate and prolongs the life of the bath as it dissociates the sulfate, chelating the iron into solution and regenerating the sulfuric acid [*7,8*]. The presence of the sequesterant thus reduces materially the time required for pickling by maintaining a higher level of free acid in the bath and, further, enhances the quality of the surface by preventing iron oxide/hydroxide precipitation on the work piece during the rinse steps.

The low corrosion rates of ammoniated citric acid solutions, and the retention of iron oxide dissolving power at pH values as high as 7.0, make these solutions attractive as pickling media in general metal finishing applications. The economic disadvantage in using organic acid as opposed to mineral acids can be significantly reduced by regenerating the solution either electrolytically [*9*] or by means of ion exchange resins [*10*].

Removing Weld Scales—Ammoniated citric acid can be effectively employed in removing weld scales from alloy steels. Using a 3 to 5 percent ammoniated citric acid solution (pH 3.5) at 80 to 90°C the characteristic blue line on electrically welded low alloy steel tube can be removed in less than 5 min. By adding a small quantity of a suitable wetting agent to this solution, light soils and oil can be removed simultaneously. The tendency to rerust after cleaning is markedly less than with mineral acid solutions.

While ammoniated citric acid solutions are less effective in removing the weld scale from higher alloys, such as 12Cr and 18-8 stainless, the use of a suitable periodic reverse electrolytic treatment (to minimize the chances of hydrogen embrittlement) allows rapid removal of weld scales from these stainless steels as well.

Electropolishing—One of the principal advantages of electrolylic polishing is that complex shaped objects, which could only be polished with difficulty using mechanical methods, may be electropolished swiftly and effectively. Solutions containing an organic acid and sulfuric acid have been found suitable for obtaining a bright polish on stainless steel using an electrolytic technique [*11*]. The composition of the solution used as the electrolyte will vary according to the type of metal being treated but, for example, satisfactory compositions for obtaining a bright reflective finish on stainless steel include:

(*a*)	citric acid	55 to 60%	temperature =	180 to 200°F
	sulfuric acid	15 to 20%		0.5 to 4 amp/ft^2
	water	30 to 20%		6 to 12 V
(*b*)	glycolic acid	55%	temperature =	170 to 190°F
	sulfuric acid	30%		0.5 to 4 amp/ft^2
	water	15%		4.9 V

When electropolishing stainless steel, the object is made the anode and a lead cathode is used. The time taken to obtain a satisfactory polish varies according to the conditions used but, as an example, stainless steel plates can be satisfactorily polished in about 5 to 10 min under the above conditions.

In the fabrication of many parts it is necessary to use a forming-lubricant, in which case it is suggested that the parts be precleaned in an alkaline cleaning solution to remove organic forming lubricants, then given a 5 to 10 min immersion in 10 to 15 percent sulfuric acid at 140 to 160°F and water rinsed before entering the polishing bath. Such a treatment will remove most surface contamination and activate the stainless surface so that electrolytic polishing can be expedited.

Alkaline Cleaning

Since solutions of citric acid, when neutralized to various pHs with ammonia or other amines or alkalies, are still capable of removing iron oxides, it is possible to prepare combinations with surfactants and penetrants which, in one operation, will remove both soils and oxide films. Such formulations must be tailored to fit the specific job, but, in general, will incorporate surfactants—nonionic or anionic or both—and an organic solvent.

In the area of highly alkaline (that is, high free caustic cleaning), the use of sodium gluconate ushered in a new era of cleaning. Mineral acids will rapidly remove rust from a metal surface but will also leave the derusted surface highly susceptible to rerusting unless it is immediately rinsed and neutralized. As noted, it is possible with organic acid cleaners to remove both scale and some organic soils in one operation if the organic soils do not contain materials which are insolubilized or precipitated by acid treatment.

However, many organic soils found on or produced on the surfaces of ferrous metals during processing contain fatty acids, but can be readily removed in alkaline, caustic soda-based cleaners. By adding sodium gluconate to these cleaners it is possible in one operation to remove both the organic soils and metal oxide deposits. In addition, the cleaned parts, since their surfaces are still alkaline, have very little tendency to rerust. The ability of gluconate to remove rust in alkaline solutions is due to its ability to form stable, water-soluble ferric gluconate complexes in alkaline solutions.

Since gluconate enables removal of rust and scale by highly alkaline solutions, it is possible to take advantage of the excellent cleaning and soil removal properties of fully formulated alkaline cleaners. Formulations which contain wetting agents, phosphates and dispersants are widely used because of their excellent degreasing, emulsifying, wetting, saponifying, water-softening and long-life properties. These formulations are quite versatile and can be used hot, cold, as soaks, sprays, ultrasonically or electrolytically [*12*].

When used electrolytically the alkaline gluconate solutions will remove rust and heavy scale several times more rapidly than when they are used as soaks. By using periodic reverse instead of simple cathodic or anodic current the cleaning is often more satisfactory, and a mild polishing effect is produced on the surface. Due to their vigorous scrubbing action the gases libertated at the electrodes during electrolytic cleaning will greatly accelerate the removal of rust. Periodic reverse current is used to reduce hydrogen absorption and subsequent embrittlement, and the cleaning is usually finished with the object as the anode. One particularly useful example of this technique is in the cleaning of cast iron glass-forming molds, because it will remove the iron oxide, silicate, and mold lubricant residues without attack on the base metal.

When used ultrasonically, alkaline gluconate solutions will also remove rust and heavy scale several times more rapidly than when they are used as soaks, but not as rapidly or effectively as when the solutions are used electrolytically. The use of ultrasonics greatly assists emulsification, and constant replenishment of the solution in contact with the surface of the object by the vigorous agitation induced by the cavitation will also assist in the removal of solid particles, such as rust, adhering to the surface. Transducers operating on magneto-strictive principles offer the greatest scope in this treatment, because they can operate for long periods at temperatures up to the boiling point of the cleaning solution.

The concentration of gluconate in soak, spray, steam, electrolytic, and ultrasonic formulations can be varied according to the amount of rust to be removed. The range of formulations and operating conditions which can be used for any of these techniques is shown in Table 3 [*13,14*].

TABLE 3—*Caustic–gluconate cleaning system.*

Concentration of caustic soda:	
sodium gluconate mixture	5 to 40%
Ratio of caustic soda to sodium gluconate in mixture	1:1 to 9:1
Wetting agent (optional)	1%
Temperature	soak: 170°F (77°C) boiling point. Electrolytic: 140°F (60°C) boiling.
Current density (for electrolytic cleaning)	25 to 100 A/ft^2
Periodic current cycle:	
direct current	10 to 30 s
reverse current	20 to 60 s
reverse current time: direct current time	2:1

Preparations containing 2 to 10 percent gluconate with alkali salts, a stable wetting agent such as Triton QS-15 (Rohm & Haas), and a dispersant will effectively remove grease, organic soil, buffing compounds, metal oxides, paints, and chromate and phosphate films in one operation. Caustic gluconate solutions are also very effective for the removal of paints and lacquers, an ability which is used to particular advantage in cleaning rusted, painted steel parts. [*14-16*].

Due to the alkalinity of the solution base, metal attack and the danger of hydrogen embrittlement is minimized. In addition, afterrusting tendencies are avoided, and there is the further advantage that the gluconate ion, by sequestering calcium and magnesium, permits using even hard water in preparing the cleaning and rinse baths.

This combined ability of caustic-gluconate solutions to clean as well as remove rust frequently makes it possible for metal processors to avoid the use of additional degreasing, derusting, and rinse tanks. Also, by preventing the formation of insoluble soap films on the surfaces being drained, gluconates improve adhesion of subsequently applied coatings or electro deposits. The fact that such savings, both in time and equipment, can be realized has led to the widespread use of gluconates for derusting in alkaline cleaners.

Oxalate Coatings

The application of oxalate coatings on metal surfaces, and particularly on stainless steels, has been employed by industry for a number of years. These coatings are applied by contacting the metal surface with an aqueous acidic solution of oxalic acid, which normally contains an activator such as a chloride or fluoride, and an accelerator such as the organic nitro compounds (picric acid/, nitroguanadine, p-nitroanaline, m-nitrobenzene sulfonic acid, etc.). Improved oxalate coatings and longer-lasting coating solutions are reportedly prepared by adding citric acid to the oxalic acid solution [*17*].

These oxalate coatings are particularly useful on surfaces which are to be subjected to a cold forming operation, since the oxalate coatings are highly effective as a lubricant carrier or a parting layer or both during the deforming operation. It should be noted, as a precautionary measure, that oxalate coatings begin to lose their effectiveness if stored longer than about three weeks before forming.

Oxalate coatings can be removed from finished parts by a hot caustic wash, followed by water rinsing, passivation in 20 percent nitric acid for 15 min and then warm water rinsing.

Conclusions

Utilization of organic acids offers the stainless steel industry an environmentally attractive alternative in many areas where mineral acids are currently employed. The economic disadvantage formerly associated with these chemicals has been substantially overcome through development of regeneration technology. The future will see increased emphasis being placed on process development to employ organic acids for the preparation and maintenance of stainless steels.

References

[*1*] Alfano, S., U. S. Patent No. 3,072,502, 1963.
[*2*] Reich, C. F., U. S. Patent No. 3,003,898, 1961.
[*3*] Mamet, A. P. and Vlasova, E. D., Investigation of solution of boiler deposits with complex-forming reagents, *Teploenergetika*, Vol. 11, No. 69 (1962).
[*4*] "Chemical Cleaning With Citric Solutions," Pfizer Data Sheet No. 557, and "Boiler Cleaning With Citric Acid and Ammonia," Pfizer Data Sheet No. 561
[*5*] Weed, R. D., U. S. Patent No. 3,496,017, 1970.
[*6*] MIL-STD-711 (SHIPS), 8 May 1959.
[*7*] Chester, A. E., U. S. Patent No. 1,995,766, 1935.
[*8*] Eck, F. and Emmericks. G. T., U. S. Patent 3,438, 799, 1969.
[*9*] Frantzis, Nicholas, U. S. Patent 3,425,920, 1969.
[*10*] Downey, J. A. and McCallion, J. J., U. S. Patent No. 3,116, 240, 1963.
Petrocelli, A. W., et al, U. S. Patent No. 3,407,129, 1968.
Wallman, H., et al, U. S. Patent No. 3,411,998, 1968.
Calmon, C. and Heit, A. H., U. S. Patent No. 3,394,068, 1968.
[*11*] McClymonds, N. L., *Metals Engineering Quarterly* Vol. 8 No. 1, 1968, pp. 27-39.
[*12*] Meyer, W. R., U. S. Patent No. 2,915,444, 1959.
[*13*] Horner, D. C., *Metal Finishing,* 1959, pp 99-105, 115.
[*14*] "Pfizer Products for Alkaline Derusting and Paint Stripping," Pfizer Data Sheet No. 593,
[*15*] L. L. Jaffee and W. L. Harris, U. S. Patent No. 2,940,977, 1960.
[*16*] Yaroch, W. L., U. S. Patent No. 2,975,140, 1961.
[*17*] Freeman, D. B. and Gill, C. A., U.S. Patent 3,459,604, 1969.

W. L. Archer[1]

Selection of a Proper Vapor Degreasing Solvent

REFERENCE: Archer, W. L., "Selection of a Proper Vapor Degreasing Solvent," *Cleaning Stainless Steel, ASTM STP 538*, American Society for Testing and Materials, 1973, pp. 54-64.

ABSTRACT: Vapor degreasing is an essential part of the manufacturing process in wide areas of the metal working industry. All the metals of construction, for example, stainless steel, mild iron, aluminum, titanium, zinc, brass, copper, and die cast, can be safely cleaned with each of the three chlorinated solvents. The vapor degreasing process is simple; when hot solvent vapors contact a cooler object, the vapors condense on the cool object into liquid solvent which warms the object and dissolves the oils and soils. When the temperature of the metal object reaches that of the vapor, vapor condensation ceases and the metal part is removed clean and dry. In the past, the vapor degreasing process has normally used trichloroethylene as the solvent of choice. Recent environmental and worker safety regulations have started, however, to cause concern among the users of trichloroethylene. This paper reviews the Clean Air Act of 1970 and Occupational Safety and Health Act (OSHA) of 1971, and their probable impact on chlorinated solvent users.

KEY WORDS: cleaning, stainless steels, vapor degreasing, metal working

There are three chlorinated solvents, 1,1,1-trichloroethane, trichloroethylene, and perchloroethylene that can be conveniently used as vapor degreasing solvents. Each solvent has advantages and disadvantages which will be discussed in the paper. The data given herein reflects both proprietary laboratory work and field experience in actual production equipment. The physical properties of each solvent will be listed and compared in view of the expected use as a metal cleaning solvent.

Recently some effort has been made to promote a special stabilized grade of methylene chloride for vapor degreasing. Methylene chloride, boiling point of 104°F, is sometimes useful for vapor degreasing where certain work soils might be "set" at the vapor temperatures of higher boiling solvents. The high solvency enables the solvent to remove paint residues and certain resins not dissolved by the other common chlorinated solvents. The low boiling point of methylene chloride will, however, necessitate extra cooling capacity when the solvent is used in vapor degreasing. The solvent's lower vapor density will also increase vapor losses due to air movements around a vapor degreaser. Methylene chloride evaporates more rapidly than the other vapor degreasing solvents; therefore, the degreaser should be covered during the nonoperating periods to prevent

---

[1] Research specialist, Inorganic Chemicals, Metal Cleaning Solvents, Dow Chemical U. S. A., Midland, Mich. 48640.

excessive solvent losses.

Methylene chloride meets all present or proposed air pollution regulations. Presently, methylene chloride has an "adopted" threshold limit value (TLV) of 500 ppm. Recently, additional toxicity information has resulted in the American Conference of Governmental Industrial Hygienists placing methylene chloride on the "intended change" list with a potential value of 250 ppm. A two year period has been established for obtaining additional data to substantiate the intended change, or to retain the present "adopted" value.

The conversion of most trichloroethylene degreasers to methylene chloride will present the problem of increased solvent losses and higher vapor concentrations in the working environment around the degreaser. In most cases, 1,1,1-trichloroethane or perchloroethylene will be the more logical choice when changing from trichloroethylene as a vapor degreasing solvent.

Environmental Concerns

> The Clean Air Act and its amendments of 1970 are aimed at establishing ambient air quality standards to force evaluation of programs to reduce pollution. "Air quality criteria for an air pollutant shall accurately reflect the latest scientific knowledge useful in indicating the kind and extent of all identifiable effects on public health or welfare which may be expected from the presence of such pollutant in the ambient air, in varying quantities."
>
> The clean air amendments of 1970 have given the responsibility to the Environmental Protection Agency (EPA) to: (1) designate air quality control regions; (2) publish air quality control criteria; (3) promulgate national primary and secondary ambient air quality standards; (4) assist states in the adoption and implementation of air quality standards; (5) enforce the Act.[*1*][2]

Ambient air standards have been set for hydrocarbons, photochemical oxidants, sulfur oxide, particulate matter, and nitrogen oxides. Chlorinated solvents are classified as hydrocarbons under this act. The reason for control of hydrocarbon emissions is that certain hydrocarbons react in the presence of the oxides of nitrogen and sunlight to form photochemical oxidants. These photochemical oxidants contribute to smog formation and accompanying eye irritation, respiratory ailments, vegetation damage, and visibility reduction. In conjunction with the federal program to reduce auto emissions, the attainment of the national primary and secondary photochemical oxidant standards may be accomplished by controlling the emission of certain organic compounds to less than 3 lb per h or 15 lb maximum per day for each piece of equipment. The regulations require that emissions in excess of these quantities be reduced by at least 85 percent. This may be accomplished by incineration, carbon adsorption, or the substitution of a solvent which is photochemically unreactive [*2*].

> Trichloroethylene is considered a photochemical oxidant generator and as such must comply with current regulations. Trichloroethylene is the only common chlorinated solvent so regulated.

---

[2] The italic numbers in brackets refer to the list of references appended to this paper.

> Chlorinated solvents which have been shown to be virtually unreactive in the formation of oxidants and are exempted from regulations by the EPA are the saturated halogenated hydrocarbons (this includes methylene chloride and 1,1,1-trichloroethane) and perchloroethylene [*3*].

State by state regulations will vary according to the photochemical oxidant problem that does exist in the particular area. The Clean Air Act standards will serve as guidelines in the individual state implementation programs to attain the federal ambient air standards. The timetable for the attainment and maintenance of these air standards is diagrammed in Fig. 1. The now famous Rule 66 of Los Angeles county served as a pattern for much of the Clean Air Act and its solvent control regulations have been incorporated into, for example, the recent city of Philadelphia's Regulation V and Ohio's Regulation AP-5-07.

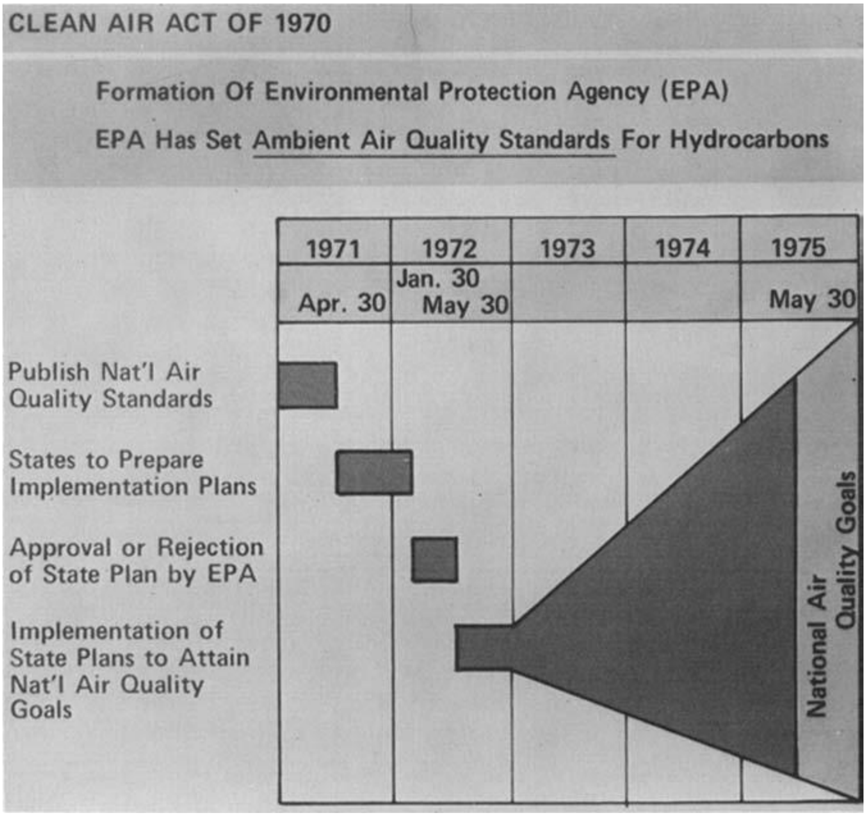


FIG. 1–*Timetable for the attainment and maintenance of the Clean Air Act standards.*

Occupational Safety and Health Act

The Occupational Safety and Health Act (OSHA) administered by the Department of Labor defines the minimum requirements for protection of workers from excessive exposure to solvent vapors. Chlorinated solvent vapor emissions into the worker's environment is thus controlled under the OSHA regulations.

The type of vapor emission standards specified in OSHA is given in the following example.

> For trichloroethylene, the standards specify a maximum time-weighted average (TWA) exposure of 100 ppm, with an acceptable ceiling concentration of 200 ppm and maximum peaks up to 300 ppm for a duration of no more than five minutes in any two hour period. Two excursions above 200 ppm in any two hours is in violation of the OSHA. In any event, the 100 ppm TWA must be satisfied. Any exposure over 300 ppm is in violation of the OSHA. In arriving at the TWA, concentrations above 100 ppm are allowed if they are of short duration and compensated for by equal periods of exposure to less than 100 ppm. The maximum peak of 300 ppm for five minutes is allowed for non-routine fluctuations, e.g., temporary leaks, spills, sudden shift in work pattern, etc.
>
> Assume a degreaser operator spends his day as follows:
>
> 6 hours at degreaser (average exposure concentration, 90 ppm)
> ½ hour at cleaning degreaser (average exposure concentration, 150 ppm)
> 1 hour sorting parts (average exposure concentration, 40 ppm)
> ½ hour lunch room (average exposure concentration, < 5 ppm)
>
> To determine his time-weighted exposure:
>
> $$\text{TWA} = 90\text{ ppm} \times \frac{6\text{ hrs}}{8\text{ hrs}} + 150\text{ ppm} \times \frac{0.5\text{ hrs}}{8\text{ hrs}} + 40\text{ ppm} \times \frac{1\text{ hr}}{8\text{ hrs}} + 5\text{ ppm} \times \frac{0.5\text{ hrs}}{8\text{ hrs}} = 82\text{ ppm}$$
>
> This would be an acceptable exposure, since the eight hours TWA is less than 100 ppm, the acceptable ceiling did not exceed 200 ppm and more than equal exposure time was spent below 100 ppm than above. If the TWA had exceeded the 100 ppm concentration, the employer would have been in violation of the OSHA [*4*].

Vapor degreasers using trichloroethylene as the solvent can be operated in a manner so as to comply with OSHA regulations. Work patterns, method of degreaser operation or unusual circumstances can, however, give excessive vapor emissions which are in violation of the OSHA standards. The chlorinated solvent emission limits as prescribed by OSHA are listed in Table 1. Table 2 lists vapor levels around small open top degreasers with each of the three common chlorinated solvents. The recorded vapor emission levels are from typical industrial installations where some 300 degreasers were surveyed. The explanation of these differences will be discussed later. The determined vapor concentrations range from perchloroethylene > trichloroethylene to 1,1,1-trichloroethane with the lowest vapor emissions.

TABLE 1–*Occupational Safety and Health Act.*

Solvent	Standards	Rules and Regulations (ppm vapor concentration in air)			
		Table G-2			
		8-hour time-weighted average	Acceptable ceiling concentration	Acceptable max peak above the acceptable ceiling concentration for an 8-h shift	
CHLOROTHENE VG[a] (1,1,1-trichloroethane)	Z37.19-1970	400	500	800	(5 min in in any 2 h)
Trichloroethylene	Z37.19-1967-ANSI	100	200	300	(5 min in any 2 h)
Methylene chloride	Z37.3-1969-ANSI	500	1000	2000	(5 min in any 2 h)
Perchloroethylene	Z37.22-1967-ANSI	100	200	300	(5 min in any 3 h)

[a] At the time this paper was written, the solvent 1,1,1-trichloroethane was listed only under Table G-1 in the OSHA Act with a threshold limit value of 350 ppm. A petition is pending (as of Oct. 1971) to have this standard listed in Table G-2 of the OSHA regulations on the basis that ANSI Z37-26-70 is a consensus standard. The values listed for 1,1,1-trichloroethane in the above Table would then apply. CHLOROTHENE is a registered trademark of The Dow Chemical Company.

TABLE 2–*Emission of solvent vapors into the work environment.*

Location of Measurement	Air Measurements of Three Hundred Industrial Vapor Degreasers[a]		
	Trichloroethylene (ppm)	1,1,1-Trichloroethane (ppm)	Perchloroethylene (ppm)
One foot above top of degreaser	150 to 215	75 to 130	180 to 310
Breathing zone of operator when lowering parts into degreaser	10 to 140	<5 to 52	30 to 215
Breathing zone of operator using spray lance	40 to 175	25 to 146	70 to 185
Breathing zone of operator raising parts to freeboard height	35 to 124	10 to 45	85 to 210
Breathing zone of operator during removal of parts from degreaser	80 to 260	25 to 110	115 to 320

[a] No ventilation vent on degreasers.

Many operational factors can contribute to excessive solvent losses from a vapor degreaser and possible violation of the OSHA regulations. Substituting 1,1,1-trichloroethane affords a wider safe operating margin and a solvent which is easier to control.

Proper adjustment of heat input and cooling capacity will minimize solvent losses. Work loads through the degreaser should not exceed machine capacity. Strong air currents across the open top degreaser will increase vapor losses. A gentle exhaust vent along the top of the degreaser may be necessary with units using trichloroethylene or perchloroethylene. While venting a degreaser can help meet OSHA standards, one must not forget possible air pollution and odor problems. Proper racking of parts in work baskets will minimize physical drag-out of solvent. Excessive water in a vapor degreaser lowers the solvent vapor density which will, in turn, greatly increase solvent losses.

The foregoing factors and others control solvent losses from a vapor degreaser. Competent advice on proper solvent usage should be available from chlorinated solvent producers. Equipment manufacturers can be consulted as to proper equipment usage. A properly run vapor degreasing operation can comply with the OSHA regulations.

Requirements of a Vapor Degreasing Solvent

The solvent of choice must have certain properties for thorough, safe, economical, and rapid metal degreasing. High solvent power, inertness to metals, and no flashpoint are important properties of the degreasing solvent. The Kauri Butanol (KB) value is one method of expressing the solvency of a solvent. Reference to Table 3 shows that the KB values for trichloroethylene and 1,1,1-trichloroethane are similar and higher than perchloroethylene. A higher KB value indicates better overall solvency.

Stresses imposed on the chlorinated solvents during vapor degreasing operations include heat, light, water, exposure to metals, metal salt catalysts, oxygen, and the miscellaneous oils and resins cleaned from the metal parts.

All three chlorinated solvents are available in specially stabilized formulations suitable for vapor degreasing. Each solvent contains an inhibitor system which distributes itself in both the vapor zone and boiling sump chamber of the degreaser, so as to provide protection against corrosion of parts being cleaned. The first stabilized grade of 1,1,1-trichloroethane for vapor degreasing was developed at Dow under the tradename CHLOROTHENE VG. The three solvents are essentially nonflammable when used with adequate ventilation. They have no fire or flash point as determined by standard laboratory methods. Under laboratory conditions, however, when the vapors are concentrated and subjected to a high energy ignition source (10 000 V), both trichloroethylene and 1,1,1-trichloroethane have ignitable limits in air. These ranges are 6.5 to 15.0 percent by volume for 1,1,1-trichloroethane and 7.3 to 41 percent by volume for trichloroethylene. When used within the recommended operating

TABLE 3–*Parameters of importance in vapor degreasing solvents.*

	1,1,1-Trichloroethane (Chlorothene VG)	Trichloroethylene	Perchloroethylene
Boiling point	165°F	189°F	250°F
Threshold limit value[a]	350 ppm	100 ppm	100 ppm
Kauri Butanol value[b]	124	129	92
Azeotrope, % H_2O	4.3%	5.4%	15.8%
Steam Pressure	1 to 6 psi	10 to 15 psi	50 psi
Condensate volume per 100 lb steel	0.98 gal	1.10 gal	1.70 gal
Heat requirements per lb steel	10.9 Btu	13.7 Btu	20.6 Btu
Consumption	1.0 (std.)	1.4	2.1

[a] Threshold Limit Value refers to a time-weighted concentration for a 7 or 8 h workday and 40-h workweek worker exposure.

[b] Kauri Butanol value (KB) is an empirical method of expressing the solvency of a solvent. Higher numbers indicate a generally higher degree of solvency.

conditions of good ventilation and away from high energy ignition sources, these solvents present no fire hazards. Perchloroethylene has no ignitable limits.

A higher solvent condensate volume per pound of metal cleaned is afforded by perchloroethylene. Cleaning of light gauge metal parts with large surface area and low mass may require the higher volume of solvent condensate afforded by perchloroethylene. Heat input required to clean a pound of steel is less with 1,1,1-trichloroethane and highest with perchloroethylene.

> The vapor pressures of typical cutting and lubricating oils, while low, are high enough to allow measurable concentrations to be present in the vapor zone above the boiling sump of a degreaser. In most vapor degreasing applications the presence of this oil can be tolerated. However, depending on the particular oil and solvent used, the concentration of the oil in this vapor zone can become high enough to require attention in critical cleaning operations. The acutal concentrations of oil vapor were 1-59 ppm (by volume) for CHLOROTHENE VG, 2-111 ppm for trichloroethylene, and 14-800 ppm for perchloroethylene, for oil concentrations of 5-30% by volume in the liquid. Three oils were evaluated; a mineral-lard oil, a sulfochlorinated-lard oil, and a sulfurized-mineral oil.[5]

Solvent consumption comparisons of the three solvents in an idling open top (24 by 58 in. opening) vapor degreaser shows that more trichloroethylene and perchloroethylene is used as compared to 1,1,1-trichloroethane. Table 4 details the daily and hourly solvent consumption rates for each solvent. The solvent losses will depend on the cross sectional area of the degreaser opening and the solvent used. The solvent losses from the stable vapor blanket in a degreaser

TABLE 4–*Solvent consumption comparison – idling vapor degreaser.*

	Consumption		
	Daily[a]	Hourly[b]	% Increase from CHLOROTHENE VG
CHLOROTHENE VG	33	0.142	...
Trichloroethylene	47	0.201	42
Perchloroethylene	68	0.293	106

[a] Daily average for 7 days (lb/day).

[b] Hourly average (lb/h/ft^2 of degreaser opening).

occurs through diffusion of solvent vapor into the overlaying air blanket. The temperature differential of this vapor-air interface determines the diffusion losses from the vapor degreaser. Thus, the losses are proportional to the boiling points of the solvent. The lower temperature of the 1,1,1-trichloroethane vapor blanket (approximately 165°F) accounts for the lower hourly consumption of 0.142 lb/h/ft^2 of degreaser opening as compared to a rate of 0.201 for trichloroethylene and 0.293 for perchloroethylene. Experience with degreasers converted from trichloroethylene or perchloroethylene to CHLOROTHENE VG support these solvent savings figures. To realize this consumption savings, one must reduce the heat input into the degreaser converted to CHLOROTHENE VG.

A vapor degreaser that is used to flash water off of metal parts should use perchloroethylene as the solvent. The higher temperature of 250°F and the 15.8 percent water azeotrope formed with perchloroethylene makes it the ideal solvent. Excessive water in a degreaser should be avoided if possible since it will cause equipment corrosion and contribute to increased solvent consumption. A properly designed and adequately sized water separator is the best method of removing intermittent water from a degreaser.

Worker Safety

While all three chlorinated solvents can produce an anesthetic effect upon inhalation, the concentrations required for this effect will vary. The threshold limit values (TLV) and ceiling limits (MAC) of the three solvents are listed in Table 5 along with the odor thresholds and typical vapor concentrations that will produce an anesthetic (light headed and dizzy) effect. Constant worker exposure that will produce this beginning anesthetic effect should not be permitted. The wider safety margin of 1,1,1-trichloroethane is easily seen in this comparison of data.

Again, we should note that vapor emissions of 1,1,1-trichloroethane are also easier to control in a vapor degreaser. What vapors that do escape into the working environment are safer in the case of 1,1,1-trichloroethane. The differences in solvent safety are reflected in the vapor emission limitations listed for each solvent in the Occupational Safety and Health Act.

TABLE 5–*Human response to chlorinated solvent vapors.*

Solvent	Odor Threshold	Anesthetic Effects (light headed, dizzy)	Limits TLV[a]	MAC[b]
Perchloroethylene	50 ppm	200 ppm, 8 h 400 ppm, 2 h 600 ppm, 10 min	100 ppm	200 ppm
Trichloroethylene	100 ppm	400 ppm, 20 min 1000 ppm, 6 min	100 ppm	200 ppm
1,1,1,-Trichloroethane	100 ppm	1000 ppm, 30 to 70 min 1500 ppm, 15 to 60 min	350 ppm	500 ppm

[a] Threshold Limit Values (TLV) from ACGIH TLV booklet, 1970.

[b] Ceiling Limits (MAC) are USASI or Dow recommended values.

Degreaser Operating Procedures

Heat input into a vapor degreaser will be determined by the amount of metal work to be cleaned, radiation losses from the degreaser, and the amount of solvent condensate produced in the degreaser. Differences in solvent boiling points will afford different "useful" amounts of heat (Btu's) for actual metal cleaning. Assume a 25 kWh (85 3000 Btu/h heat input into a 6 by 3 by 6 ft (90 ft^2 area) open top degreaser at an ambient temperature of 70°F. Radiation losses from the degreaser can be calculated from the equation:

$$\text{Btu/h heat loss} = (\text{solvent BP} - 70^\circ\text{F})\,(90\ \text{ft}^2)\,(2.33\ \text{Btu/ft}^2/^\circ\text{F/h})$$

The "useful" heat available for metal cleaning is the difference between the 85 300 Btu input and the heat loss through radiation. This "useful" heat is used to raise the temperature of the metal to the solvent vapor temperature. These values for all three solvents are listed in Table 6.

TABLE 6–*Heat balance for a 6 by 3 by 6 ft open top degreaser with a 25 kWh (85 300 Btu/h) heat input.*

Solvent	Radiation Loss, Btu's	Heat Available for work, Btu's	Pounds of Steel Cleaned
CHLOROTHENE VG	20 000	65 300	6000
Trichloroethylene	25 000	60 300	4400
Perchloroethylene	38 000	47 300	2300

To determine how much metal, for example, steel, that can be cleaned with the "useful" available heat, one uses the following equation:

$$\text{pounds of steel cleaned} = \frac{85\,300\ \text{Btu} - \text{radiation loss}}{(0.115\ \text{Btu}/^{\circ}\text{F/lb steel})\ (\text{solvent BP} - 70^{\circ}\text{F})}$$

Reference to Table 6 shows that more steel can be cleaned (36 percent more) with CHLOROTHENE VG as compared to trichloroethylene. The higher boiling point of perchloroethylene and high radiation losses from the degreaser drastically decreases the cleaning capacity of perchloroethylene per unit of heat input. It should be noted that 40 to 50 psi steam pressure is necessary to boil perchloroethylene in a vapor degreaser.

Heat input into the degreaser should be adjusted to reflect the solvent being used. Steam is the common heating source. The recommended steam pressures for the three solvents are: CHLOROTHENE VG, 1 to 6 psi; trichloroethylene, 10 to 15 psi; and perchloroethylene, 40 to 50 psi. Electrically heated or gas fired degreasers are adjusted so that excessive heat input does not occur. A solvent like CHLOROTHENE VG will continue to boil at 165°F even if excessive heat is put into the degreaser. However, excessive heat will cause turbulent boiling and will increase vapor losses from the machine.

An external still can be used to distill oil contaminated chlorinated solvents. Proper operations will ensure a good quality distilled solvent. During the distillation of 1,1,1-trichloroethane or trichloroethylene, the flow of distillate will cease when the solvent-oil mixture temperature reaches 205 to 210°F. In the case of 1,1,1-trichloroethane, the distillation is then complete. For trichloroethylene the injection of steam into the solvent-oil sludge is necessary for complete solvent recovery. The cut off temperature for perchloroethylene distillation is 265 to 270°F followed by steam injection into the still/residue.

Summary

Trichloroethylene has a long and successful history as a vapor degreasing solvent. Trichloroethylene was the only practical choice in many cases, until the recent introduction of a specially inhibited grade of 1,1,1-trichloroethane (CHLOROTHENE VG) for vapor degreasing. Recently, air pollution and worker safety regulations have now afforded an incentive to industry to find a suitable replacement for trichloroethylene. In many cases, 1,1,1-trichloroethane is the best substitute for trichloroethylene in vapor degreasing. The advantages and disadvantages of each solvent are listed here for comparison purposes.

Trichloroethylene

Advantages

1. High solvency.
2. Long history of industrial use.
3. Can be used with carbon adsorption.

Disadvantages

1. Air pollution regulations control trichloroethylene use in many areas.
2. New OSHA regulations limit vapor emissions.

3. Not recommended for cold cleaning because of low threshold limit value (TLV).
4. Will swell or dissolve some plastics.
5. Need steam injection for proper recovery in solvent still.

Perchloroethylene

Advantages

1. Recommended for wet systems.
2. Useful for high melting waxes.
3. High condensate volume useful with light gauge parts.
4. Meets all air pollution regulations.

Disadvantages

1. High heat input, for example, needs 40 to 50 psi steam.
2. Higher solvent consumption.
3. High temperature of cleaned parts.
4. Plastic components may warp or melt.

CHLOROTHENE VG (inhibited 1,1,1-trichloroethane)

Advantages

1. Wider safety margin, threshold limit value = 350 ppm.
2. Solvent versatility—use cold and hot.
3. Lower solvent consumption in vapor degreasing.
4. Reduced utilities for degreasing.
5. Greater operator comfort.
6. Optimum solvent action.
7. Meets all air pollution regulations.

Disadvantages

1. Cannot use present carbon adsorption vapor recovery systems.
2. Gross water contamination is not recommended.

References

[*1*] "Dow Chlorinated Solvents and the Clean Air Act," Form No. 100-5325-72, Dow Chemical publication, 1972, p. 1.

[*2*] *Federal Register*, Vol. 36, No. 158, 14 Aug. 1971, p. 15497.

[*3*] "Dow Chlorinated Solvents and the Clean Air Act," Form No. 100-5325-72, Dow Chemical publication, 1972, p. 3.

[*4*] "Dow Chlorinated Solvents and the Occupational Safety and Health Act," Form No. 100-5270-71, Dow Chemical publication, 1971, p. 3.

[*5*] "How to Select Your Vapor Degreasing Solvent," Form No. 100-5321-72, Dow Chemical publication, 1972, p. 5; see also, article by McIntyre, J.A. and McDonald, R.A., *Plating Journal,* June 1973, pp. 633-635.

R. A. Gorski[1]

Stability of Trichlorotrifluoroethane – Stainless Steel Systems

REFERENCE: Gorski, R. A., "Stability of Trichlorotrifluoroethane-Stainless Steel Systems," *Cleaning Stainless Steel, ASTM STP 538*, American Society for Testing and Materials, 1973, pp. 65–76.

ABSTRACT: The stabilities of trichlorotrifluoroethane metal systems are discussed under simulated solvent-cleaning conditions and under solvent-vapor entrapment conditions at temperatures up to 450°F. Comparisons are made with other systems containing water, acetone, trichlorethylene, and 1,1,1-trichloroethane. The data show (1) the systems with trichlorotrifluoroethane are chemically stable, and (2) the solvent can be used to clean austenitic stainless steels regardless of heat sensitization and degree of stress. With reasonable cleaning practices, residual solvent vapors in entrapment configurations are not expected to cause difficulties with austenitic stainless steels at elevated temperatures.

KEY WORDS: stainless steels, cleaning, solvents, surfactants, contamination

Oils, greases, and other soils may be removed from stainless steels with a variety of solvents—some of which have caused stress cracking. In some cases, the cracking has been due to inorganic-chloride ion impurities in surfactants. In other cases, it has been due to the generation of inorganic-chloride ions because of the decomposition of chlorinated solvents. Because of this situation, some solvent users have tended to choose flammable hydrocarbon solvents to clean austenitic stainless steels and to exclude all halogen-containing solvents.

Objective

It is the objective of this paper to present experimental data which demonstrates that fluorocarbon-113 (FC-113, trichlorotrifluoroethane[2]) does not harm heat sensitized and highly stressed austenitic stainless steels under simulated vapor-degreasing conditions and solvent-vapor entrapment conditions up to 450°F.

The data presented here represent only a small part of the experience available regarding the compatibility of FC-113 with stainless steels that has resulted in the broad use of stainless steel in contact with FC-113. Examples are:

---

[1] Senior research chemist, Organic Chemicals Dept., Freon Products Laboratory, E. I. du Pont de Nemours & Company, Inc., Wilmington, Del. 19898.

[2] Known as Freon® TF solvent or Freon® PCA, the white-room grade of Freon® TF solvent. This chemical is sold also as "Genesolv" D, "Ucon" 113, and "Isotron" 113. The typical analyses shown in Table 1 were made with Freon® PCA solvent. Freon® TF solvent was used in the solvent-grade FC-113 tests with metals.

1. FC-113 is manufactured and transported in stainless steel equipment.
2. FC-113 is used in stainless steel vapor degreasers, ultrasonic units, cold-dip tanks, and water displacement units.
3. FC-113 is used, with other chlorofluorocarbons, in stainless steel laboratory pressure vessels over a broad temperature range of -320 to +200°F.
4. FC-113 is used to clean austenitic stainless steels in the NASA program and in the grade-A cleaning of primary cooling piping and components of nuclear-power plants [*1, 2*].[3]

Typical analysis of white-room grade FC-113 is shown in Table 1 [*3*]. This grade is used for flushing inaccessible areas containing critical surfaces and crevices since its particulate-matter content is controlled. For other cleaning applications, solvent-grade FC-113 is used. Its quality is essentially identical to the white-room grade, except that its particulate-matter content is not controlled. Some properties of FC-113 are compared to those of other solvents in Table 2 [*4-12*]. Table 3 summarizes the metals compatible with FC-113 under cleaning conditions. These data are based on experimental data [*13*] as well as practical experience.

TABLE 1—*Typical analyses of white-room grade FC-113.*

Appearance	Clear, Water-White
B.P. (°F)	117.6
Purity (min, weight percent)	99.99
Water (max, weight ppm)	10
Organic-inorganic residue (max/ave, weight ppm)	0.5/0.3
Metals (weight ppm)[a]	0.003
Estimated max[b]	
Cl^- (weight ppm)	0.007
F^- (weight ppm)	0.004
Chloride ion (max/ave, weight ppm)[c]	0.05/0.02
Inhibitors	None
Particulate matter (max number of particles/100 ml)[d]	
25 to 100 microns range	100
larger than 100 microns	10

[a] Single determination.
[b] Based on metals analysis.
[c] Calculated as chloride ion by aqueous conductance.
[d] Product specification.

---

[3] The italic numbers in brackets refer to the list of references appended to this paper.

TABLE 2–*Properties of solvents.*

	FC-113	Trichloro-ethylene	1,1,1-Trichloro-ethane	Acetone	Water
Formula	$CF_2ClCFCl_2$	$CHCl{=}CCl_2$	CCl_3CH_3	$(CH_3)_2CO$	H_2O
Boiling point, °F	118	190	180	133	212
Relative evaporation rate	49	13	16	25	1
Surface tension (dynes/cm)	18	29	26	24	72
Flash point, °F tag closed cup	None	None	None	0	None
Flammable vapor concentrations in air, volume %	None	11 to 90	10 to 16	3 to 13	None
Vapor toxicity–TLV, ppm by volume in air	1000	100	350	1000	. . .

TABLE 3–*Metals compatible with FC-113 under cleaning conditions.*

Magnesium alloys	Mg/Al/Zn - 96/3/1, Mg/Li/Al/Zn - 70/13/2/15
Beryllium	pure metal
Aluminum and its alloys	1100, 6061, 7075, 2219[a]
Titanium alloys	6 Al-4V, 5Al-2.5 Sn, 8Al-1 Mo-1V, 13V-11Cr-3Al
Zirconium alloy	Zr/Sn - 98.5/1.5
Zinc	pure metal
Steel	1010, 1020 cold-rolled
Nickel	pure metal
Stainless steel alloys	304, 316, 321, 347
High-Nickel content alloys	Ni/Cu/Fe - 66/1.4/31.5, Ni/Cr/Fe - 76/15.8/7.2
Tin	pure metal
Tin/Lead solders	63/37, 5/95
Copper	pure metal
Silver	pure metal
Silver solder (1602)	composition unknown

[a] Bare, alodine-coated, and anodized.

Test and Evaluation Methods

Two types of test specimens were used to determine the stability of solvent-metal combinations: (*a*) Unstressed metals in sealed Pyrex tubes. The test method has been described previously [*14*]. (*b*) U-bends under 100 percent of the 75°F yield stress. Stability was determined by the following means:

1. Measurement of inorganic chlorides generated due to the decomposition of the halogenated solvents. Three weight percent sulfuric acid was used to scavenge the chloride ions generated in both types of tests. The amount of chlorides was determined potentiometrically by titration with silver nitrate. An improved method for chloride-ion determination in sealed tube tests is referenced here [*15*]. The method utilizes 3 weight percent nitric acid to scavenge the chloride ions from the test system and avoids the insolubility problems associated with silver sulfate. The chlorides are determined colorimetrically by titrating with mercuric acetate using s-diphenylcarbazone as a colorimetric end-point indicator. Further details will follow later.

2. Determination of the metal corrosion rate based on weight changes. Before the metal strips were weighed at the start and finish of each sealed-tube test, their surfaces were: (*a*) cleaned with a neoprene stopper wet with distilled water and then with CP-grade acetone, (*b*) rinsed well with both solvents in the same order, and (*c*) desiccated over anhydrous calcium sulfate at 75°F for 24 h.

Prior to the U-bend tests, the metal surfaces were: (*a*) scrubbed with a nylon bristle brush in 2 weight percent "Tide" (a mixture of sodium lauryl sulfate and alkyl benzyl sulfonates) in 130°F tap water, (*b*) rinsed in 130°F tap water and 75°F distilled water, (*c*) dried with a lint-free cotton towel, and (*d*) desiccated over anhydrous calcium sulfate at 75°F for 24 h. At the end of the U-bend tests, the surface was rinsed with reagent-grade methanol and desiccated for corrosion rate determination. The corrosion products were left on the metal surface in these tests.

3. Visual appearance of solvent and metal. These test components were examined by the naked eye before and after the test to serve as a supplementary semiquantitative evaluation of test system stability.

4. Microscopic examination (x10) of stressed areas on U-bends. The surfaces were examined along the edges and on the outer curved surfaces with a stereomicroscope to supplement Item 3.

Experimental Procedure and Results of Sealed-Tube Tests

The components of the tests are shown in Table 4. Briefly, the tube loading method is as follows. The metal is first placed in a tube. The tube is necked down to a capillary to facilitate later sealing. Next, 2 ml of solvent is placed in the tube and the tube is sealed from the atmosphere with a temporary seal. The tube contents are then frozen with liquid nitrogen. The tube is then sealed in the necked down area.

At the end of the test, the tube contents are processed for inorganic chlorides by freezing the tube contents with liquid nitrogen, breaking the tube open at the sealed tip, and transfering the liquid contents to an alcohol/distilled water (50/50 volume ratio (v/v)) solution. The tube interior and metal surfaces are then scrubbed with 3 weight percent acid in distilled water. This acid is then combined with the alcohol-water solution and thoroughly agitated. The resultant

TABLE 4–*Components in sealed Pyrex tubes.*

1.	Sealed Pyrex tube	
	Inside diameter	7/16 in.
	Length	5-1/2 in.
	Volume	12 ml
2.	Volume of test liquid	2 ml
3.	Metal specimen	
	Dimensions	2-3/8 by 1/4 by 1/16 in.
	Surface finish	120 grit
4.	Air pressure in vapor space	About 1 atm at 75°F

aqueous phase is separated from the halogenated solvent and analyzed for inorganic chlorides.

Results of the tests are summarized in the Tables 5, 6, and 7. In these tests, the following solvents were used: solvent-grade FC-113, inhibited 1,1,1-trichloroethane, and distilled water (<0.1 ppm chloride ion). Metals other than stainless steels have been included to broaden the perspective. The results in Table 5 are given in terms of stability ratings, as described in the footnotes.

Table 5 shows that after 100 days at 130°F [*13*]: Systems with FC-113 were more stable than those with water. FC-113 systems with insoluble water gave stabilities comparable to water alone. FC-113 remained clean, water-white with no corrosion-product precipitates in all tests. Zinc and steel discolored slightly with FC-113. The latter was probably caused by tramp moisture. In the water tests, the water changed color (a brown) only in the test with steel. Water caused moderate-to-severe quantities of corrosion-product precipitates with steel, magnesium, and zinc.

Table 6 shows that under hydrolytic conditions at 250°F for 11 days [*13*], FC-113 was significantly more stable than inhibited 1,1,1-trichloroethane in terms of solvent decomposition and metal corrosion rates. The FC-113 with stainless steel-304 gave results which were significantly better than with mild steel. The corrosion rates of the stainless steel and steel with FC-113 were low and comparable to those obtained with water.

Table 7 shows, in two-year tests, that [*13*]: FC-113 decomposed slightly with stainless steel, mild steel, and aluminum at 300°F; and FC-113 decomposed significantly with copper at 300°F.

Experimental Procedure and Results of U-Bend Tests

The test components are illustrated in Fig. 1. The container on the left is a Pyrex flask equipped with a glass flange sealed with a polytetrafluoroethylene (PTFE) gasket, a water-cooled condenser, and a heating mantle. It contained a boiling solvent and six different metals as U-bends. One of each was present in the liquid and vapor phases. These U-bends were independently suspended in the flask by means of a PTFE support structure and tape. The container on the right is a high-pressure flanged Pyrex tube. It was sealed with a PTFE gasket and a stainless steel cap and valve. In this case, one each of the six metals as U-bends were supported one above the other with a PTFE rod and tape. These tests were run with the solvents in the gaseous state only.

In the original study, the objective of the analyses for inorganic chlorides was to determine the total chlorides generated, and not to determine specifically the concentration of the chlorides in the solvent and on the metal surfaces. To better appreciate the location of the chlorides in the test system, the chlorides have been assigned to these two locations. This has been done as follows. The total chlorides is known and the chlorides in the solvent has been determined directly [*15*], thus, the difference in chlorides may be assigned to the metal surface. This assignment, however, may be on the high side, since these chlorides

TABLE 5–*The stability of systems containing FC-113 or distilled water or both.*

	100 Days/130°F With Air		
	Stability Rating[a]		
	FC-113	FC-113/Water (99/1 v/v or 99.36/0.64 w/w)[e]	Water
SS-304	0	0	1
Ni	0	1	0
Monel 400	0	1	0
Cu	0	1	2
Al-1100	0	2	2
Zn	1	2	4
Mg AZ31B	0	3	3
Steel-1020 cold rolled	1	3	3

[a] Key to ratings–

Rating	% FC-113[b] Decomposed	Corrosion Rate, mils/year	Appearance Changes of Solvent and Metal
0	<0.002	<0.1	none
1	0.002-0.01	0.1-0.5	very, very slight (insignificant)
2[c]	0.01 -0.1	0.5-1.0	very slight (borderline)
3[d]	0.1 -0.5	1-5	slight (significant)
4[d]	0.5 -1.0	5-30	moderate
5[d]	>1	>30	severe

[b] As determined by inorganic chlorides analysis.

[c] The rating includes test system stabilities in the range of probably acceptable to probably unacceptable.

[d] These ratings indicate unstable systems.

[e] Water solubility in FC-113 at 130°F is 0.026 weight percent.

TABLE 6–*Hydrolytic stability of FC-113 and 1,1,1,-trichloroethane.*

11 Days at 250°F with Air
Solvent/Water Ratio = 99/1 v/v [a,b]

	Metal		
	SS-304	Steel 1020CR	None
Solvent Decomposed, %			
FC-113	0.04	0.22	<0.002
1,1,1-Trichloroethane	22	28	0.006
Metal Corrosion Rate, mils/Year			
FC-113	0.2	1.3	. . .
1,1,1-Trichloroethane	10	11	. . .
Distilled Water[c]	0.1	0.9	. . .

[a] The equivalent on a weight ratio basis is:

FC-113/Water	99.36/0.64
1,1,1-trichloroethane/water	99.28/0.72

[b] Approximate solubility of water in solvents at 250°F is:

FC-113	0.11 weight percent
1,1,1-trichloroethane	0.36 weight percent

[c] Less than 0.1 ppm by weight of chloride ion.

TABLE 7–*Stability of FC-113 at elevated temperatures.*

2-Year Test with No Air[a]

	% FC-113 Decomposed	
	At 250°F	At 300°F
SS-316	<0.002	0.03
Steel 1020CR	0.005	0.04
Al-1100	<0.002	0.008
Cu	. . .	0.13

[a] Long-term data in the presence of air are not available. At this time, no significance should be attached to the lack of air in these tests.

include the chlorides (1) from the surface of the test vessel, (2) dissolved in the insoluble water phase (if present), and (3) on the metal surfaces. Since the six test metals in each test were scrubbed in a single acid solution, the inorganic chlorides on the metals are reported as averages.

The volumes of the reagent chemicals used to scavenge the inorganic chlorides from the test system were as follows:

Test	Methanol or Methanol/Distilled Water (50/50 v/v)	3% Acid Solution
Reflux test	400 ml	450 ml
450°F test	250 ml	250 ml

The solvents tested were solvent-grade FC-113; CP-grade acetone and inhibited trichloroethylene. In these particular tests, the acetone and trichloroethylene were selected as controls for the following reasons. Acetone is specified for critical cleaning of inaccessible areas of nuclear components made of austenitic stainless steels. Trichloroethylene is not allowed for this application.

Details for the two test conditions are summarized in Table 8. Under the reflux conditions, two water levels were tested. In the 450°F test, note that 0.0263 moles of solvent vapors were tested in a volume of 550 ml. This amount of FC-113 solvent-vapor is about 10 000 times higher than normally expected in entrapment configurations. When reasonable care is exercised to remove residual liquid and vapor from entrapment configurations, vapor concentrations of less than 100 ppm by volume are easily attained.

The primary details for the U-bends are in Table 9. Supplementary details are: the Inconel and steel were Heli-arc welded with Inconel and low carbon

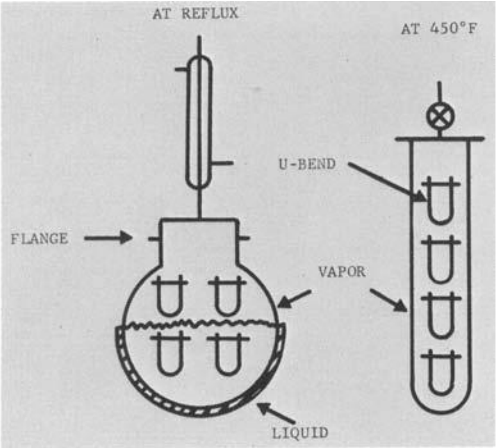


FIG. 1–*Illustration of Pyrex equipment used in U-bend tests.*

TABLE 8–*Test conditions.*

	Reflux Test	450°F Test
System volume, ML	2500	550
Solvent		
ml	1000	. . .
mol fraction	. . .	0.35 (0.0263 moles)
Water		
ml	0 and 30[a]	. . .
mol fraction	. . .	0.35
Air		
mol fraction	. . .	0.30
System pressure, psia	14.7	84
Number of U-bends		
vapor phase	6	6
liquid phase	6	. . .
Metal types	6	6

[a] This is equivalent to 3 volume percent water. On a weight basis, this is equal to the following in these halogenated solvents.

FC-113	1.9 percent
Trichloroethylene	2.1 percent

The solubilities of water in these solvents at reflux temperature are:

FC-113	0.02 weight percent
Trichloroethylene	0.14 weight percent

TABLE 9–*U-bend details.*

Original Metal Details
1. Flat specimen dimensions, 4 by 3/4 by 1/8 in.
2. Stainless steels and Inconel 600, solution annealed
3. Surface finish, 120 grit

Additional Treatment of Metals in Sheet Form

1. Stainless steels 304 and 316	Heat sensitized at 1250°F for 1/2 h, no welds
2. Stainless steels 321 and 347	Heat treated as above, no welds
3. Inconel 600 and Steel 1020CR	Welds in maximum stress area

U-Bend Details
1. Bend radius, 7/16 in.
2. U-Bend stress, 100% of yield stress at 75°F

steel-1010 welding rods, respectively. The welds were smoothed prior to surface-finishing, cleaning, and bending. The nuts and bolts used with the indicated U-bends specimens were made of low carbon steel for steel-1020CR, stainless steel 316 for the same alloy, and stainless steel-304 for the other metals.

Table 10 shows that after eleven days of solvent refluxing [*13*] : (*a*) With no insoluble water lying on top of FC-113 (the normal situation), no inorganic chlorides were generated and the metal corrosion rates were negligible. (The minimum detectable corrosion rate is equivalent to ±0.01 mils/year.) (*b*) Both dry and wet FC-113 and dry trichloroethylene gave results equivalent to the control (acetone) in both chlorides and corrosion rates. The very small increase in chloride-ion content of the final acetone may have been due to trace quantities of inorganic chlorides on the surfaces of the test vessel prior to initiation of the tests or to the decomposition of chlorine-containing organic impurities in the acetone. (*c*) Wet trichloroethylene developed a comparatively high inorganic chloride-ion content on the metals. The steel was the prime attack surface, as reflected by its slight negative corrosion rate (rust). This was the only test in which surface corrosion was evident. The corrosion occurred on the curved surfaces of the U-bends near the welds in both the liquid and vapor phases. (*d*) None of the solvents caused stress-cracking.

As a supplement to the previous points, the liquids in the FC-113 and acetone tests remained clear and water-white. In the tests with trichloroethylene, the color changes from the initial clear and water-white were (*a*) dry tests—clear, light brownish-yellow, and (*b*) wet tests—cloudy, light yellow.

Table 11 shows results after eleven days at 450°F [*13*]. (*a*) FC-113 and acetone vapors gave comparable and acceptable results in terms of chloride-ion

TABLE 10—*Eleven-day reflux tests—inorganic chlorides before and after test.*

	FC-113		Trichloroethylene		CP-Grade Acetone	
	Dry	Wet	Dry	Wet	Dry	Wet
Inorganic Chlorides						
1. in solvent (weight ppm)						
original	<0.2	...	1.3	...	0.3	...
final	<0.2	<0.2	1.1	<0.2	1.1	0.9
2. average on metal, μg/in^2						
final	<4	13^a	8	640^a	7	9
Metal Corrosion Rate, mils/year						
Avg for stainless steels and Inconel-600^b	0.06	0.12	0.04	0.06	0.06	0.12
Steel-1020CR	0.07	-0.18	0.03	-4.4	0.05	0.16
Stress-cracking	none at X10 magnification					

[a] Total on metal and in insoluble water.
[b] Average of metals in liquid and vapor phase.

TABLE 11–*Eleven-day tests at 450°F with solvent and water vapors plus air.*

	FC-113	Trichloroethylene	Acetone
1. Total solvent decomposition, %	0.03	1.5	. . .
2. Chlorides on metals, (μg/in.^{2})	22[a]	960[a]	23
3. Corrosion rates, mils/year			
Stainless Steel 304	0.01	-0.79	0.04
Stainless Steel 316	0.04	-0.28	<0.01
Stainless Steel 321	0.02	-0.55	0.02
Stainless Steel 347	-0.02	-0.28	<0.01
Inconel 600	0.02	0.05	0.01
Steel 1020CR	0.31	-1.0	-0.19
4. Stress cracking (x10)		none	

[a] Based on the above chloride-ion analysis.

content and metal-corrosion rate. Steel 1020CR gave the highest corrosion rate in both cases. (*b*) Trichloroethylene decomposed significantly more than FC-113. This, as a consequence, has caused negative corrosion rates (corrosion-product deposition) with all metals except Inconel. Despite these corrosion rates, no surface corrosion was evident. (*c*) None of the solvents cause stress-cracking.

Summary

These experimental data show that FC-113 (1) is compatible with austenitic stainless steels even when these alloys are highly stressed and heat-sensitized under simulated (*a*) cleaning conditions, and (*b*) vapor-entrapment conditions up to 450°F, (2) is as stable as acetone, and (3) is significantly more stable than the two tested chlorosolvents and distilled water.

Conclusion

FC-113 (trichlorotrifluoroethane) can be used to clean austenitic stainless steels regardless of heat sensitization and degree of stress. With reasonable cleaning practices, residual solvent vapors in entrapment configurations are not expected to cause difficultues with austenitic stainless steels at elevated temperatures.

References

[*1*] Cleaning Requirements for Special Purpose Equipment, including Piping Systems (FOR OFFICIAL USE ONLY), MIL-STD-767A (SHIPS), Nov. 1964.

[*2*] Cleaning and Cleanliness Requirements for Nuclear Components, AEC-RTD-F5-1T, Feb. 1972.

[*3*] "Freon® Precision Cleaning Agent," Freon® Technical Bulletin FSP-1, E. I. du Pont de Nemours & Co., Inc., June 1963.

[*4*] "Solvent Properties Comparison Chart," Freon® Technical Bulletin FS-6, E. I. du Pont de Nemours & Co., Inc., March 1970.

[5] "Freon® TF Solvent," Freon® Technical Bulletin FST-1, E. I. du Pont de Nemours & Co., Inc., Oct. 1972.

[*6*] Scott, G. S., et al, "Review of Fire and Explosion Hazards of Flight Vehicle Combustibles," Technical Document ASD-TR-61-278, Supplement 1, Bureau of Mines for Wright-Patterson Air Force Base, Oct. 1962.

[7] "Review of Fire and Explosion Hazards of Flight Vehicle Combustibles," Quarterly Progress Report No. 3, Bureau of Mines, 1 July to 30 Sept. 1964.

[*8*] Scott, G. S., "Flammability of Trichloroethylene," Bureau of Mines Report RI-6190, Bureau of Mines, 1963.

[*9*] Torkelson, T. R., et al, *Industrial Hygiene Association Journal*, Oct. 1958, pp. 353-362.

[*10*] Threshold limit values adopted by American Conference of Governmental Industrial Hygienists for 1970.

[*11*] Ramsey, R. B., "Vapor Degreasing with Trichlorotrifluoroethane," ASTM paper 139, presented at the 4th Pacific Area National Meeting of the American Society for Testing and Materials, Los Angeles, Calif., 1-5 Oct. 1962.

[*12*] ASTM Test for Relative Evaporation Time of Halogenated Hydrocarbon Solvents and Their Admixtures (D 1901-67). Note–The method was modified for water so that the total evaporation surface was wet. The distilled water was poured onto the evaporation surface, while held in the horizontal position, before it was put into the standard inclined position for the evaporation test.)

[*13*] Thirteen Freon® Products Technical Reports.

[*14*] Kvalnes, D. E., "The Sealed Tube Test for Refrigeration Oils," American Society of Heating, Refrigerating and Air-Conditioning Engineers, Semiannual Meeting, Chicago, 25-28 Jan. 1965.

[*15*] Armstrong, T. D., "Chloride Analysis as a Measure for the Evaluation of Sealed Tube Tests," American Society of Heating, Refrigerating and Air-Conditioning Engineers, Semiannual Meeting, Chicago, 25-28 Jan. 1965.

W. J. Roberts[1]

Acid Cleaning of Stainless Steel

REFERENCE: Roberts, W. J., "Acid Cleaning of Stainless Steel," *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 77–89.

ABSTRACT: This paper discusses the basic chemistry of acid cleaning, with specific ideas on 300 series stainless steel. Examples of acid cleaner ingredients, why they are employed, and how they can be applied to remove specific soils are given.

KEY WORDS: stainless steels, cleaning, acid treatment, electroplating, metal finishing, heat treatment

Cleaning is regarded as the removal of all contaminants from the base metal surface. This includes oils, fats, foreign metals, radioactive soils, bacteria, thin film oxides, weld scale, etc. Cleaning is usually accomplished with no removal of the base metal, but in special cases a minimum of metal is removed to produce a clean surface.

The methods used to clean stainless steels cover a wide variety of chemical and mechanical techniques. Mechanical cleaning such as buffing, wire brushing, grinding, sand blasting, grit blasting, etc. will not be covered in this paper. Typical chemical cleaning procedures are outlined in Table 1.

This paper will expand upon the acid cleaners used to remove contaminants from the surface of AISI 300 series stainless steels.

What Is Acid Cleaning?

Acid cleaning by strict definition is removing contaminants from stainless steel surfaces with cleaners having a pH less than 7.0. In practical terms it is also cleaning procedures used to remove both organic (for example, lubricating oils) and inorganic (oxides, free iron) soils in the same operation. Furthermore, this same cleaning step is usually designed to enhance the clean base metal surface in terms of corrosion resistance, brightness, etc. [*1*].[2]

Why Acid Clean Stainless Steel?

A wide variety of stainless steels are cleaned with acid products to remove acid-soluble contaminants, both hydrophilic (a substance attracted to water) and hydrophobic (a substance repelled by water), because this simply represents the

---

[1] Manager, Metal Industries Dept., Chemical-ways Corporation, Lake Buff, Ill. 60044.

[2] The italic numbers in brackets refer to the list of references appended to this paper.

TABLE 1—*Chemical cleaning procedures for stainless steels.*

Type	Time	Temperature, °F	Conc.	Pressure	Polarity	Current Density	Voltage	Foam	Frequency	Part Agitation
Acid soak	4-5 min	110-140	10-20% volume	N/C[a]	N/C	N/C	N/C	high	N/C	yes
Acid, spray	30-60 s	120-160	2-3 oz/gal	30-60 psi	N/C	N/C	N/C	low	N/C	no
Acid, electrolytic	30-120 s	65-75	20-30%	. . .	cathodic	20-60 asf	6 V	medium	N/C	no
Acid, manual wipe	60-120 s	60-75	20-50% volume	N/C	N/C	N/C	N/C	high	N/C	yes
Alkaline, soak	3-5 min	140-180	6-8 oz/gal	N/C	N/C	N/C	N/C	high	N/C	yes
Alkaline, spray	60-90 s	130-160	3-4 oz/gal	30-80 psi	N/C	N/C	N/C	low	N/C	no
Alkaline, electroclean	30-60 s	140-160	6-8 oz/gal	N/C	anodic	50-100 asf	6 V	low	N/C	no
Alkaline, ultrasonic	1-2 min	120-140	2-3 oz/gal.	N/C	N/C	N/C	N/C	low	25-50 Ke	no
Diphase, soak	3-5 min	140-180	6-8 oz/gal	N/C	N/C	N/C	N/C	medium	N/C	yes
Emulsion, soak	5-10 min	70-130	5-10% volume	N/C	N/C	N/C	N/C	medium	N/C	yes
Molten salt	5-10 min	700-800	100% salt	N/C	N/C	N/C	N/C	medium	N/C	yes
Solvent manual wipe	3-5 min	65-75	100% solvent	N/C	N/C	N/C	N/C	low	N/C	no
Vapor Degreaser	2-4 min	180-220	100% solvent	N/C	N/C	N/C	N/C	low	N/C	yes

[a] N/C = Not applicable.

most efficient, economical, and practical approach. In general, alkaline cleaners are not suitable for removing oxides and other similar inorganic soils. Vapor degreasing, solvent-wipe, and emulsion cleaners are also limited in this respect.

The molten salt bath, and similar high temperature (300 to 700°F) baths are excellent for removing heavy oxides (heat treat scale). However, organic marking inks, baked-on lube oils, etc., tend to be only partially removed. Quite often the hydrophilic soils are rendered more difficult to remove. Consequently, parts should be first cleaned to remove organic soils (oils, etc.) before treatment in a molten salt bath to receive best results. The removal of both inorganic (silicates, solder-flux) and organic type soils requires an acid cleaner as well as an alkaline cleaner and a cold water rinse (70 to 75°F).

General Chemistry of Acid Cleaning

Acid cleaning of stainless steel follows four basic steps to producing a clean water-break-free surface.

As the soiled metal surface is contacted with the cleaning solution, the surface is wetted by intimate contact between acid cleaner ingredients and the part to be cleaned. This is accomplished by lowering the surface tension of the cleaning solution below that of the soiled metal surface. The greater the difference between the free energy of the cleaning solution and the soiled stainless steel surface, the greater the wetting effect and ultimate cleaning.

Once the surface is wetted, the cleaner, with the aid of a part agitation and elevated solution temperature (120 to 160°F), begins to penetrate the (hydrophobic) soil layer. As the penetration of the soil layer to the base metal continues, the fatty type soil begins to form small globules on the surface. This "balling-up" effect is produced by the wetting phenomena. Briefly, the tendency for fat to form small globules on the metal surface is to present the minimum exposed surface area to the cleaning solution. This minimum surface area strives for a minimum surface energy. All parts try to lower their total free surface energy within a given system. That is why a metal surface with high free surface energy rapidly allows a cleaning solution of low free surface energy to "wet" (or contact) the surface. The overall marriage produces a total system having much lower free surface energy. All cleaning systems will tend to obtain the lowest free surface energy. This, in turn produces the overall cleaning results. The driving force in most cleaning mechanisms is to produce the lowest possible free surface energy for the entire metal surface/cleaning solution system [*2-4*].

As the hydrophobic soil is being penetrated and balled-up, a third step in the cleaning mechanism, displacement, takes place. The cleaner chemical will replace the fat globules on the stainless steel surface, allowing these spheres to "float" in solution. This "exchange" between cleaning ingredients (surface active agents) and hydrophobic soils exposes inorganic soils normally inhibited (or protected) by hydrophobic soils from the acid cleaner. By using the correct acid cleaner, the foreign metal oxides, finger prints, marking inks, and other acid soluble soils are also wetted, penetrated, and displaced into solution, in the same manner. This double cleaning effect produces a stainless steel surface essentially free of both hydrophilic and hydrophobic soils.

In special cleaning applications, a minimum amount of attack on the stainless surface is desirable to produce a smooth level surface. This cleaning operation usually involves more than one step and will remove both organic and inorganic soils. The big advantage to a minimum amount of surface attack is to expose a new or "virgin" base metal and to microfinish the surface with a more theoretical surface area. This small amount of attack also produces some surface gassing that will tend to mechanically scrub the surface. A small amount of surface attack, to produce a brighter smoother surface, is very desirable in stainless steel cleaning with acid cleaning processes [*5,6*].

The displaced soils are suspended in the cleaning solution by dispersing the solid particulate matter and emulsifying the oils and similar hydrophobic soils. Suspending the displaced soils prevents their redeposition back onto the clean stainless steel surface. A disadvantage of acid cleaners is they will not "hold" or suspend the same quantity of soils as the standard high pH alkaline soak cleaner. When the solution end-point is reached, the soils tend to come out of solution to form an oil layer on the solution surface. This oil layer can be skimmed or the entire cleaning solution replaced, depending on the economics or the overall cleaning requirements [7].

Acid Cleaners

These acid cleaner additives are detailed in Table 2. The variety of acid cleaners is almost limitless, depending on: (1) soils to be removed, (2) stainless steel to be cleaned, (3) required inhibiting effects, (4) desired final surface properties, (5) waste disposal requirements, and (6) overall economic considerations. A standard acid cleaner will include one or more of the chemical ingredients listed in Table 3 based on the considerations just mentioned.

Most acid cleaners are based on phosphoric acid, as testified by its many references in the literature. This is due to relative low cost, good compatability with other cleaner ingredients, and its ability to exert a very strong synergistic cleaning affect. The trend toward phosphate-free cleaners will eventually produce an equally popular phosphate-free alternate.

Other acids can be used to obtain special cleaning affects on stainless steels. Just a few are listed here:

1. Phosphoric acid
2. Nitric acid
3. Acetic acid
4. Boric acid
5. Sodium acid phosphate
6. Citric acid
7. Oxalic acid
8. Sulfuric acid
9. Hydrofluoric acid
10. Hydrochloric acid
11. Alkyl ARYL sulfonic acid
12. Formic acid
13. Sulfonic acid
14. Hydroxyacetic acid
15. Sodium bisulfate
16. Gluconic acid

In most cases these acids are used in combination rather than alone, and are incorporated into a special cleaner system. Much has been accomplished with the

TABLE 2–*Acid cleaner characteristics [1-3, 5, 13].*

Chemical Ingredient	Function of Chemical
Mineral acid	Attack metal oxides also base metal in special cases
Organic acid	Solubilize organic contaminants
Wetting agents	Lower solution surface tension, promote soil penetration
Solvents	Aid in removal of hydrophobic soils
Inhibitors	Control surface attack of base metal
Defoamers	Prevent foam or foam build up on solution surface
Water	Key cleaner ingredient
Thickner (acid stable)	Allow cleaner to adhere (cling) to vertical surface
Fume suppressant	Prevent toxic fumes from leaving solution or solution surface
Sequestrant	Promote good draining and eliminate hard water spotting
Passivator	Protect surface against environmental attack
Biocides	Controls odor problems, kills harmful bacteria
Buffer, (pH control)	Helps maintain the correct pH at varying product concentrations

versatility of acid cleaners that could not have been handled economically by other means [*8*].

Applied Acid Cleaning

Following are examples of practical applications of acid cleaners for pretreating and post-treating stainless steels. They are based on actual field usage and should be used as a guide toward better cleaning of stainless steel products.

Acid Cleaning Pre-Treatments (Before)

Adhesive Bonding

The "art" of adhesive bonding can be significantly reduced by always bonding the adhesive (epoxy) to a clean activated (slightly acidic) surface. Stainless steel represents a class of materials that are less difficult to bond and will provide excellent results under adverse environmental conditions when properly cleaned and activated. One process that has been used to satisfactorily process stainless steels for adhesive bonding is shown in the following [*9*].

1. Acid clean in phosphoric acid/detergent system at 20 to 25 percent by volume at 140 to 150°F for 3 to 5 min.
2. Cold water rinse at 60 to 70°F for 1 to 2 min. If water breaks are observed, repeat Step No. 1.

TABLE 3–*Soil removal from stainless steel [5,6,11,13,14].*

Contaminants	Recommended Type Cleaner
Grease (hydrocarbon)	Liquid alkaline solvent
Oils (animal/vegetable)	Sodium acid phosphate, detergent
Fingerprints	Phosphoric acid/detergent
Free iron	Oxalic acid/detergent
Rust (oxide)	Sulfonic acid/detergent
Iron oxide scale	Hydrochloric acid/inhibitor
Grease pencil	Liquid silicate/detergent
Food protein	Diversol plus acid rinse[a]
Marking inks	Acetic/phosphoric/solvent
Weld splatter	Sodium acid sulfate/abrasive
Burned-on detergents	Alkyl sulfonic acid/solvent
Oxidized paint	Methylene chloride/formic acid
Smut (carbon)	Nitric/hydrochloric acid
Hard water scale	Citric/phosphoric acid/detergent
Soldering flux	Boric acid/detergent
Copper disposition	Nitric/phosphoric/inhibitor
Burnt-on carbon	Nitric/hydrofluoric acid
Dried-on silicates	Hydrochloric/phosphoric acid detergent
Drawing oils (hydro)	Emulsion cleaner plus phosphoric acid rinse
Food processing (residuals)	Diversol plus phosphoric rinse acid[a]
Shop dirt (dust)	
Zyglo	Phosphoric/detergent/solvent
Chromium oxides	Sulfuric/hydrochloric/detergent
Titanium splattering	Hydrochloric/inhibitor
Buffing compounds	Phosphoric/gluconic/detergent
Casting scale	Nitric/hydrofluoric or DS9-314

[a] Alkaline chlorinated cleaner.

3. Acid deoxidize and activate in sulfuric-hydrofluoric-nitric acid/detergent system, 70-90°F for 3 to 5 min.
4. Cold water rinse. Check for smut with tissue wipe. Surface should be desmutted before next step.
5. Distilled water rinse and oven dry at 120 to 130°F.
6. Adhesive bond.

Chemical Polishing

Chemical polishing produces a bright smooth surface, without the use of electric current, conforming electrodes, etc. It is a simple immersion process operated at 170 to 180°F, contact time 5 to 10 min with slow part agitation.

The process will economically handle a wide variety of shapes and sizes to produce satisfactory polishing if properly pretreated. A typical pretreatment is shown in the following.

1. Alkaline clean with silicated cleaner at 6 to 8 oz/gal, 160 to 170°F for 5 to 7 min.
2. Cold water rinse.
3. Scale condition with caustic permanganate inhibitor blend at 14 to 16 oz/gal, 190 to 200°F for 10 to 15 min.
4. Cold water running rinse.
5. Acid clean (deoxidize) in 25 to 30 percent by volume solution of inhibited hydrochloric acid at 70 to 80°F for 3 to 5 min.
6. Cold water rinse.
7. Chemical polish in DS-9-314 (propietary blend of inorganic acids and organic brighteners) or a similar product at 170 to 180°F for 5 to 7 min. Slow part agitation is highly desirable.

Electroplating

Stainless steels are usually passive and must be properly cleaned and activated to obtain satisfactory electroplating. This requires a water-break-free surface, completely deoxidized followed by electrocleaning and acid activation in diluted hydrochloric acid. A typical process for preparing stainless steel for electroplating is detailed in the following.

1. Acid clean with phosphoric acid/detergent product at 10 to 15 percent by volume at 140 to 170°F for 5 to 10 min.
2. Cold water rinse.
3. Alkaline soak clean with high caustic nonsilicated product at 6 to 8 oz/gal, 160 to 170°F for 5 to 10 min.
4. Cold water rinse.
5. Electroclean using a high caustic cleaner at 4 to 6 oz/gal making the part anodic for 30 to 60 s.
6. Cold water running rinse.
7. Acid activate with hydrochloric acid at 3 to 5 percent by volume, 70 to 80°F for 1 to 3 min.
8. Cold water rinse.
9. Electroplate immediately.

Electropolishing

The standard electropolishing bath uses an optimum blend of phosphoric and sulfuric acids along with various additives. The stainless steel should be completely free of hydrophobic (oils) and hydrophilic (oxides) soils to obtain good electropolishing. A good pre-treatment process is shown in the following.

1. Alkaline soak clean in a silicated cleaner at 6 to 8 oz/gal, 150 to 160°F for 3 to 5 min.
2. Cold water running rinse.

3. Acid clean and in a phosphoric-hydrochloric acid detergent product at 10 to 15 percent by volume, 120°F, for 3 to 4 min.
4. Cold water rinse.
5. Acid activate in 5 percent by volume nitric acid, 70 to 80°F as required.
6. Cold water rinse.
7. Electropolish

Heat Treating

Many heat treat soil problems (burnt-on soils, crayon marks) can be easily eliminated by properly cleaning before heat treating. An important aspect in cleaning prior to heat treating is to also completely remove cleaning residuals (silicates, solvents), that are known to detract from heat treating. Strong acids (sulfuric) should also be thoroughly rinsed to avoid pitting the surface. A cleaning procedure for a residual free surface is outlined in the following [*10*].

1. Emulsion clean with a 5 to 10 percent by volume solvent emulsion product at 70 to 90°F for 5 to 10 min, with good part agitation.
2. Alkaline clean with a nonsilicated product at 6 to 8 oz/gal, 150 to 160°F for 3 to 5 min.
3. Cold water running rinse.
4. Acid clean in phosphoric nitric acid solution product at 10 to 12 percent by volume, 90 to 120°F for 3 to 4 min.
5. Cold water running rinse, air blow dry.

Nondestructive Testing

The proper pretreatment of stainless steel components prior to nondestructive testing for hair line cracks can significantly increase the ease of detecting these surface flaws. By chemically polishing the surface, minute flaws are developed that can sometimes be detected, before actual testing, with the naked eye. A process for developing a more sensitive surface for nondestructive testing is shown in the following.

1. Alkaline clean in high caustic cleaner, 6 to 8 oz/gal, 170 to 180°F for 3 to 5 min. Good part agitation is desirable to promote rapid soil removal.
2. Cold water running rinse.
3. If the part is heavily scaled, scale condition in caustic permanganate inhibitor blend, at 16 oz/gal for 15 to 20 min.
4. Acid clean (neutralize) in nitric phosphoric acid cleaner at 5 to 8 percent by volume 70 to 80°F for 3 to 4 min.
5. Microfinish (level) in DS-9-314 at 170 to 180°F for 4 to 5 min.
6. Cold water rinse.
7. Distilled water rinse and air blow dry.

Passivation

Passivating stainless steel usually involves nitric acid, with or without chromic acid, at temperatures varying from 70 to 150°F. To properly passivate against an attacking environment, the proper pretreatment must be employed to clean, deoxidize, and activate the surface. Chlorides (hydrochloric acid), due to their corrosive nature, are eliminated and good rinsing between each step will help ensure complete uniform passivation. A pre-treatment is outlined in the following [*6*].

1. Alkaline soak clean with non-silicated product at 6 to 8 oz/gal, 160 to 170°F for 3 to 5 min.
2. Cold water rinse.
3. Acid clean and activate in phosphoric/gluconic acid detergent, 10 to 15 percent by volume, 130 to 140°F for 3 to 5 min.
4. Cold water running rinse.
5. Passivate in 25 percent by volume 42° baume nitric acid and 4 to 5 oz/gal sodium dichromate solution at 130 to 140°F for 10 to 20 min.
6. Cold water running rinse for 5 min and air dry.

Welding

Many welding failures, regardless of the type welding, can be attributed to inclusions in the weld, due to poor surface preparation. Quite often the chemical cleaning should be preceeded by wire brushing to loosen scale and solid contaminants in the weld zone. If the work (pipe, sheet, etc.) has been stored outdoors, wire brushing to remove loose dust is strongly recommended. The recommended procedure for cleaning and preparing stainless steel for standard welding operator is as follows [*11*].

1. Alkaline clean with non-silicated cleaner at 7 to 8 oz/gal, 160 to 170°F for 5 to 10 min.
2. Cold water rinse.
3. Acid clean in phosphoric/hydrochloric acid product, 10 to 12 percent by volume, 120 to 130°F for 2 to 3 min.
4. Cold water rinse. Check for water break free surface. If the rinse water does not rinse in a continuous sheet, repeat Steps 1 through 4.
5. Air dry.

Acid Cleaning Post-Treatments (After)

Buffing

Buffed stainless steel can be readily cleaned if the buffing compound is not allowed to "set" over a 24 to 48 h period. The longer the time between buffing and the final cleaning operation, the more difficult the cleaning job. A satisfactory cleaning procedure is shown below.

1. Alkaline soak clean at 160 to 170°F, 4 to 5 min with some solution agitation.
2. Cold water rinse (70 to 80°F, 2 to 3 min).
3. Acid clean using a phosphoric/nitric acid type cleaner at 15 to 20 percent by volume, 130 to 140°F for 5 to 10 min.
4. Cold water running rinse.

5. Deionized water rinse (70 to 80°F).

Heat Treated Parts

Stainless steel components cleaned before heat treating usually present few post-cleaning problems. However, heat treating before removing crayon markings, acid finger prints, corrosion inhibiting oils, and adhering shop soils leads to enumerable problems. The process to restore the final finish requires more steps than simple acid cleaning. However, this process will remove the burnt-on (oxidized) soils and restore the surface to its original luster.

1. Acid clean in phosphoric acid detergent solvent system at 140 to 150°F for 10 to 15 min, 10 to 15 percent by volume.
2. Cold water running rinse (60 to 70°F) for 3 to 5 min. Check for water break free surface. If water breaks, repeat Step 1.
3. Soak in scale conditioner (deoxidizer) caustic permanganate inhibitor blend at 14 to 16 oz/gal, 200°F for 15 to 20 min. A scale conditioner designed not to etch or attack the surface should be used.
4. Cold water running rinse (60 to 70°F), for 5 to 10 min.
5. Acid clean in inhibited hydrochloric acid detergent system (pickle) 15 to 20 percent by volume, at room temperature (70 to 80°F) for 3 to 4 min. Part agitation will increase dissolution of soils.
6. Cold water running rinse.
7. Microfinish in chemical polishing bath, DS-9-314 at 170 to 180°F for 3 to 5 min. Once again part agitation will speed leveling action. A longer dwell time (5 to 10 min) will produce a brighter surface.
8. Cold water running rinse and air blow dry. If water stains present problems, follow Step 8 with a distilled water rinse and alcohol dry.

Machined Parts

The cutting oils, adhering metal clips, and heavy shop soils quite often make this a tough cleaning operation. This sometimes requires an emulsion cleaner, followed by a heavy duty alkaline (30 to 40 percent caustic) cleaner. Using an acid cleaner, even one containing a high percentage of solvent and emulsifiers, could lead to limited soil-load problems. If the cutting oils are water soluble, foam generated could contaminate the following rinses and cleaning steps. The loose adhering clips usually are dislodged by solution or part agitation. Burrs or rough edges can be eliminated by chemical polishing, depending on the end use of the machined parts. A good cleaning procedure is outlined.

1. Alkaline emulsion clean at 130 to 150°F, 4 to 5 min, 5 to 10 percent by volume.
2. Alkaline soak clean at 150 to 160°F, 4 to 5 min, 6 to 8 oz/gal.
3. Cold water running rinse for 3 to 4 min (70 to 75°F).
4. Acid clean in inhibited hydrochloric-phosphoric acid detergent system at room temperature (70 to 80°F) 10 to 20 percent by volume for 3 to 4 min.
5. Cold water rinse and air blow dry.

Smut Removal

When smut is produced during a metal finishing operation, it can be readily removed using the following process.

1. Soak clean with a high pH (10 to 11) alkaline soak cleaner at 6 to 8 oz/gal, 150 to 170°F for 3 to 5 min.
2. Cold water rinse.
3. Soak in caustic permanganate inhibitor blend solution at 6 to 8 oz/gal, 130 to 140°F for 5 to 10 min with part agitation.
4. Cold water running rinse for 8 to 10 min, at 60 to 80°F. Part will be light brown in color after this step.
5. Dip in acid neutralizer (inhibited muriatic/nitric acid) solution at 8 to 12 percent by volume concentration, 70 to 80°F for 30 to 90 s with good part agitation.
6. Cold water running rinse, 60 to 80°F for 3 to 4 min.
7. Neutralize in 4 to 6 oz/gal solution of sodium bicarbonate or mild alkaline (pH 8 to 10) soak cleaner.
8. Cold water rinse.

Smut is generally defined as the black residue remaining on the surface after chemical attack; for instance, after acid pickling on stainless steel part. Chemically, smut is the carbon and metal compounds (oxide) that are insoluble or just sparingly soluble in the attacking chemical media (hot sulfuric acid). To remove these "insolubles" that produce a composite black to dark brown smut, they are first chemically converted into more soluble oxides through hydration and oxidation to a higher valence state. Once converted into more acid soluble compounds they are quickly removed in the proper stainless steel acid desmutter. A common test for smut on stainless steel is to wipe the surface with a dry clean tissue and examine the tissue for the presence of the black residual called smut. If smut is still present after rinsing through Step 6, simply repeat Steps, 3, 4, 5, and 6 to complete desmutting the part [*5*].

Soldering

Solder flux, splatter, and the resulting oxide film can cause a cleaning problem, especially where manual cleaning is not economically feasible. Based on actual field experience, to first remove most of the solder residue, use a very dilute solution of boric acid and nonionic surfactants at 140 to 160°F. Many soldering fluxes are actually "set" by alkaline cleaners, making them even more difficult to remove. The splatter can be removed chemically, but sometimes responds better to wire brushing, if possible. Most of the hard solders used for stainless steels contain nickel, iron, silicates, boron, and carbon. A few special hard solders will also contain manganese, chromium, silver pallandium, and copper nickle gold composites. The soft solders, not common to such high melting material as stainless steel, contain zinc, lead, tin, and cadmium (low melting metals). These contaminants are not considered as severe a cleaning problem.

To handle this wide variety of contaminants requires a process using acid cleaning. Alkaline cleaners, quite often, will set the solder residues, making the cleaning job more difficult. A recommended cleaning process for handling these soils is as follows [*12*].

1. Clean in a 4 to 6 oz/gal boric acid detergent solution at 140 to 150°F for 10 to 15 min.
2. Cold water running rinse.
3. Convert the oxides, and mixed solder splatter to more acid soluble soils in a scale conditioner solution, with a product similar to caustic permanganate inhibitor blend at 14 to 16 oz/gal, 190 to 200°F for 10 to 20 min.
4. Cold water running rinse.
5. Deoxidize in a 10 to 15 percent by volume solution of an inhibited nitric/hydrochloric acid system at 110 to 130°F for 3 to 5 min.
6. Cold water running rinse.
7. Microfinish with DS9-314 or a similar product at 160 to 170°F for 3 to 5 min.
8. Cold water running rinse for 3 to 5 min.
9. Neutralize in low pH (7 to 10) alkaline cleaner or sodium bicarbonate at 3 to 4 oz/gal, 70 to 80°F for 3 to 4 min.
10. Cold water running rinse.

Welding

Weld splatter, discoloration (thin film oxide), and welding oxides are most easily cleaned with acid cleaners or mechanical means using wire brushes. The acid cleaning techniques can be divided into manual and soak tank operations.

The manual cleaning operation uses an abrasive powder cleaner based on sodium acid sulfate, abrasive power (aluminum oxide), inhibitors, and surfactants. This composition powder is mixed with a small amount of water and rubbed into the weld areas as a paste. This abrasive acid paste will remove the oxides and also polish the welded area. This paste should not be allowed to sit or remain on the welded area for any length of time (more than 5 min) or the welded joint will become blackened. Use the paste as a manual abrasive and flush off the welded surface with water when finished [*11*].

The soak tank operation is often required for large welded tank sections, or parts with welded recessed areas that cannot be cleaned by hand. A satisfactory soak tank operation is shown below.

1. Soak clean with a nonsilicated alkaline cleaner at 6 to 8 oz/gal, 150 to 160°F for 5 to 10 min.
2. Cold water rinse.
3. Soak in scale conditioner, similar to caustic permanganate inhibitor blend at 14 to 16 oz/gal for 10 to 15 min at 180 to 200°F.
4. Cold water running rinse.
5. Acid clean (deoxidize) with an inhibited muriatic acid detergent product at 8 to 12 percent by volume, 70 to 75°F for 5 to 8 min.
6. Cold water running rinse (60 to 70°F) for 3 to 5 min.

7. Neutralize the completely deoxidized surface with a mild alkaline cleaner (pH 8 to 10) or sodium bicarbonate at 6 to 8 oz/gal, 70 to 80°F (room temperature) for 1 to 2 min. This solution should be dumped daily or more, depending on the work load to prevent the neutralizing solutions from becoming contaminated with chlorides.

Conclusion

The 300 series stainless steels are most efficiently cleaned and chemically finished in acid media. This data is presented with the sincere hope that it will enable our industry to better utilize this technology.

Acknowledgments

My sincere thanks to Ralph Pettit and Floyd Mickelson for helping make this paper possible.

References

[*1*] Linford, H. B. and Sanbestre, E., *Plating*, Vol. 38, No. 4, 1951, pp. 367-376.

[*2*] Gould, R. F., "Contact Angel, Wettability and Adhesion," American Chemical Society, Washington, D. C., 1964, pp. 74-87; 147-157.

[*3*] Schwartz and Perry, *Surface Active Agents,* Vol. 1. Interscience Publishers, 1949, pp. 25-30; 241-270.

[*4*] Trevoy, D. J. and Hollister, J., *Journal of Physical Chemistry,* Vol. 62, No. 7, 1958, pp. 833-837.

[*5*] Private communication, R. E. Pettit, Diversey Metal Finishing Consultant, Lombard, Ill., 1970-1971.

[*6*] Uhlig, H. H., *The Corrosion Handbook,* Wiley, New York, 1948, pp. 125-194.

[*7*] Clayton, W., *The Theory of Emulsions and Their Technical Treatment,* Blakeston, New York, 1954, pp. 192-295.

[*8*] Weast, R. C., *Handbook of Chemistry and Physics,* Chemical Rubber Company, Cleveland, Ohio, 1967, pp. F204-F226; F134; C75-C597.

[*9*] Cagle, V., *Adhesive Bonding,* McGraw Hill, New York, 1968, pp. 86-123.

[*10*] Grossman, M. A., *Principles of Heat Treatment,* American Society for Metals, Cleveland, Ohio, 1940, pp. 126-144.

[*11*] *Welding Handbook,* American Welding Society, New York, 1950, pp. 648-686; 498-515.

[*12*] *Properties and Selections of Metals,* American Society for Metals, Vol. 1, pp. 408-438.

[*13*] Kopecki, E., "Cleanability of Stainless Steels," AISI Dairy Industry Management, American Iron and Steel Institute, June 1965.

[*14*] *1968 Annual Book of ASTM Standards,* Part 3, Metal Test Methods.

Michael Henthorne[1] *and R. J. Yinger*[1]

Passivation Treatments for Resulfurized, Free Machining Stainless Steels

REFERENCE: Henthorne, Michael and Yinger, R. J., "Passivation Treatments for Resulfurized, Free Machining Stainless Steels," *Cleaning Stainless Steel, ASTM STP 538*, American Society for Testing and Materials, 1973, pp. 90–105.

ABSTRACT: The practical aspects of nitric acid passivation are reviewed and new data on the effect of passivation variables on subsequent corrosion resistance are reported. Solution composition and temperature, passivation time, and double acid and alkaline treatments were investigated. Commercial heats of 12Cr (0.5 and 2 percent varieties) and 18Cr-9Ni resulfurized stainless were tested at 95°F (35°C) in either 95 percent humidity or 5 percent salt spray after receiving the various passivation treatments. The variables having the most significant effect were (1) the manganese content of the steel, (2) whether a cross or a long section of a bar was being investigated, and (3) an alkaline post passivation treatment. Without passivation, the low manganese 12Cr alloy has superior corrosion resistance to the high manganese grade. After passivation, the low manganese alloys lost some of their corrosion resistance, whereas the high manganese materials sometimes showed improved resistance. The loss of resistance after passivation is attributed to the retention of acid in partially removed sulfides and it can be minimized with the alkaline treatment. It is also noted that highly oxidizing passivation solutions are required to avoid attack during the passivation treatment itself and that these solutions do not dissolve tool steels, particles of which might be embedded in the stainless surface during machining.

KEY WORDS: stainless steels, cleaning, passivity, corrosion prevention, oxidation

A passivation treatment is the immersion of stainless steel parts or equipment in an oxidizing solution such as 20 percent nitric acid (HNO_3). Early in the history of stainless steel these treatments were used with the aim of providing an optimum oxide film on the stainless surface. Since a clean (for example, pickled) surface will quite readily passivate in air, the use of nitric acid to achieve this end is unjustifiable. Also, the film formed during the passivation treatment will not be maintained on exposure to new media.

Later, it was generally conceded that the most important feature of passivation was to clean the steel surface by dissolving inclusions in the steel or iron particles imbedded in the surface during fabrication and that pickling would also achieve this [*1,2*].[2] There have been several investigations into the effect of

---

[1] Manager, Corrosion and Welding, Research and Development, and senior corrosion engineer, Corrosion Research, respectively, Carpenter Technology Corp., R & D Center, Reading, Pa. 19603.

[2] The italic numbers in brackets refer to the list of references appended to this paper.

passivation on corrosion resistance, and they show it to be generally beneficial, especially when there is subsequent exposure to acid media [*3-7*].

Resulfurized, free machining stainless steels (for example, AISI Types 416, 430, and 303) which contain about 0.3 percent sulfur are a special case so far as passivation is concerned. They contain sulfide inclusions which become elongated in the hot working direction, as shown in Fig. 1. Sulfides are deleterious to the corrosion resistance of ordinary steel [*8*] and in some media they increase the corrosion susceptibility of stainless steel [*9*]. The role of sulfides in the corrosion of stainless steels is dependent upon their composition [*9,10*]. Low manganese steels (say, 0.5 percent manganese) contain chromium rich sulfides such as $(Mn_{.4}Cr_{.5}Fe_{.1})S$ and these are more corrosion resistant than the manganese sulfide (MnS) which predominates in the high manganese grades (for example, 2 percent manganese).

The resulfurized stainless steels are frequently passivated with the reasoning that (1) they contain sulfide inclusions which might, to advantage, be removed during the passivation, and (2) they generally have been machined and so might contain imbedded tool steel particles.

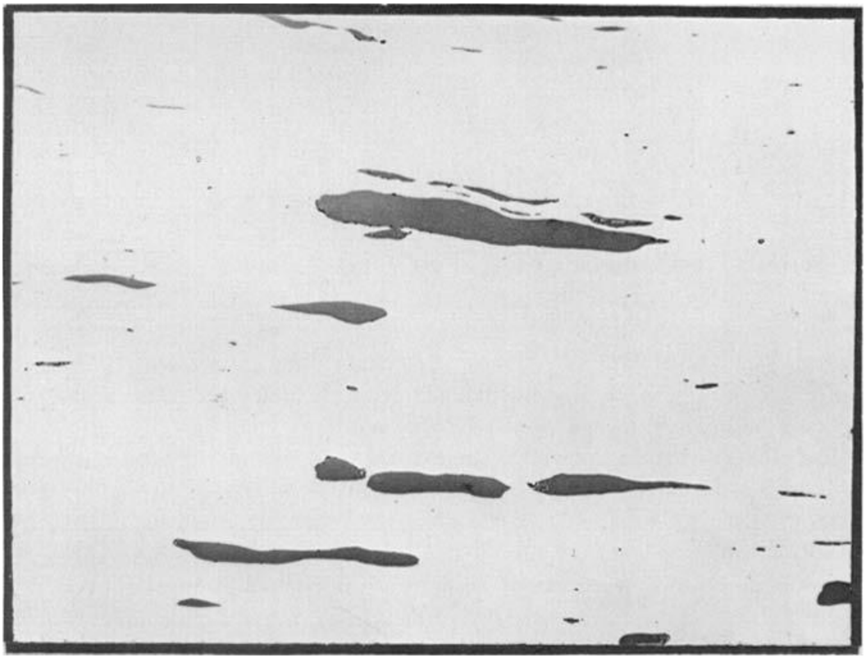


FIG. 1–*Sulfides in resulfurized, free machining stainless steel, longitudinal section (x500).*

The Passivation Treatment Itself

Large or small stainless steel articles may be passivated, but the most common situation will involve the passivation of many small machined parts, fittings, etc. Problems, when they occur, are of two types–unwanted attack of the stainless steel during the treatment or unsatisfactory corrosion performance after passivation. In this section we shall discuss the former.

The attack usually will start immediately after immersion of the parts in the solution or suddenly within the first minute of immersion. The sudden nature of the attack has led to it commonly being called "flash attack." The steel is etched grey or black and the attack may continue vigorously or abate after a few seconds. Experience has shown that the problem can be related to either the acid or the steel. Table 1 is a checklist of items to consider.

TABLE 1–*Passivation–Practical points to check.*

1. Acid concentration
2. Chloride contamination
3. Temperature
4. Grease on steel
5. Scale on steel
6. Nitrided or carburized surfaces
7. Galvanic effects
8. Metallurgical condition of steel
9. Rinsing and drying
10. Location of bath

The most commonly used passivation solution for ordinary stainless steels is 20 percent HNO_3, typically for 30 min at 130°F (54°C). This solution will usually cause flash attack with the resulfurized grades so it is necessary to increase the oxidizing power of the bath by increasing the concentration of the nitric acid (to say 40 or 50 percent), adding an oxidizing agent (for example, 2 percent sodium dichromate ($Na_2Cr_2O_7$)) or both.

The relative oxidizing power of some of the more common solutions is shown in Fig. 2. A 50 percent HNO_3 solution is sometimes used as an alternative to 20 percent HNO_3 + 2 percent $Na_2Cr_2O_7$. It has the advantage of creating less pollution problems when a bath has to be disposed of but the disadvantages of more fuming during use and the need for close control to avoid dilution to a concentration that will cause flash attack. The nitric acid content can be measured by titrating against a standard sodium hydroxide (NaOH) solution with phenolphthalein as an indicator.

Tap water is usually adequate for making up the acid although high chloride content (greater than several hundred ppm) could be deleterious in a borderline situation.

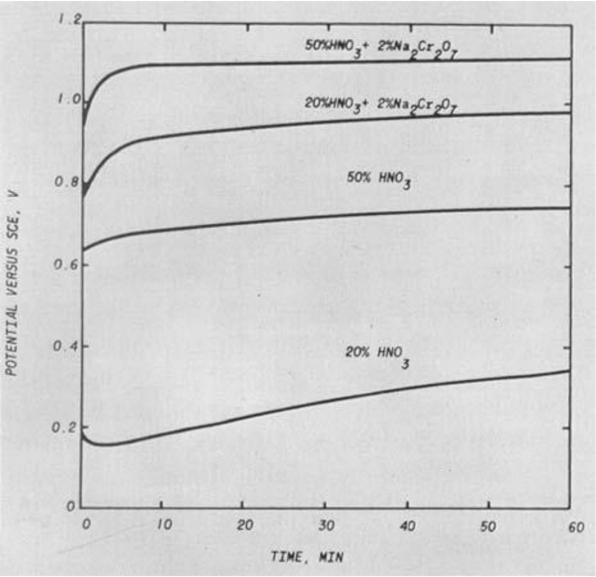


FIG. 2–*Potential time curves for Type 304 stainless (longitudinal sections) in four passivation solutions at 120°F.*

The recommended temperature is usually about 130°F (54°C). Ambient temperature solutions are sometimes used but they are slightly less oxidizing. High temperature (> about 170°F, 77°C) may cause staining of the parts being passivated. It should also be noted that if stainless steel equipment is used in the construction of the bath, then the hot solutions containing sodium dichromate can cause it to be intergranularly attacked (this is another potential advantage of the straight 50 percent HNO_3).

Parts with large cross section areas (relative to the bar they were machined from) are more prone to attack in the acid than those with large long sections. Highly polished material is also more susceptible to attack. It is essential to remove all grease and oil prior to passivation. The passivation solution will not do this, and prior degreasing in an alkaline cleaner or organic degreaser is desirable. Neither will the passivation bath remove heat treatment scale. Remnants of the latter can increase the tendency to attack in the passivation solution as can heavily carburized or nitrided surfaces. In a borderline situation, galvanic effects between different types of stainless steel being passivated or between a more noble metal basket could increase the likelihood of attack.

Metallurgical condition will not usually be a factor in deciding whether flash attack occurs but in a borderline situation, it may be relevant. For example Type 416 tempered in the region of about 900 to 1000°F (482 to 538°C), Type 430F "sensitized" by treatment above about 1700°F (927°C) or Type 303 sensitized by treating in the 1200°F (649°C) region could all be slightly more susceptible to attack in a borderline situation than in the annealed (and in the case of the Type 416, full hardened) condition.

As in any chemical treatment, it is essential to have adequate washing procedures to remove residual acid. The advantages of an alkaline treatment after the acid will be discussed later. After washing and drying, the parts should be stored in a clean area. Locating a passivation bath in the region of a pickling solution is not a good idea, particularly if hot hydrochloric acid (HCl) pickling is involved.

Effect of Passivation on Corrosion Resistance

The influence of the more common passivation treatments on the corrosion resistance of Types 416, 430F, and 303 stainless has been reported previously [*9*]. It was shown that passivation is generally beneficial, especially in the high (1 to 2 percent) manganese grades. The manganese rich sulfides in the latter are removed more completely during the passivation process than are the chromium rich sulfides in the low manganese alloys. There were also indications that passivation could be detrimental to the subsequent corrosion resistance of cross sections, especially for the low manganese alloys.

The aims of the current work were to (*a*) confirm the previous findings, (*b*) investigate several different passivation solutions and the effect of temperature and time, (*c*) determine the reason for differences between long and cross sections, and (*d*) evaluate the effectiveness of double acid and alkaline treatments.

Commercial heats of 12Cr (0.5 and 2 Mn) and 18Cr-9Ni (Type 303) were used (see Table 2 for analyses). Three different heats were used for each alloy and all material was in the form of mill annealed bars 1 to 1 1/4 in. diameter. Machine ground cross and long sections were studied and, in some cases, parts machined on an automatic screw machine were evaluated. The test specimens used are shown in Fig. 3.

All specimens were given the following cleaning cycle just prior to passivation: vapor degrease in inhibited III trichloroethane, ultrasonically clean in methanol for 5 min and then methanol rinse. Samples were tested in this condition or

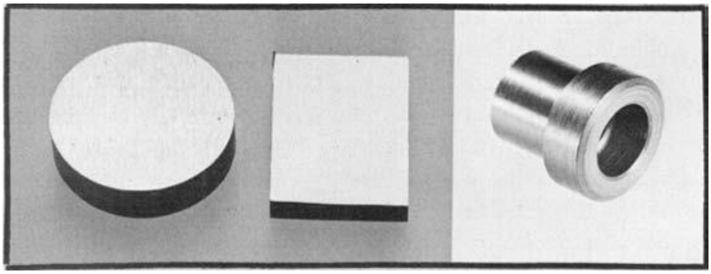


FIG. 3—*Test specimens used for corrosion tests,* (left) *machine ground cross section,* (center) *machine ground long section, and* (right) *part from automatic screw machine (x0.75).*

TABLE 2–*Analysis of resulfurized stainless steels tested.*

Alloy	Heat No.	C	Mn	Si	P	S	Cr	Ni	Mo	Cu
High Mn 12Cr	A	0.107	2.30	0.53	0.021	0.38	12.83	0.21	0.02	0.09
	B	0.115	1.86	0.48	0.021	0.33	13.40	0.31	0.18	0.12
	C	0.117	1.86	0.48	0.024	0.35	13.50	0.21	0.19	0.10
Low Mn 12Cr (Type 416)	D	0.096	0.40	0.70	0.018	0.34	12.89	0.21	0.02	0.07
	E	0.096	0.50	0.54	0.029	0.35	13.08	0.24	0.06	0.11
	F	0.100	0.35	0.63	0.017	0.36	13.19	0.20	0.05	0.05
Type 303	G	0.066	1.59	0.50	0.029	0.35	17.71	8.85	0.41	0.26
	H	0.062	1.74	0.61	0.029	0.34	17.10	8.72	0.22	0.23
	L	0.076	1.56	0.57	0.027	0.31	17.39	8.71	0.32	0.23

given one of twelve different passivation treatments.

After passivation (within 24 h of it) the 12Cr alloys were tested for one week in 95 percent humidity at 95°F (35°C) and the Type 303 was tested as per ASTM Salt Spray (Fog) Testing (B 117-64) for 24 h in neutral 5 percent salt spray at 95°F (35°C). Triplicate specimens were tested for each condition. The test pieces were held with the ground surface at 45 deg to the vertical and were randomly positioned in the test area of the fog chamber. After testing, the samples were rated visually for the degree of corrosion.

The results for the 12Cr alloys in high humidity are shown in Tables 3 and 4. These results show:

1. In the "as cleaned" condition, the low manganese material is superior to high manganese. This confirms previous work [*9*].
2. Passivation improves the high manganese alloys but can make low manganese material worse than "as cleaned." This is particularly true of cross sections and again confirms the previous data.
3. The alkaline-acid-alkaline combination (Treatment 9) is generally the best passivation treatment.
4. Variations in the time, temperature, composition of the passivation solution, and double acid treatments had relatively minor effects.
5. Cross sections are generally more prone to corrosion than long and are more sensitive to passivation effects.

Machined parts of the 12Cr alloys were also tested in humidity. The results (Table 5) show similar trends to those just described for the machine ground sections. For example, passivation improves the high manganese alloy but in some cases was deleterious to low manganese material. However, the alkaline-acid-alkaline treatment was not too effective on these machined parts.

The Type 303 salt spray results for machine ground specimens (see Table 6) show:

1. There is considerable scatter in the data with passivation being beneficial in some cases and detrimental in others.
2. The alkaline-acid-alkaline treatment is superior to the regular passivation treatments (see also Fig. 4 and 5).
3. Cross sections were attacked more than long sections particularly after the regular passivation (see also Fig. 4 and 5).
4. Variation in the temperature, time, composition of the passivation solution, and double acid treatments had relatively minor effects. There was, however, an indication that the 10 min and 75°F (24°C) passivations (Treatments 3 and 5) were somewhat superior to the regular 30 min and 130°F (54°C). This is probably due to less attack of the more resistant sulfides and therefore less acid entrapment (see later for discussion of the latter).

Discussion of Passivation Effects

The preceding section raises several questions. (1) Why are the effects of passivation related to the manganese content of the steel? (2) Why does passivation sometimes increase the corrosion in humidity and salt spray? (3)

TABLE 3–*Corrosion of low manganese 12Cr steel in 95 percent humidity at 95°F (35°C).*

Prior Treatment				Degree of Corrosion After One Week[a]							
				Cross Sections				Long Sections			
No.	Solution[b]	Tempera-ture, °F	Time, min	Heat D	Heat E	Heat F	Av	Heat D	Heat E	Heat F	Av
1.	None	...	...	0,0,0	1,0,0	1,1,1	0	2,2,1	1,1,0	1,2,2	1
2.	20HNO$_3$+2Na$_2$Cr$_2$O$_7$	130	30	5,3,4	3,1,2	3,3,2	3	2,1,2	1,1,0	0,2,0	1
3.	20HNO$_3$+2Na$_2$Cr$_2$O$_7$	72	30	4,4,4	3,2,2	2,3,2	3	2,2,2	2,2,2	1,4,1	1
4.	20HNO$_3$+2Na$_2$Cr$_2$O$_7$	170	30	5,5,4	2,3,2	3,3,3	3	0,2,2	0,2,2	0,0,1	1
5.	20HNO$_3$+2Na$_2$Cr$_2$O$_7$	130	10	5,5,5	2,2,2	2,1,2	3	2,2,1	2,1,1	1,3,1	2
6.	20HNO$_3$+2Na$_2$Cr$_2$O$_7$	130	60	5,5,5	1,3,2	3,4,3	3	2,2,1	2,2,0	1,1,2	1
7.	20HNO$_2$+2Na$_2$Cr$_2$O$_7$	130	120	5,6,4	3,3,1	2,3,3	3	2,2,1	2,0,1	1,2,1	1
8.	5NaOH plus	170	30	5,4,5	1,2,0	2,2,2	3	2,2,2	1,2,1	0,2,1	1
	20HNO$_3$+2Na$_2$Cr$_2$O$_7$	130	30								
9.	5NaOH plus	170	30	2,2,3	0,1,1	2,2,0	1	0,1,0	0,0,0	1,1,2	1
	20HNO$_3$+2Na$_2$Cr$_2$O$_7$ plus	130	30								
	5NaOH	170	30								
10.	50HNO$_3$	130	30	5,3,5	1,4,3	5,4,3	4	0,0,1	2,2,1	0,2,0	1
11.	50HNO$_3$+2Na$_2$Cr$_2$O$_7$	130	30	4,4,4	1,0,1	4,3,3	3	0,2,2	0,0,1	1,1,0	1
12.	20HNO$_3$+2Na$_2$Cr$_2$O$_7$ plus	130	30	6,5,5	2,2,3	3,3,2	3	3,1,2	2,2,0	2,2,3	2
	10HNO$_3$	130	30								
13.	20HNO$_3$+2Na$_2$Cr$_2$O$_7$ plus	130	30	6,6,6	3,4,2	4,4,3	4	3,1,1	2,0,2	2,3,2	2
	20HNO$_3$	130	30								

[a] 1X evaluation of each of the triplicate samples. Rating 0 is no visible attack. Rating 9 represents corrosion product on almost the entire specimen surface.

[b] Weight percent.

TABLE 4–*Corrosion of high manganese 12Cr Steel in 95 percent humidity at 95°F (35°C).*

Prior Treatment				Degree of Corrosion After One Week[a]							
				Cross Sections				Long Sections			
No.	Solution[b]	Temperature, °F	Time min	Heat A	Heat B	Heat C	Av	Heat A	Heat B	Heat C	Av
1.	None	. . .	. . .	5,4,5	4,3,3	6,6,6	5	5,5,5	2,5,5	3,4,4	4
2.	$20HNO_3+2Na_2Cr_2O_7$	130	30	. . .	. . .	0,0,2	1	0,0,0	0,2,1	2,0,0	1
3.	$20HNO_3+2Na_2Cr_2O_7$	72	30	. . .	. . .	0,...,0	0	0,0,0	0,0,1	...,2,1	1
4.	$20HNO_3+2Na_2Cr_2O_7$	170	30	. . .	. . .	0,0,0	0	0,0,2	0,0,0	0,1,1	0
5.	$20HNO_3+2Na_2Cr_2O_7$	130	10	. . .	. . .	0,2,1	1	0,0,0	$0,0,0^c$	$1,0,0^c$	0
6.	$20HNO_3+2Na_2Cr_2O_7$	130	60	. . .	. . .	2,1,2	2	2,2,1	2,0,2	2,2,0	1
7.	$20HNO_3+2Na_2Cr_2O_7$	130	120	. . .	. . .	0,1,0	0	$0,0^c,0^c$	$0^c,0,0^c$	2,2,0	0
8.	5NaOH plus	170	30	. . .	. . .	0,0,2	1	2,2,0	0,0,2	0,0,0	1
	$20HNO_3+2Na_2Cr_2O_7$	130	30								
9.	5NaOH plus	170	30	2,3,4	1,2,4	0,0,0	2	1,1,0	0,0,0	0,0,0	0
	$20HNO_3+2Na_2Cr_2O_7$ plus	130	30								
	5NaOH	170	30								
10.	$5OHNO_3$	130	30	$3^c,2^c,2^c$	$2,2^c,2$	3,2,4	2	0,0,2	2,2,2	0,1,0	1
11.	$5OHNO_3+2Na_2Cr_2O_7$	130	30	0,2,2	0,1,2	2,2,3	2	0,1,2	2,0,2	1,0,0	1
12.	$20HNO_3+2Na_2Cr_2O_7$ plus	130	30	. . .	. . .	. . .	. . .	2,1,1	$0,0^c,0$	$1^c,0,0$	1
	$10HNO_3$	130	30								
13.	$20HNO_3+2Na_2Cr_2O_7$ plus	130	30	. . .	. . .	1,2,2	2	...,2,2	$1,0^c,0^c$	0,0,0	1
	$20HNO_3$	130	30								

[a] 1X evaluation of each of the triplicate samples. Rating 0 is no visible attack. Rating 9 represents corrosion product on almost the entire specimen surface. Where there is no data given, this signifies severe attack during passivation so specimens were not tested.

[b] Weight percent.

[c] Some etching of specimen during passivation.

TABLE 5–*Influence of passivation on corrosion of machined parts in 95 percent humidity, 95°F (35°C).*

				Degree of Corrosion After One Week[a]						
Prior Treatment				Low Mn 12Cr Steel			High Mn 12Cr Steel			
No.	Solution[b]	Temperature, °F	Time min	Heat D	Heat E	Av	Heat A	Heat B	Heat C	Av
1.	None	...	...	3,7,2	2,3,2	3	9,8,10	3,10,8	7,9,7	8
2.	$20HNO_3+2Na_2Cr_2O_7$	130	30	4,7,7	6,2,6	5	1,1,3	2,6,1	2,2,2	2
3.	$20HNO_3+2Na_2Cr_2O_7$	72	30	5,5,8	3,6,4	5	2,1,3	2,1,4	2,1,2	2
4.	$20HNO_3+2Na_2Cr_2O_7$	170	30	5,6,4	4,2,4	4	1,1,2	2,2,5	2,3,2	2
5.	$20HNO_3+2Na_2Cr_2O_7$	130	10	8,2,5	5,4,5	5	4,2,6	2,1,2	3,1,1	2
6.	$20HNO_3+2Na_2Cr_2O_7$	130	60	5,3,5	2,2,2	3	1,6,2	4,5,1	2,2,2	3
7.	$20HNO_3+2Na_2Cr_2O_7$	130	120	5,5,4	2,6,3	4	1,1,2	2,5,1	1,2,2	2
8.	5NaOH plus $20HNO_3+2Na_2Cr_2O_7$	170 130	30 30	4,6,7	5,3,7	5	3,2,2	3,2,2	3,3,3	3
9.	5NaOH plus $20HNO_3+2Na_2Cr_2O_7$ plus 5NaOH	170 130 170	30 30 30	6,8,2	4,4,3	5	5,2,2	3,1,1	3,2,3	2
10.	$50HNO_3$	130	30	2,6,7	3,4,3	4	8,4,7	3,7,5	4,5,3	5
11.	$50HNO_3+2Na_2Cr_2O_7$	130	30	4,3,2	2,2,1	2	8,4,6	2,3,4	4,4,4	4
12.	$20HNO_3+2Na_2Cr_2O_7$ plus $10HNO_3$	130 130	30 30	8,8,4	5,5,4	6	3,2,2	3,4,2	2,2,3	3
13.	$20HNO_3+2Na_2Cr_2O_7$ plus $20HNO_3$	130 130	30 30	6,4,8	6,5,4	6	5,2,2	1,2,3	5,4,1	3

[a] 1X evaluation of each of the triplicate test samples. Rating system 1 to 10 with increasing corrosion at the higher numbers. NOTE–This is not identical rating system to that used for ground sections (Tables 3 and 4).

[b] Weight percent.

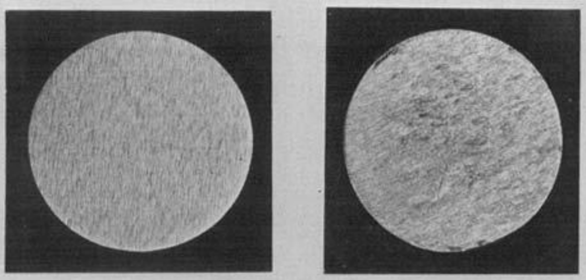
TABLE 6—*Corrosion of Type 303 in 5 percent salt spray at 95°F (35°C).*

	Prior Treatment			Degree of Corrosion After One Week[a]							
				Cross Sections				Long Sections			
No.	Solution[b]	Tempera-ture, °F	Time, min	Heat G	Heat H	Heat L	Av	Heat G	Heat H	Heat L	Av
1.	None	. . .	. . .	9,9,9	4,3,7	4,4,4	6	7,4,2	3,2,3	1,2,2	3
2.	$20HNO_3+2Na_2Cr_2O_7$	130	30	9,9,9	. . .	9,9,9	9	3,4,3	3,3,3	3,4,4	3
3.	$20HNO_3+2Na_2Cr_2O_7$	72	30	9,7,7	...,...,3	5,5,5	6	2,2,2	1,2,2	3,4,4	2
4.	$20HNO_3+2Na_2Cr_2O_7$	170	30	9,9,9	6,7,...	7,8,9	8	3,3,2	2,3,2	2,3,2	3
5.	$20HNO_3+2Na_2Cr_2O_7$	130	10	6,6,7	. . .	7,9,7	7	1,2,1	3,3,3	2,3,4	2
6.	$20HNO_3+2Na_2Cr_2O_7$	130	60	9,9,9	. . .	9,8,8	9	4,3,3	3,3,3	3,4,4	3
7.	$20HNO_3+2Na_2Cr_2O_7$	130	120	9,9,9	. . .	7,8,8	8	4,3,4	3,3,2	2,2,2	3
8.	5NaOH plus	170	30	6[c],6[c],6[c]	6,6,8	7,7,7	7	5,5,5	2,3,2	4,4,4	4
	$20HNO_3+2Na_2Cr_2O_7$	130	30								
9.	5NaOH plus	170	30	4,5,5	1,2,2	2,1,0	2	0,0,1	1,1,1	0,0,0	0
	$20HNO_3+2Na_2Cr_2O_7$ plus	130	30								
	5NaOH	170	30								
10.	$50HNO_3$	130	30	8,8,8	3,2,2	2,3,3	4	3,4,2	2,3,2	6,6,6	4
11.	$50HNO_3+Na_2Cr_2O_7$	130	30	7,7,9	2,3,2	8,8,8	6	4,3,4	3,3,4	5,2,5	4
12.	$20HNO_3+2Na_2Cr_2O_7$ plus	130	30	9,9,8	. . .	8,8,8	8	3,2,4	4,4,4	5,4,5	4
	$10HNO_3$	130	30								
13.	$20HNO_3+2Na_2Cr_2O_7$ plus	130	30	9,8,9	. . .	8,9,9	9	4,4,3	2,2,3	4,4,5	3
	$20HNO_3$	130	30								

[a] 1X evaluation of each of the triplicate samples. Rating 0 is no visible attack. Rating 9 represents corrosion product on almost the entire specimen surface. Where there is no data given, this signifies severe attack during passivation so specimens were not tested.

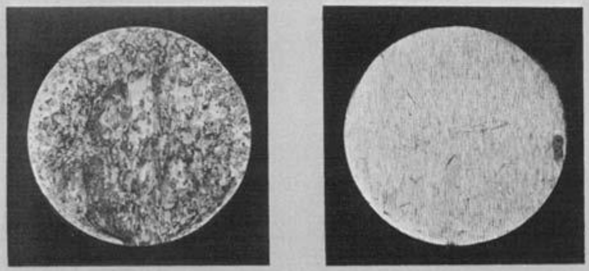
[b] Weight percent.

[c] Some etching of specimen during passivation.



Not Tested

Tested as ground
and cleaned



Tested after passivation
in 20%HNO_3+2%$Na_2Cr_2O_7$
at 130F, 30 min.

Tested after alkaline clean,
passivation & alkaline
clean(5%NaOH,170F,30min)

FIG. 4–*Type 303 stainless cross sections (Heat L) after 24 h in 5 percent salt spray at 95°F (x0.75).*

Why do cross sections respond differently to long sections? (4) Why is the alkaline-acid-alkaline treatment generally much superior to regular passivation? The answer to all of these questions is believed to be related to the composition and geometry of the sulfides.

In the absence of passivation, the high manganese steels are more susceptible to corrosion than low manganese material because the manganese sulfides in the former are readily attacked by mild media. Passivation generally improves these high manganese steels because the deleterious sulfides are more completely removed during the passivation.[3]

Sulfides in the low manganese alloys are chromium rich and inherently more corrosion resistant than manganese sulfide. This is beneficial when the steel is used without passivation but is the probable cause of the sometimes seen decrease in corrosion resistance when material is passivated. The nitric acid-sodium dichromate treatments do not completely remove all the sulfides. This is

---

[3] However, it should be remembered that the very removal of these sulfides during the passivation treatment can cause the "flash attack" problems described earlier in this paper. In practice. therefore, the 20 percent HNO_3 + 2 percent $Na_2Cr_2O_7$ solutions will not be useable for the high manganese 12Cr alloys. A higher nitric acid content (Treatment 11) will have to be used and generally it does not bring about the same improvement in corrosion resistance because it does not remove sulfides as effectively.

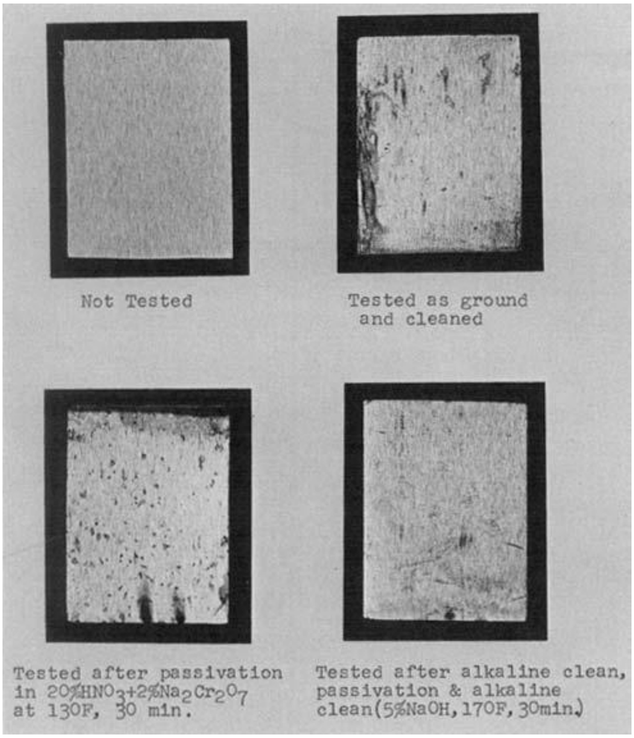


FIG. 5—Type 303 stainless long sections (Heat L) after 24 h in 5 percent neutral salt spray at 95°F (x0.75).

particularly true on cross sections because the sulfides are elongated in the longitudinal direction. Thus, to remove a sulfide on a cross section, the acid may have to dissolve a 5μ diameter sulfide to a depth of 50μ.

This partial removal of sulfides is believed to be the reason why passivation treatments can be deleterious to subsequent corrosion resistance. This is because normal washing procedures after passivation do not completely remove all the acid from the partially attacked sulfide. To verify this, the following experiment was run on micropolished cross sections of Type 303 (Heat G).

Ten specimens were ultrasonically cleaned in methanol and then passivated in 20 percent HNO_3 plus 2 percent $Na_2Cr_2O_7$ (Treatment 2). Five of these were then rinsed twice in water and ultrasonically cleaned in a small volume of distilled water at pH 5. After 2 min the pH had decreased to 4, indicating the presence of acid on the twice rinsed specimens. The other five specimens were immersed in 5 percent NaOH at 170°F for 30 min after passivating and rinsing. Following this treatment, they were double rinsed in water identically to the first five and then ultrasonically cleaned in distilled water at pH 5. In 2 min the pH had risen to 6.5, indicating the neutralization of residual acid and the retention of some alkali.

This provides a logical explanation for the sometimes detrimental effects of passivation, the benefits of the alkaline post passivation treatment and the dependence of passivation effects on whether a cross or long section is involved.

Another possible explanation for the detrimental effect of passivation exists and was investigated. It has been suggested that passivating a stainless steel surface to a potential higher than its pitting potential in a given chloride media could result in spontaneous pitting on immersing the passivated steel in that media [*11*]. This assumes that the high passivation solution potential would be maintained long enough in the chloride solution for pitting to initiate, and this is questionable. However, this mechanism would explain the deleterious effect of passivation and the benefits of the alkaline treatment because the latter lowers the potential very significantly (see Fig. 6) and, in fact, makes it active to that achieved in water and sodium chloride media. To further investigate whether this was a valid theory, the visible film on micropolished cross sections of passivated Type 303 was wiped off with a paper tissue and then they were tested in salt spray. These specimens still corroded more than unpassivated material even though the high potential condition presumably had been removed with the wiping. This again indicates that the problem is related to conditions within the sulfide cavities and is consistent with the residual acid theory.

If a resulfurized stainless steel is passivated, a post alkaline treatment is recommended.

Dissolution of Tool Steels in Passivation Solutions

Historically, the main justification for passivating stainless steel has been to remove embedded iron from fabrication processes, for example, machine tool

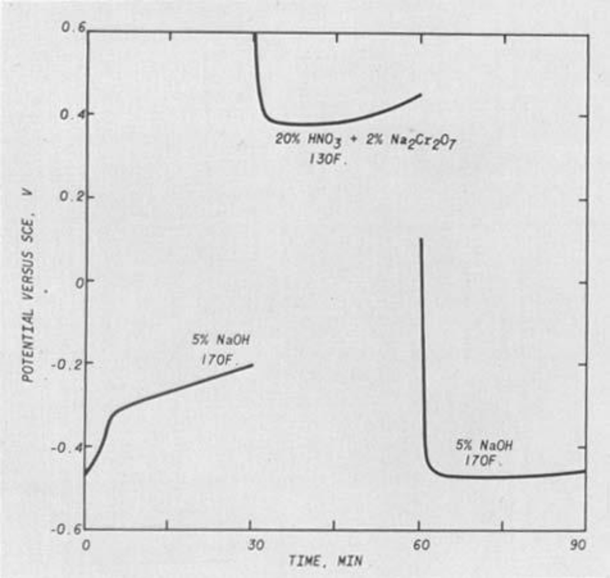


FIG. 6—*Potential time measurements during alkaline-acid-alkaline passivation treatment. Machine ground cross sections of Type 303 (Heat G).*

particles. Iron and steel dissolve readily in the dilute nitric acid solutions (for example, 20 percent HNO_3) used to passivate ordinary stainless.

As noted earlier, more oxidizing solutions (for example, 50 percent HNO_3 or 20 percent HNO_3 + 2 percent $Na_2Cr_2O_7$) must be used for the free machining grades to avoid their being attacked during the passivation. It has generally been assumed that these solutions also dissolve iron and steel particles. This was recently shown to be untrue [9]. The present work confirmed this and some additional tests were done to simulate the behavior of isolated particles on a stainless surface.

A 0.2C, 1.3Mn, 0.2Si steel was tested as well as samples cut from M2, T1, T5, and T15 tool bits. The samples were approximately 1 by 0.2 by 0.2 cm and they were tested alone or in contact with a 10 by 10 cm Type 304 sheet as shown in Fig. 7. The results are given in Table 7.

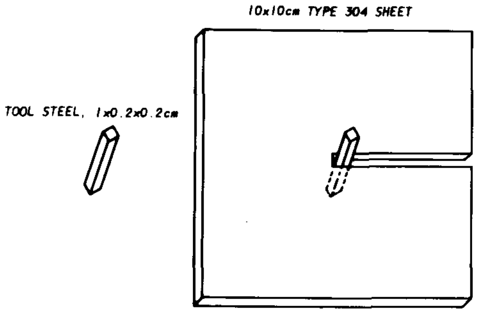


FIG. 7—*Tool steel specimen for corrosion testing with and without contact with Type 304 sheet.*

TABLE 7—*Dissolution of tool steels in passivation solutions.*

	Weight Loss[a] in 10 min Test, mg/cm^2			
	20% HNO_3,120°F		20% HNO_3+2% $Na_2Cr_2O_7$,120°F	
Steel	No Contact	Contact with Type 304	No Contact	Contact with Type 304
0.2C Steel	260	170	52/Nil	Nil[b]
M2	122	93	Nil	Nil
T1	95	89	Nil	Nil
T5	35	51	43/Nil	Nil
T15	129	76	Nil	Nil

[a] Average of duplicate tests given except where very poor duplication. 100 mg/cm^2/10 min is equivalent to about 185 000 mpy.

[b] Nil is <0.2

All of the steels dissolved rapidly in 20 percent HNO_3, as expected. Contact with a much larger area of stainless steel did not have a major influence but generally there was some decrease in dissolution rate. One might at first expect galvanic action to have the opposite effect, but it can be argued that the large cathode area provided by the stainless gave a sufficiently high current density to passivate some areas of the tool steel. The fact that the T5 steel showed the lowest dissolution rate and a reverse effect of contact is consistent with this.

None of the steels dissolved consistently in the 20 percent HNO_3 + 2 percent $Na_2Cr_2O_7$ solution. Passivating a resulfurized stainless steel will not therefore dissolve embedded iron or tool steel particles although, of course, the passivation and rinsing procedures may mechanically remove loose particles.

References

[1] LaQue, F. L., *Proceedings,* American Society for Testing and Materials, Vol. 46, 1946, pp. 175-178.
[2] Fontana, M. G. and Beck F. H., *Metal Progress,* Vol. 17, 1947, pp. 939-944.
[3] Guitton, L., *Metal Treatment,* Vol. 15, 1948, pp. 3-13.
[4] Renshaw, W. G. and Ferree, J. A., *Corrosion,* Vol. 7, 1951, pp. 353-360.
[5] Berge, P., *Corrosion et Anticorrosion,* Vol. 15, 1967, pp. 3-8.
[6] Bäcker, L. and Herzog, E., *Corrosion–Traitements · Protection · Finition,* Vol. 15, 1967, pp. 117-125.
[7] Bäcker, L., Herzog, E., and Valéro, A. M., *Revue de Métallurgie,* Vol. 62, 1965, pp. 823-833.
[8] Wranglén, G., *Corrosion Science,* Vol. 9, 1969, pp. 585-602.
[9] Henthorne, M., *Corrosion,* Vol. 26, 1970, pp. 511-528.
[10] Kovach, C. W. and Moskowitz, A., *Transactions,* Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Vol. 245, 1969, pp. 2157-2164.
[11] Defranoux, J. M., *Corrosion–Traitements · Protection · Finition,* Vol. 19, No. 7, 1971, pp. 404-410.

R. H. Shoemaker[1]

New Molten Salt Systems for Cleaning Stainless Steels

REFERENCE: Shoemaker, R. H., "New Molten Salt Systems for Cleaning Stainless Steels," *Cleaning Stainless Steels, ASTM STP 538*, American Society for Testing and Materials, 1973, pp. 106–117.

ABSTRACT: Operating conditions determine the application of acid pickling, mechanical abrasion, and salt bath conditioning for cleaning stainless steel strip. Ecology requirements favor the use of molten salt baths as conditioning agents. Reductions in the concentration of pickling acids required can be accomplished by the chemical reactions of molten salts with the oxidized surface. The combination of electrical energy and highly active chemical salt baths is an effective method of continuously descaling stainless steel strip. A new low temperature and electrolytic process which operates at 400°F (204°C) is also quite effective. The construction of salt bath equipment from carbon steel and the inclusion of sludge collection and removal systems is recommended. A system of minimizing salt drag-out on a moving strip involves the use of high pressure steam as a scrubbing media. Synchronized roll drives are a new development in continuous strip processing through a molten salt bath. Molten salt spray systems are another new addition to the processing of continuous strip. High speed lines in the future may utilize all of these developments and clean pickling without the use of strong acids remains a distinct possibility.

KEY WORDS: stainless steels, cleaning, scale removal, descaling, chemical cleaning, salt baths

Molten cleaning salts have, for many years, been a basic part of metal finishing operations in stainless, alloy, and titanium metals. The processing of bar, rod, wire, and strip on a production basis would be seriously retarded without the conditioning obtained in salt baths. The operating temperature of these baths, 400°F (204°C) to 900°F (482°C), assures the high chemical activity required for the removal of the complex oxides and scales developed in hot forming operations.

Scale Removal

The thin passivating films developed on stainless steels at room temperatures are quite chemically resistant. It is this property that permits these materials to exist for acceptable periods under corrosive environmental conditions. Oxides of these metals from hot forming at 1900°F (1038°C) or annealing at 1500°F (816°C) and 2000°F (1093°C) are also slowly soluble in conventional pickling acids. Because of these inert properties, volume production requires the use of mechanical methods or highly active chemical treatments in conjunction with

---

[1] President, Kolene Corp., Detroit, Mich. 48223.

acid baths to effect rapid scale removal. Various suggested combinations are shown in Table 1.

TABLE 1–*Scale removal methods.*

Acid pickling
Mechanical abrasion
Salt baths
Salt bath conditioning and acid pickling
Mechanical abrasion, salt bath conditioning, and acid pickling

Pickling Acids

The solubility of metal oxides in any pickle solution is proportional to the concentration of the acid and its operating temperature. The reaction rate also changes as a function of time since it varies with metal ion concentration.

Frequently, a rectified d-c current source is used in conjunction with sulfuric (H_2SO_4) and nitric (HNO_3) acid solutions to obtain specific surface properties.

Sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCL), and nitric-hydrofluoric acid (HNO_3-HF) are the mineral acids commonly used in pickling tanks. The nitric-hydrofluoric (HNO_3-HF) mixture is probably the most effective pickling media on highly alloyed material. Unfortunately, scale removal is not always a uniform rate process over a complete area. Exposed metal surfaces are subject to selective attack by aggressive acid solutions.

Most acid pickle tanks operate in a temperature range of 100°F (38°C) to 180°F (82°C) with limitations developed from the volatilization characteristics of the water-acid mixtures.

Prolonged acid pickling which can occur on heavy or difficult scales presents a problem unique to the operation. The solution of metal oxides in acids generates, through acid base reactions, considerable volumes of nascent hydrogen which may contribute to an embrittled condition.

Disposal of spent acid and rinse water is also an important economic factor. Simple neutralization of acid waste to an acceptable pH value is not a serious problem. However, the precipitation of metallic hydroxides which results from this action develops complex separation problems. These flocculent compounds are difficult to filter since they tend to form very thin impenetrable filter cakes. Consequently, large settling ponds are frequently required for separation. Table 2 lists some of the characteristics of acid pickling baths.

Mechanical Methods

Scale removal by shot blast, grinding, and flapper wheel is frequently specified in lieu of acid if oxides must be removed at very rapid rates. These systems are well suited for continuous operations because they can be placed in-line without

TABLE 2–*Acid pickling baths.*

Advantages	Disadvantages
Low temperature cleaning	Base metal attack
Rapid attack of some scales	Descaling efficiency subject to concentration
	Hydrogen embrittlement problems
	High disposal costs

jeopardizing production speeds. Chemical composition of the oxide is of little importance since removal is independent of anything but physical contact between the abrasive and the metal surface.

It would appear initially that any process which fulfills all of these requirements would be superior to other scale removal methods. Actually, there are problems with abrasive scale removal systems. First, costs can be rather high, depending upon the physical characteristics of the oxide films–breakdown of abrasive in any form is directly related to the surface hardness. Second, abrasion tends to remove only scales which can be contacted at the point of impingement–lapped areas and those sheltered by slivers are not penetrated or removed. A third factor to be considered involves the surface stresses introduced by cold working–these can be harmful to future operations. Finally, finishes resulting from abrasive action may be unsatisfactory in certain applications. Table 3 summarizes the advantages and disadvantages associated with mechanical scale removal methods.

TABLE 3–*Mechanical methods.*

Advantages	Disadvantages
Effective on all types of scale.	High maintenance costs
Rapid scale removal	Peened-in scales
Surface leveling effect	Work hardening effects
	Surface finish

Salt Bath Conditioning and Cleaning

At the present time molten salt baths are not complete cleaning systems. They must be used in conjunction with acid pickling solutions. They do drastically reduce the concentration of acids required as shown in Table 4. The data in this table was obtained from an operating anneal and pickle line processing stainless steel on a continuous basis. The acid reduction achieved with the installation not only reduces operating costs but also effects substantial savings in metal loss.

TABLE 4–*Acid concentrations before and after salt bath installation.*

	Tank 1	Tank 2	Tank 3
Before	12% HNO_3 electrolytic	18-25% HNO_3 + HF at 150-190°F (65-88°C)	6-8% HNO_3 at 70°F (21°C)
After	6-8 H_2SO_4 electrolytic	8-10% HNO_3 + HF at 125-150°F (52-65°C)	1-2% HNO_3 at 70°F (21°C)

Present and future work in the area of combined mechanical abrasion, salt bath conditioning, and pickling solutions should result in greater reductions in acid concentrations. Complete elimination of acid pickling is in the foreseeable future.

Molten salt conditioning baths are alkaline base compounds operating in the range of 400°F (204°C) to 900°F (482°C). They may be strongly oxidizing, strongly reducing, or neutral, and activated by electrical input.

The chemical reactions promoting salt conditioning are:

$$2MO + NaNO_3 = M_2O_3 + NaNO_2 \tag{1}$$

$$NaNO_2 + 0.5O_2 = NaNO_3 \tag{2}$$

$$MO + 2Na^+ = M + Na_2O \tag{3}$$

$$MO + NaH = M + NaOH \tag{4}$$

Equation 1 shows the conversion of a metal rich in oxide to a more soluble gas rich oxide by oxidation in a conditioning bath. Equation 2 indicates that regeneration of the oxidizing potential of the bath is possible by contact with atmospheric oxygen and, thereby, selective depletion of the bath is avoided. Equation 3 is the reduction of metal oxides by the sodium ion concentrated in the work area when the work load has a negative polarity—in an electrolytic salt bath operation. Equation 4 is a reduction of the metallic oxide by sodium hydride in a reducing bath producing the base metal plus sodium hydroxide.

Reactions of Molten Salts

The chemistry shown develops quite rapidly because of the temperatures involved. Immersion times can vary between 30 and 90 s which is acceptable for normal production requirements. The reactions listed in Table 5 are characteristic of all types of conditioning salts.

All molten cleaning salts have excellent solvency and complexing characteristics. They are also good wetting solutions and can penetrate even minute openings or cracks in the scaled surface. The nature of the chemical conversion resulting from salt bath treatment is dependent upon bath composition as shown in Reactions 1 through 4. Sudden cooling of conditioned scales emphasizes existing differences in expansion coefficients between the metal and its oxide resulting in spalling and cracking of the oxide film. A combination of these

TABLE 5–*Reactions of molten salt descaling baths.*

1. Solvency of glass lubricant residues or fusion with complex oxides or both.
2. Wetting and penetration of any surface irregularities in the oxide-metal interface.
3. Conversion of metal rich oxides to more soluble gas rich oxides or complete reduction to metal fines.
4. Thermal shock developed by rapid temperature change influence on oxides and base metal.
5. Little or no reaction with common base metals.

reactions produces a surface on which the oxide pattern has been eliminated or greatly reduced. Some of the most apparent factors associated with salt baths are listed in Table 6. All grades of stainless steel, including 301, 302, 304, 309, 316, 410, 430, 431, and 434, are generally conditioned in molten salt baths, followed by an acid pickle.

TABLE 6–*Salt bath conditioning and cleaning.*

Advantages	Disadvantages
Penetrates recessed scale areas	Additional operation in-line
Reacts with all types of scale	High temperature process equipment involved
No attack on base metal	Personnel resistance to operating temperatures
Minimum hydrogen pick-up	
Reduces acid consumption and disposal problems	

Salt Bath Equipment

Salt bath equipment (Fig. 1), to be fully effective, requires good engineering design to fit the individual cleaning operation. The complete system, wherever possible, should be hooded and vented for the safety and comfort of operating personnel. Either gas fired immersion tubes or electric heating may be used, with the former preferred because of energy costs. Additional developments in salt bath design, many of which have been pioneered in the past few years, include sludge collection systems, electrolytic salt bath processing, steam wipe, synchronized roll drives, and sonic spray.

Sludge Collection Systems

An efficient sludge collection system should incorporate the basic principles shown in Fig. 2. Controlled directional agitation sweeps the molten salt bath through the heat zone and back into the work zone, thereby effecting constant heat transfer and uniform temperatures in the bath. The agitation produces a

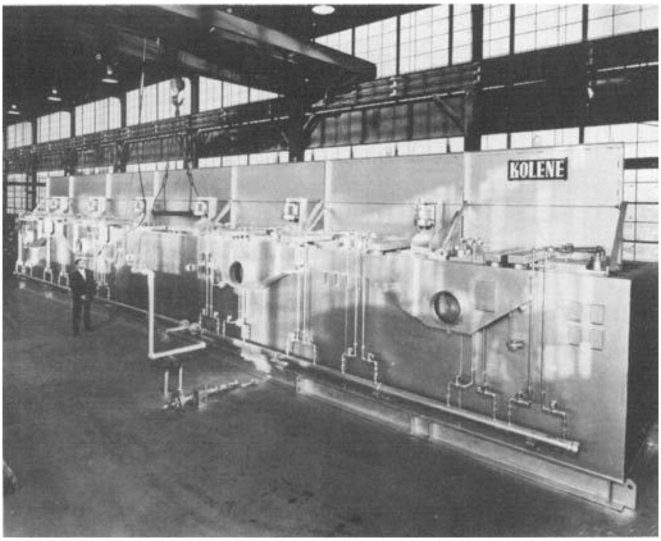


FIG. 1–*Molten salt bath processing equipment.*

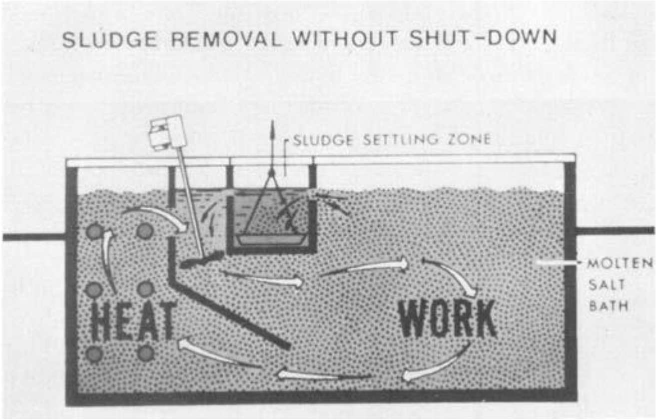


FIG. 2–*Sludge collection system diagram.*

turbulent movement throughout the work zone and the heat zone, preventing any suspended particles from settling. This aids in rapid and efficient cleaning of the work.

Concurrent with the work cycle, some of the bath passes through a small opening from the work area into the settling zone. A gate controls the rate of flow here to suit requirements. Movement of the bath in this area is slowed sufficiently for sludge to settle into a pan which rests at the bottom of the compartment. The pan is removed, emptied, and replaced periodically without interruption of the cycle. The force of the propeller causes movement but no turbulence as the clean solution leaves the settling zone through another small opening where it is drawn back into the work cycle. The effectiveness of such a system is shown in Table 7.

TABLE 7–*Simultaneous analysis of salt and sludge.*

	Na_2CO_3, %	TiO_2, %	Fe, %
Salt	9.44	0.36	0.059
Sludge	7.56	16.42	0.98
Salt	10.67	0.057	0.435
Sludge	11.40	1.07	0.37
Salt	10.79	0.335	0.047
Sludge	9.15	3.39	8.72
Salt	6.99	0.317	0.039
Sludge	10.27	4.34	0.85

An efficient desludging system not only maintains the effectiveness of the bath by continuously eliminating all waste products, but also helps to remove reaction products from the surface of the work, thereby increasing reaction rates. Since these salt baths are regenerative in nature with the oxidation potential being maintained by atmospheric contact, the removal of waste products assures maximum longevity of the bath. Numerous continuous stainless steel cleaning installations have been in operation for several years using the original salt charge.

Until quite recently, removal and disposal of the accumulated sludge has been a manual operation. Problems arose in baths subject to heavy sludge deposits if the operator neglected to pull the pan on a regular basis. To overcome this difficulty, a programmed sludge dumping system has been devised. The system operates on a preset time cycle activating an elevator type hoist which removes the pan and empties it into an accumulator. The empty pan is then returned to the sludge zone and the time cycle is automatically reset.

Electrolytic Salt Bath Processing

Salt baths which are neither chemically oxidizing nor chemically reducing can be activated to produce these conditions by the input of electrical energy. The electrical system involved is rather simple. It employs a d-c source of current, a reversing switch, a positive and a negative pole which can be either the furnace wall or the work, and a conducting media which is the molten salt bath.

The entire operation can be performed in a single salt bath furnace. However, because of the conductivity characteristics of molten salt baths, it has been found that a two furnace system is more efficient for cleaning alloy strip on a continuous basis. Here a reversing switch is not required and the strip is positively charged in the first furnace through a negative pair of grids and negatively charged in the second chamber passing through a positive set of grids. Conversion of the strip oxide is effected in the first chamber according to the following equation.

$$2MO + 2HO^- = M_2O_3 + H_2O \tag{5}$$

Scale removal is effected in the second compartment according to the following reaction.

$$M_2O_3 + 6Na^+ = 2M + 3Na_2O \tag{6}$$

A line diagram of a complete electrolytic salt bath descaling system is shown in Fig. 3. Starting from the left hand side of the figure we see the strip leaving the uncoiler, through the leveler, spot welder, looping pit, preheat, annealing furnace, and quench prior to salt bath cleaning; then through the immersion rolls and the electrodes in the first salt furnace where the strip is charged anodically, and into the second salt pot where the strip is charged cathodically and the scale removal is accomplished; finally into a water rinse, acid pickle, which may be electrolytic or nonelectrolytic, scrubbing, drying, inspection, and recoiling. Continuous strip lines of this design are presently cleaning large tonnage of stainless steel and superalloys.

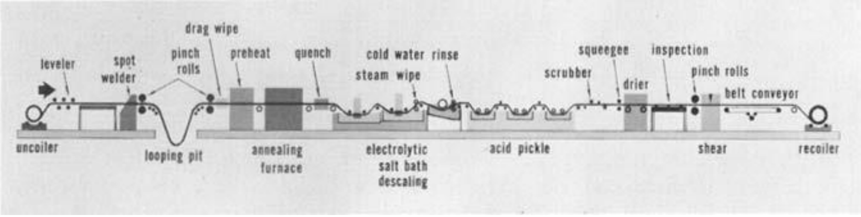


FIG. 3—*Continuous annealing, descaling, and pickling of stainless steel strip.*

Low Temperature Salt Bath Processing

A recent innovation of salt bath cleaning involves a 400°F (204°C) salt bath for conditioning stainless steel strip. The advantages inherent in a low temperature operation are numerous when one considers the flexibility possible in equipment design. Processing of light gauge strip is also simplified at these temperatures. An added bonus is the elimination of nitric hydrofluoric pickling with this system. Savings in both initial chemical requirements and in disposal costs are quite substantial.

The process is electrolytic, but final conditioning is accomplished with the strip at an anodic polarity. Unlike the high temperature electrolytic baths, reduction to base metal is not part of the system. A rather strong anodizing effect achieved under the oxidizing conditions converts the surface oxide and separates the film from the base metal. After water rinsing in a dilute sulfuric acid pickle, the strip is chemically clean and oxide free.

The 400°F (204°C) operating temperature is sufficiently low to allow the use of Teflon as an insulating material. A one salt furnace system is thus possible with the anodic and cathodic areas separated by a Teflon shield. Additional confinement of current is obtained by insulating the cathodic strip compartment to prevent flow from the electrodes to the furnace wall. Teflon roll covers aid in good strip travel and eliminate roll marks and scratching.

Steam Wipe

The viscosity of molten salt baths is quite low at operating temperature. They do have excellent wetting properties and are inclined to completely coat metal surfaces. At strip travel speeds of 50 ft/min (15.24 m) to 100 ft/min (30.48 m) a continuous strip would tend to drag out large volumes of salt. Originally, wiper rolls were used at the exit end of strip lines to force some of the salt back into the furnace. Their effectiveness was limited by the temperature of the operation and the required roll construction which was too rigid to produce good wiping action. In addition, any entrapped waste products in the salt bath could create surface problems when trapped between the roll and the moving strip.

Another approach to minimizing salt dragout is a high pressure air blast directed at the top and bottom surface of the strip at the exit end of the salt furnace. This system has been tried numerous times and, although quite effective in reducing salt consumption, it has the adverse effect of changing the chemistry of the salt bath according to the following reaction.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O \qquad (7)$$

Because the availability of carbon dioxide atmosphere in a mill is almost without limit, and because the molten alkaline based salt bath is a prime reactant with CO_2, a more efficient method has been developed.

Use of high pressure steam, which is inert to the salt bath and can be generated at a temperature above the melting temperature of the salt, has been found to be the most effective process. Steam is relatively inexpensive and can be brought to temperature with minimum cost. It is extremely effective not only in reducing costs by minimizing salt dragout, but also aiding in pollution control by reducing the solids content of the rinse water.

Synchronized Roll Drives

The use of free-turning metal rolls beneath the surface of a salt bath to guide the strip travel through the salt bath furnace is a required approach to continuous processing. This is a very simplified system and under certain conditions will operate without serious problems. The nonpositive drive does depend on the friction generated between the roll and the strip faces to cause rotation. When thin strip is being processed, the tension is necessarily low, and roll turning may be minimized or actually eliminated. Under these conditions, the pulling of the strip across the face of a stationary roll can result in serious surface damage generating large quantities of scrap.

Helper drives have been used in the past in an attempt to apply extra torque to the roll. Again, however, this system is not positive. The delicate balance between the torque applied to turn the roll and the torque applied by the strip can easily result in nonuniform travel, slippage, scratching, and marking.

The Honeywell EGT system for rotating dunking rolls in a salt pot is shown in Fig. 4. With this arrangement everything is positive and the rolls are exactly synchronized. Strip surface speed and roll surface speed are identical and nonuniform turning is eliminated. With the three axis system illustrated, no scratching is experienced as the strip travels through the salt bath and scrap generation from surface marking has been eliminated.

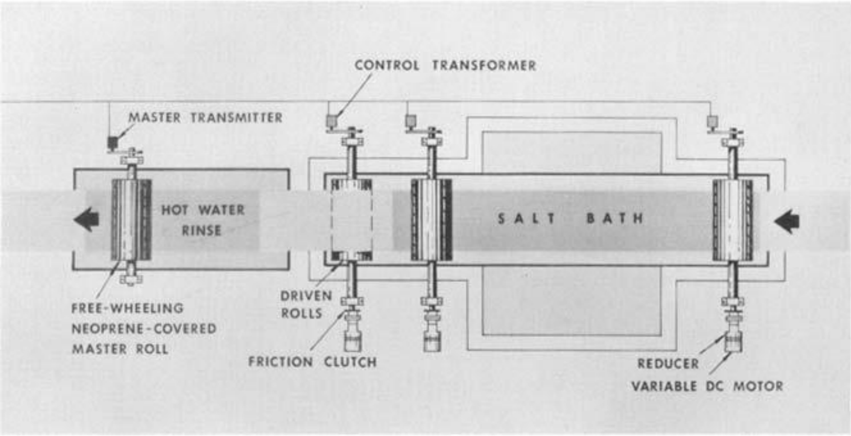


FIG. 4—*Synchronized roll drive system.*

Molten Salt Spray

Another approach to roll contact problems within a molten salt bath is one in which the rolls are completely eliminated. Figure 5 shows a system for applying molten salt to a continuous strip through ultrasonic spray nozzles. The only roll contact with the strip is at the entrance and exit end of the salt chamber, that is, from the annealing furnace and in the water rinse. Any possibility of entrapment of abrasive particles from salt bath waste products is completely eliminated.

The salt supply is maintained as a flake product in the storage area indicated and conveyed to the melting area by a lifting conveyor. The salt furnace itself is a small electrically heated melting chamber which supplies the spray nozzles by gravity feed. Steam, 800°F (427°C) to 900°F (482°C), is introduced through the nozzles to aid in salt dispersion and to maintain temperature within the chamber above the melting point of the salt mixture. The reaction of the molten oxidizing salt with the strip takes place between the point of application at the nozzles and the entrance end of the water rinse. Although this system was primarily designed to eliminate any problems with surface contact, the end

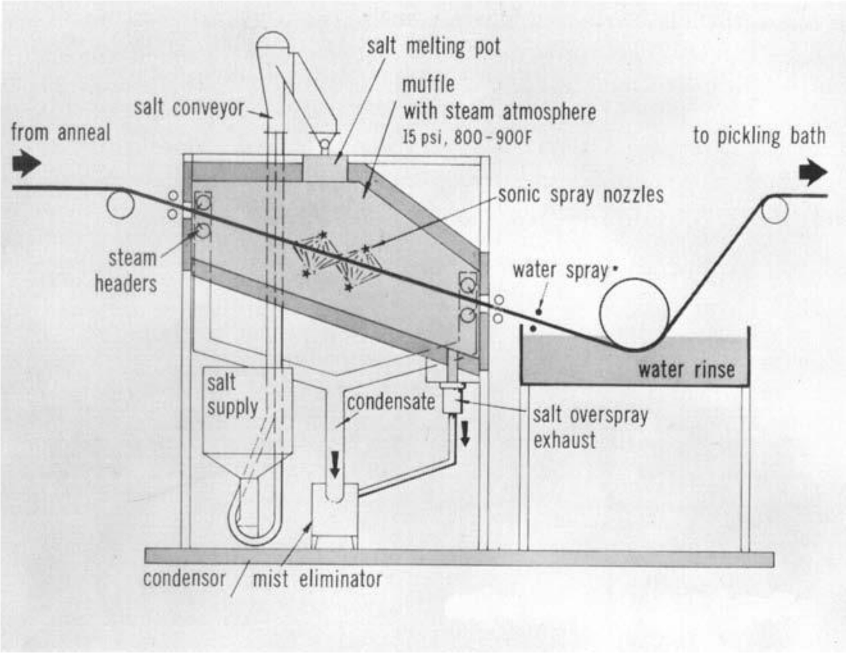


FIG. 5–*Molten salt spray descaling.*

product required a minimum pickle to obtain a clean surface. Prospects for this system appear to hold considerable promise.

Future Continuous Anneal and Pickle

Production requirements which are obsoleting present speeds will be the prime factors influencing future anneal and pickle line designs. Many of the developments just described will find wide application because of the demands for high speed lines.

Environmental control is another important consideration in the construction of cleaning facilities. The characteristics of the converted scale resulting from electrolytic salt bath processing, steam wiping, or salt spray may well influence the type of equipment included in the design. Minimum acid consumption is definitely a future goal of all metal processing technical staffs. Work is now progressing in treating converted salt bath scales with nonacid pickling solutions from which reclamation of both metal and pickle solutions is possible, as shown in Fig. 6.

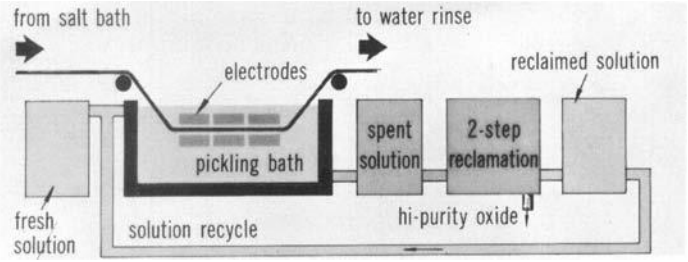


FIG. 6–*Non-acid cleaning with closed cycle reclamation.*

Conclusion

The cleaning salt bath operations described are expected to become increasingly important as ecology requirements become more complex. The manner in which a particular cleaning operation is accomplished and the waste products involved are certain to take precedence over the costs involved in replacing existing equipment. When this hurdle has been overcome, operating costs of molten salt systems will compare favorably with other methods which generate pollutants.

Jane Sorensen[1] *and George Shepard*[1]

Anodic Treatment Improves Surface Properties of Stainless Steel

REFERENCE: Sorensen, Jane, and Shepard, George, "**Anodic Treatment Improves Surface Properties of Stainless Steel,**" *Cleaning Stainless Steel, ASTM STP 538*, American Society for Testing and Materials, 1973, pp. 118–125.

ABSTRACT: Bright annealing, that is, annealing under a reducing atmosphere, is an economical method of annealing stainless steel; it has the added advantage that it prevents a chromium depleted surface such as is produced by air annealing and pickling. However, bright annealing does result in poor bright chromium platability and decreased pitting resistance. It is necessary to alter the film on bright annealed stainless steel before chromium flashing since failure to do so results in a chromium plate that has a dull gray or hazy appearance. This problem can be overcome by buffing the surface prior to chromium plating. This paper discusses a new electrolytic treatment for bright annealed stainless steel (AISI 400 series) by which the stainless steel may be plated directly with chromium without first buffing. Results of a series of experiments performed to determine the range of current density, treatment time, temperature, and pH that can be used to obtain a bright platable surface will be reported.

KEY WORDS: stainless steels, chromium coatings, anodic coatings, polarimetry, bright annealing, pitting, corrosion, cleaning

To develop the desired mechanical properties after cold rolling, stainless steel strip must be annealed for many applications so that the desired mechanical properties are developed. In conventional air annealing, chromium in the steel is oxidized preferentially and an adherent chromium-rich oxide film forms on the surface. Subsequent acid pickling operations to remove this scale may result in a chromium depleted surface that is vulnerable to corrosion [*1*].[2] Both the scaling and the reaction of the acid with the underlying metal dull the surface. After pickling, the strip is given a temper pass which may restore some, but not all of the original luster of the stainless steel. An alternative to air annealing is bright annealing, that is, annealing in a protective atmosphere to prevent formation of the oxide. No oxide scale forms during bright annealing; hence, pickling is unnecessary. Because the resultant surface is not deficient in chromium, the general corrosion resistance is superior to that of air-annealed and acid-pickled stainless steel. A temper pass will further enhance specularity or reflectivity.

Although bright annealed stainless steel (AISI Type 434) is preferred for automotive trim applications because of its corrosion resistance and relatively

---

[1] Corrosion technologist and processing technologist, respectively, Republic Steel Corp., Independence, Ohio 44131.

[2] The italic numbers in brackets refer to the list of references appended to this paper.

low cost, it too has certain disadvantages. Bright annealing reduces paintability, solderability, and pitting resistance of the stainless steel. Also of importance is the bright chrome platability. Because there is a noticeable difference in color between stainless steel and chromium plated steel, auto trim fabricators often plate the formed trim pieces with 10 to 20 μin. of chromium. This results in uniform color on all trim and matching parts. It has been found, however, that when bright annealed stainless steel of the AISI Type 400 series is chromium flashed without special treatment of the surface, the chromium plate has a dull gray or hazy appearance. This problem can be overcome by buffing the surface prior to chromium plating. The problem with buffing the stainless steel is twofold: (1) the buffing is relatively expensive, and (2) unsightly buffing lines are left on the strip. Less aggressive buffing, which would eliminate these lines, does not alter the surface sufficiently to produce good chromium plating.

Effect of Bright Annealing

To explain the effect of bright annealing, the oxide film on the surface of the steel was studied electrochemically and ellipsometrically. The latter technique was used to monitor film thickness. Figure 1 shows the potential-time behavior of bright annealed and buffed Type 434 stainless steel during activation in $1N$ H_2SO_4 (hydrogen sulfate). It can be seen that the bright annealed sample exhibited a minimum in the potential before a steady-state corrosion potential was reached. Such behavior was previously observed in borate-hydrochloric acid buffer solution by Caplan and Cohen [*2*] for iron-chromium alloys (chromium content > 11 percent) treated under oxidizing conditions. The minimum was attributed to the cathodic reaction during activation of a highly cation deficient chromium oxide layer containing Cr^{+6} ions, and to the fact that the hydrogen overvoltage must be large on the highly imperfect oxide. The existence of a defect oxide film on the bright annealed stainless steel seems to be consistent with the observations just discussed. A nonuniformly conducting film could lead to a hazy chrome plate; also the defect oxide lattice could provide readily available paths for chloride penetration, thereby leading to increased susceptibility to pitting attack.

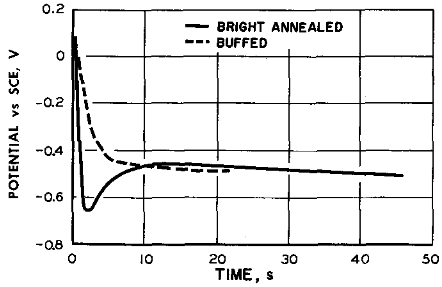


FIG. 1—*Activation curves for AISI Type 434 stainless steel in 1N H_2SO_4.*

To explain the formation of a defect oxide film on bright annealed stainless steel, a simulated bright anneal was carried out in the laboratory. Specimens of Type 434 stainless steel were heated under flowing hydrogen in an ultra-high vacuum system (Varian Associates). Temperatures in the range 250 to 950°C (484 to 1742°F) were employed. Windows in the vacuum system allowed the film thickness to be monitored ellipsometrically. Figure 2 shows the results of a typical experiment. It was found that to obtain complete reduction, temperatures higher than those ordinarily used in commercial bright annealing were necessary. From this it was concluded that bright annealing results in reduction of the less stable oxide constituents of the film, thereby leaving a defect oxide on the surface. Work recently reported by Bianchi, et al [*3*] seems to support this conclusion. They found that thermal treatments on Type 304 stainless steel markedly influenced the pitting susceptibility of the underlying metal. In particular, heating the steel for 2 h at 300°C (572°F) in dry air or 4 h at 150°C (302°F) in hydrogen resulted in an oxygen-defective nonstoichiometric film displaying *n*-type conductivity and high pitting susceptibility. Subsequent thermal treatment at 150°C in dry air for an extended period (~120 h) transformed the film into a metal defective nonstoichiometric oxide film displaying *p*-type conductivity and low pitting susceptibility.

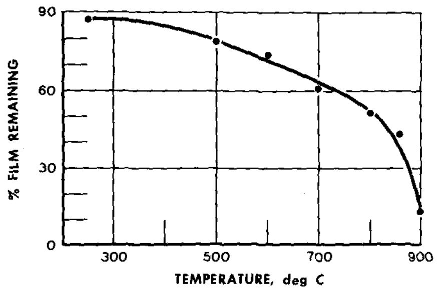


FIG. 2–*Relationship between extent of film reduction and reduction temperature for AISI Type 434 stainless steel.*

Development of an Anodic Pretreatment

Because buffing is not a completely satisfactory means for removing the film on bright annealed stainless steel, an alternative method was sought. An electrolytic method for treating bright annealed stainless steel (Type 400 series) has been developed by which the stainless steel is bright plated with chromium without first buffing the steel (see Republic Steel Corporation's U. S. Patent No. 3,642,586). The steel is treated anodically in the electrolytic bath which consists of an aqueous solution of alkali metal hydroxides buffered to a pH between 12 and 13.5. The following bath composition was used in developing treatment parameters for obtaining acceptable bright chromium plates:

Compound	*Weight*
sodium carbonate (Na_2CO_3)	40 g/liter
trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	30 g/liter
sodium hydroxide (NaOH)	20 g/liter

The effect of treatment temperature on the specularity of the subsequent chromium plate is shown in Table 1. Based on these data, a treatment temperature of 180°F (82°C) was chosen for further study because at this temperature chrome plates were bright at both high and low current densities and times. Figure 3 shows the effect of current density and time of pretreatment on the bright chrome plate range. It is evident that as the current density is increased, the bright plating range becomes narrower. Beyond 50 A/ft^2 there is no bright range. It was found also that too long a treatment time will affect the chrome plate. Long treatment times result in chrome misses, that is, areas where chromium does not plate out at all.

TABLE 1–*Effect of temperature, current density, and treatment time on the bright chromium platability of AISI Type 434 stainless steel.*

T, °F	Current Density, A/ft^2	Time, min	Specularity of Chromium Plate
120	3.7	4	hazy
140	3.7	4	hazy
160	3.7	4	hazy
180	3.7	4	excellent
200	3.7	4	excellent
120	3.7	8	hazy streaks
140	3.7	8	slight haze
160	3.7	8	very slight haze
180	3.7	8	excellent
200	3.7	8	excellent
120	7.2	4	hazy
140	7.2	4	hazy
160	7.2	4	slight haze
180	7.2	4	excellent
200	7.2	4	excellent
120	7.2	8	hazy
140	7.2	8	slight haze
160	7.2	8	very slight haze
180	7.2	8	excellent
200	7.2	8	excellent

Data concerning the acceptable range of NaOH concentrations are given in Table 2. The listed pH values were obtained by adding the required amount of NaOH to a bath containing 40 g/liter of Na_2CO_3 and 30 g/liter of $Na_3PO_4 \cdot 12H_2O$.

Following the development of the pretreatment procedure, immersion tests were run on bright annealed and pretreated materials to determine their relative

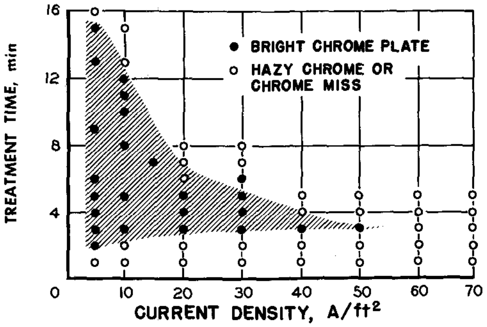


FIG. 3—*Relationship between anodic treatment time and bright chromium platability.*

TABLE 2—*Effect of treatment bath pH on the bright chromium platability of AISI Type 434 stainless steel.*

Bath pH	Specularity of Chromium Plate
11.0	hazy
11.5	slight haze
12.0	excellent
13.0	excellent
13.5	excellent
> 13.5	hazy streaks, chrome miss

pitting resistances. The results of tests carried out in two acidified ferric chloride ($FeCl_3$) solutions are shown in Table 3. Examination of the specimens undergoing the tests showed that the bright annealed samples had deep pits on both sides, whereas the pretreated panels were virtually unattacked except on the cut edges. The second immersion test employed was the "dip dry" test [*4*]. In this test 2-in.-square stainless steel panels were dipped for 1 s into a solution containing calcium chloride ($CaCl_2$), sodium chloride (NaCl), sodium sulfate

TABLE 3—*Weight loss and pit density of AISI Type 434 stainless steel in acidified ferric chloride immersion tests.*

	Solution 1[a]		Solution 2[b]	
Surface Condition	Weight Loss, $mg/in^2 \cdot hr$	Pit Density, $Pits/in^2$	Weight Loss, $mg/in^2 \cdot hr$	Pit Density, $Pits/in^2$
Bright annealed	3.0	25	20.5	250
Pretreated	0.1	0	1.0	< 1

[a] 27 g $FeCl_3 \cdot 6H_2O$ + 1.05 ml conc. HCl dissolved in one liter of distilled water.
[b] 106 g $FeCl_3 \cdot 6H_2O$ + 4.2 ml conc. HCl dissolved in one liter of distilled water.

(Na_2SO_4), sodium sulfite (Na_2SO_3), and sodium thiosulfate ($Na_2S_2O_3$). The panels then were withdrawn from the solution and allowed to dry for 100 s under a battery of heat lamps. This cycle was repeated for a period of 3 h. This procedure represents a slight modification of the original test procedure calling for only 100 cycles. As in the ferric chloride test, pits were observed on the bright annealed stainless steel but not on the pretreated material.

The effect of the anodic pretreatment on the paintability of stainless steel was evaluated. The test assemblies consisted of 6-in. lengths of painted stainless auto trim (AISI Type 434) bolted to painted 4 in. by 12 in. cold rolled steel panels by means of steel bolts. The test solution was 5 percent NaCl with a pH between 6.5 and 7.2. Typical test results are shown in Fig. 4. The test piece labeled "Production Stock" is untreated, bright annealed Type 434. It is evident from this test that pretreatment greatly enhances the paintability of the stainless steel.

FIG. 4—*Results of paintability tests on AISI Type 434 production stock (bright annealed) and laboratory treated stock.*

Effect of Anodic Pretreatment

To elucidate the effect of the anodic pretreatment on bright annealed Type 400 series stainless steel, the surface was studied electrochemically and ellipsometrically. Figure 5 shows the potential-time behavior of bright annealed and pretreated Type 434 stainless steel during activation in 1*N* H_2SO_4. It can be seen that pretreatment eliminates the minimum seen previously in the bright anneal curve and yields a number of potential arrests. These arrests are attributed to an increased amount of readily reducible oxides in the film. Electrochemical measurements show that during pretreatment the potential of the stainless steel is between +0.400 and +0.500 V (versus SCE). At these potentials the steel is transpassive (pH = 12.5 to 13). The changes in the film thickness were monitored ellipsometrically as the pretreatment progressed. During the pretreatment the Type 434 stainless steel specimen was removed from the solution periodically and ellipsometer readings taken. The data obtained are shown graphically in Fig. 6. The specimen referred to as "MgO polished" was bright annealed stainless steel that was polished with magnesium oxide prior to pretreatment to reduce the initial film thickness. Δ, a directly

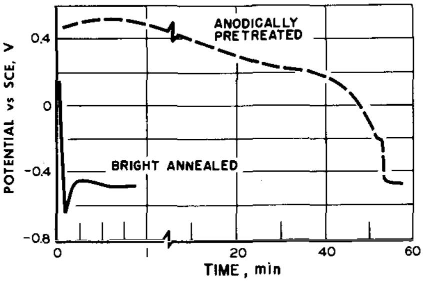


FIG. 5—*Activation curves for AISI Type 434 stainless steel in 1N* H_2SO_4.

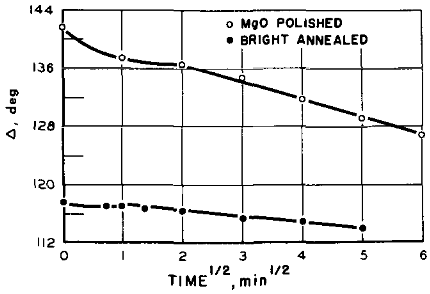


FIG. 6—*Rate of film growth during anodic oxidation of AISI Type 434 stainless steel.*

measurable quantity, is the phase difference of the polarized light. For the relatively thin films of interest here (<200 Å), it was assumed that Δ decreases linearly with an increase in film thickness. In the early stages of the reaction the film grows slowly or not at all, depending on the initial film thickness. It is postulated that this is a result of competing reactions involving film growth (diffusion of ions into the film) and film dissolution (formation of $CrO_4^=$ and $FeO_4^=$). The former tends to "heal" the defect lattice while the latter tends to remove it from the surface. Finally, a uniform film is established over the entire surface and the steel will now take a bright chromium plate. Apparently, the uniformity of the film also results in increasing the pitting resistance of the steel. Following this, a linear dependence of Δ on $t^{1/2}$ is observed. If film growth is allowed to continue, the surface is so affected that chrome "misses" are observed. It is possible that the relatively thick oxide film that results from long treatment times changes the efficiencies of the cathodic processes taking place on the surface during chrome plating.

Conclusions

Ellipsometric and electrochemical studies have shown that bright annealing AISI Type 434 stainless steel results in an oxygen-deficient film on the surface of the steel. It is this film that is responsible for the decreased bright chromium platability and decreased pitting resistance of bright annealed stainless steel. A method of anodically pretreating the bright annealed stainless steel in a caustic bath has been developed. This anodic pretreatment changes the oxide film on the surface in such a manner as to improve the bright chromium platability and pitting resistance of the steel. It has also been found that the pretreatment improves the paintability of the stainless steel.

References

[*1*] Trax, R. V. and Holzwarth, J. C., *Corrosion*, Vol. 16, No. 6, June 1960, pp. 271t-274t.

[*2*] Caplan, D. and Cohen, M., *Journal of the Electrochemical Society*, Vol. 108, 1961, pp. 1005-1008.

[*3*] Bianchi, G., Cerquetti, A., Mazza, F. and Torchio, S., *Corrosion Science*, Vol. 12, 1972, pp. 495-502.

[*4*] General Motors Product Engineering Test Method #1025.

T. L. Griffin[1]

Vibratory Cleaning, Descaling, and Deburring of Stainless Steel Parts

REFERENCE: Griffin, T. L., "Vibratory Cleaning, Descaling, and Deburring of Stainless Steel Parts," *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 126–134.

ABSTRACT: There are four basic types of mass finishing machines used in producing clean, burr-free, stainless steel parts: rotary, centrifugal, spindle, and vibratory. This paper traces the history of the development of the equipment and techniques from early Egyptian times and discusses the relative merits of each. The paper reviews new developments in handling equipment, which allow systems to be automated, and it examines several basic types of compounds and abrasive media used for cleaning, descaling, deburring, and burnishing stainless steel parts.

KEY WORDS: cleaning, stainless steels, descaling, deburring, finishing

In olden times artisans fabricated metal into functional parts for use on such items as knight's armor. While functional, these parts also had to look well. Larger parts were sanded and polished by hand, but smaller parts presented more of a problem for the finisher—they were hard to grip and many times had various designs worked into them that were difficult to finish, resulting in many hours of laborious handwork to produce one finished part. At some undetermined point in time, one of the more enterprising artisans found that when he put these small parts into a keg filled with sand, and caused the keg to be rolled, back and forth, along the ground for a given length of time, the small parts were smoothed and polished much more satisfactorily than anyone had been able to do by the most painstaking hand method. Another unidentified craftsman discovered that the results were even better, with less work, if he hitched the keg to a water wheel. Thus, the art of mass finishing was born, and even today, there is at least one water-driven "tumbling" barrel at work grinding and polishing semiprecious stones for the "rock hounds" fraternity in the New England area.

This system of finishing has been refined through the years to the point where it has become an indispensable tool for the modern finishing engineer. Although we call this process mass finishing, terms such as "tumbling," "rattling," "rolling," "tubbing," "rumbling," and others have also been used to describe the same basic process. In a somewhat simplified form, all these processes use some kind of a machine to move a load of parts, media, and compound for a given time to produce a smooth, uniformly burr-free part at a relatively low unit cost.

---

[1] Product manager, Hubbard-Hall Chemical Co., Waterbury, Conn. 06720.

The various types of modern-day finishing machines will be presented, along with commentary on media, compounds, and other aspects of the mass finishing process.

The Tumbling Barrel

For many years mass finishing was done with a machine that incorporated a hexagonal, or octagonal, shaped barrel mounted on a central axle and rotated by an outside power source—in very early times by water power, later by belts driven by steam engines, and in more recent years by self-contained electric motor drives. These modern tumbling barrels, or more properly, tumble finishing machines, have safety guards to stop the rotation of the barrel automatically to protect the operator from becoming entangled in the mechanism, have fully variable speed drive systems for better control, and provide very economical and trouble-free operation. Work on the parts is performed as the barrel revolves, which produces a sliding action on the parts and media as they "tumble" from the top of the slide to the bottom where they "tuck under" and ride back to the top of the slide again—very much as people ride on a Ferris wheel. As the parts proceed down the sliding layer the media "scrubs" them to remove sharp edges and, given sufficient time, produces smooth, burr-free parts. The major disadvantage of this type of equipment becomes evident during the loading and unloading portions of the cycle. Loading of quantities of parts, particularly large sized parts, to satisfy large volume production requirements, resulted in tumbling barrels of as much as 100 f^3 capacity and more. This, in turn, requiring much larger overhead cranes and hoisting systems to handle the large loads.

The greatest difficulty was experienced when it came time to rinse the load. On the majority of tumble-finishing machines a removable door is provided on one of the flat sides of the barrel for loading and unloading purposes. Although these doors are provided with gaskets to prevent leakage, the gaskets are invariably damaged, causing the solution of water and compound in the barrel to leak out during the finishing cycle, thus producing poor results. During the tumble-finishing cycle, the grinding action of the media and parts produces small particles of metal and abrasive which are called "fines." In order to obtain clean parts these fines must be removed from the barrel by a rinsing process. To accomplish this on a large tumble-finishing machine is no easy feat. The solid door of the barrel is replaced by a door with a perforated panel to allow the solution of water and compound, but not the parts and media, to drain from the barrel. Then the barrel is refilled with water, rotated several times to agitate the fines inside, stopped, and allowed to drain again. Unfortunately, the load consisting of parts and media in the average tumbling barrel acts as a very efficient gravel type filter bed. Thus, the fines remain trapped in the load even though the rinsing process is repeated several times. Since all of the fines were not removed, the pores of the abrasive media would become clogged with fines, or "glazed." Glazing prevents the abrasive media from performing its normal cutting action and results in a drop in efficiency in the finishing department. The result of this meant that, although adoption of tumble-finishing machines for deburring, descaling, etc. resulted in substantial cost savings over laborious hand finishing methods, there was still a great deal of expensive direct labor required for loading, unloading, and rinsing, and it took considerable manual effort to manipulate the large size loads involved.

Centrifugal Finishing Machines

The centrifugal finishing machine is a fairly modern development in the finishing field, coming into prominence in the early 1960s. There is at least one example of this type of finishing machine, which still exists, that was used in the late 1800s for finishing spinning rings in the textile industry. This type of machine is used today primarily for finishing very small parts, such as miniature precision bearings, or parts that require very small sized media to perform the required finishing operation.

In practice, the parts and media, along with water and a suitable compound, are placed into a cylinder that is constructed along the same lines as a standard tumbling barrel. Instead of revolving about a central axis, however, this container is mounted on the periphery of a large disc—usually in diametrically opposed pairs to maintain a balanced condition. The disc is then rotated at a relatively high speed, on the order of 250 rpm for a 48 in. diameter disc, which produces a centrifugal force on the contents of the barrel forcing the contents to the outside wall of the barrels. The barrels are then rotated, by a connecting mechanical drive system, so that the parts and media "tumble" under the forces created by the centrifugal action. In this type of machine the media can have an effective weight of as much as 25 times its own "normal" weight, which then allows it to "scrub" the parts very effectively. The average deburring time in the centrifugal machine is measured in terms of a few minutes in most cases. Because of this very short finishing time the direct labor cost factor is generally higher for this type of machine then for either the tumble-finisher or vibrator. The centrifugal method is utilized mainly for parts that do not lend themselves to tumbling or vibratory finishing.

Spindle Finishing Machines

Spindle-finishing machines have been developed to provide a low-cost means of finishing large, expensive, precision parts, such as gears, turbine wheels, etc. In most cases a very fine abrasive media that "form-fits" itself to the contours of the part is swirled past a "form-fitting grinding wheel." The part is fixtured to a rotating spindle which is lowered into the abrasive mass as it, in turn, is moved in a circular pattern by means of a rotating tub to "scrub" all surfaces of the part. To reduce direct labor costs there are usually two spindles provided so that the operator can be changing one part while the machine is processing a second part. These are also somewhat specialized units designed to handle parts that are not really suited to mass finishing techniques in tumble-finishers or vibratory units.

It should be pointed out that both the centrifugal and the spindle finishing machines can be very valuable tools in aiding the finishing engineer in reducing costs, if the parts that he is responsible for are suited to either of these machines. This can be determined very easily by submitting sample parts to the manufacturers of these machines for experimental finishing purposes. Most manufacturers provide this service free of charge.

Vibratory Finishing Machines

The first vibratory finishing machines appeared on the scene in the mid-1950s. The very early models, like the tumbling barrel, continued the practice of unloading by turning the work container, most commonly called the "tub," on its side. Rinsing was accomplished by filling the tub with water, agitating the load briefly, installing a perforated cover, and turning the tub on its side to allow the water to drain out. Unfortunately this, again, produced a very efficient gravel pack filter bed, and rinsing in those early vibrators was no more effective than in the tumbling barrel. The open top tub made loading the machine a little easier, and the fact that the load could be observed while the machine was operating provided a means of inspecting the parts to determine if the necessary work had been performed at any time during the cycle. This is not possible in tumbling where the machine has to be stopped and the door removed before the work can be inspected. The vibratory unit also does the same amount of work in a much shorter time period, due to the fact that the scrubbing action of the media on the parts takes place 100 percent of the time instead of the approximately 30 percent of the time that work actually is done in the sliding layer of the tumbling barrel. The vibratory machine will also accomplish work on internal, or protected, areas of parts that cannot be done in a tumbling barrel.

Many engineering changes have taken place in the vibratory units and today the modern vibratory finishing machine is one of the lowest cost and most efficient mass finishing methods available. Modern vibratory units are trouble-free and require a relatively small amount of maintenance. Most are provided with automatic lubrication devices to assure proper lubrication of the bearings which are the heart of any vibratory unit. Vibratory machines are built in two basic types—the tub type and the bowl type. Both types utilize built-in drains to allow a solution of water and compound to be continuously metered into the load and carry out the fines to a sump where the fines settle out. The fines are removed at regular intervals and disposed of—most probably in a sanitary land-fill. This system produces a constantly clean load of parts and media. The media remains clean and sharp to provide maximum finishing efficiency. Because the parts remain clean the direct labor cost formerly required for rinsing in the tumbling barrel operations is completely eliminated. Various types of metering devices have been developed which will feed the chemical solutions automatically and allow changing from one solution to another as required. Material handling devices have also been developed which further allow the vibratory machine to be semi or fully automated, thus helping to reduce direct labor costs even further. With the use of these various devices it is now possible to engineer the equipment to load the media, add the parts, add a descaling compound for 20 min, rinse for 3 min, and neutralize, then burnish for 30 min, including reducing the speed of the machine automatically to provide a more gentle action for burnishing. The machine will then unload itself, separate the media from the parts and reset itself for the next batch of parts. Heavy-duty machinery now allows the use of steel media, where applicable, and loads of 300 lb per ft^3 are not uncommon today.

Media

Finishing media is available in a wide assortment of types, sizes, and shapes to fit just about any requirement, and they are divided into four basic groups: manufactured, natural, metallic, and agricultural. Manufactured abrasives used for mass finishing are mainly aluminum oxide and silicon carbide, both products of the electric furnace, which are crushed into chunks, washed, screened, and packed in a range of sizes from approximately 1 1/2 in. in diameter down to the fine flour sizes. Random shaped aluminum oxide media remains the most economical material for use in mass finishing. The major disadvantage to the random shaped material it its tendency to become lodged in slots, holes, etc., in the more intricately shaped parts which are being processed in vibratory finishing machines. The added costs for hand removal of lodged media resulted in the development of "preshaped" media. These are manufactured from various combinations of abrasive grain and bond types. One of the first combinations was the triangular shaped media using a vitrified, or ceramic, bonding material. These are manufactured by mixing the abrasive with a clay type material, pressing them to the desired shape, and firing them in a kiln to fuse the clay-like bonding material into a glassy ceramic matrix which contains the abrasive particles. The main advantage of these materials is to eliminate wedging and lodging, and to enable the media to remove burrs from protected areas that could not be accomplished by random shaped materials. Many new shapes have been introduced in recent years until today the finishing engineer can choose from a wide variety of shapes and sizes and is almost sure to find at least one to suit the requirements of the job. Silicon carbide abrasives are also used in manufacturing these preshaped products and, in some instances, have eliminated certain problems seemingly inherent in the use of aluminum oxide material, as in the electronics industry. Plastics have become increasingly popular as a bonding material and have been used widely with the lighter metals such as aluminum. The use of a plastic bonding material gives the media engineer much more freedom to design special shapes for certain jobs—shapes that would not be economical to produce in ceramic bonded media, mainly because a very large run of a given size of ceramic media is required to justify the use of the cost of operating the kiln. Plastics are self-curing and eliminate the cost of the kiln, and are, as would be expected, not as costly to produce.

Natural abrasives are used less today as media, although limestone and granite are still used to some extent primarily for such jobs as descaling axe-heads (a very rough, tough, job that has to be done fast and at minimum cost). The natural abrasives are being used more in combination with the plastic bonding materials for use on such metals as aluminum to provide an economical, yet very effective media.

Metallic media is used in only limited cases in vibratory equipment. Most vibratory machines today are sturdy enough to stand up under the heavy loads imposed by the use of steel media, and the combination is being used more and more by such industries as the hardware industry to produce economically a burnished part prior to plating or, in the case of brass plated on steel, to burnish to a high luster after plating. Metallic media is also available in the stainless steel alloys for use in such jobs as burnishing stainless steel bathroom fixtures.

The agricultural materials are primarily sawdust or ground corn-cob or both, and they are used mainly to dry parts after the finishing operation. Some industries, such as the plastic industry, use these products as carriers for abrasives, etc. for processing their parts without water and, in that case, the agricultural products are certainly a key material.

Compounds

Detergents, soaps, abrasives, and other constituents, are blended in various proportions to form what we refer to as "compounds." These compounds are divided into several basic categories and we will explore each of the categories in this paper.

The first category, and probably the most widely used, is the detergent type of compounds which are designed to keep the abrasive media open and free-cutting, provide lubricity, and prevent corrosion of the metal—a somewhat secondary consideration in the case of stainless steel parts. The detergent types are sometimes called "cutting" compounds, even though they contain no abrasives themselves because of the manner in which they promote the "cutting," or grinding, action of the abrasive media which are most commonly used in the deburring operation. These compounds are available in powder or liquid form and are formulated with a pH ranging from mildly acidic (5.0 to 6.0) through neutral to highly alkaline (12.0 to 13.5). The highly alkaline materials are used on ferrous metal parts because they are very efficient cleaners, provide corrosion protection, and are economical. Neutral and slightly acidic compounds are designed for use with the nonferrous metals and suit the stainless alloys quite well. Formulations of these compounds vary widely and the choice of the "best" compound for a given job is determined by the type of part, burr condition, surface finish requirement, and soils. Careful consideration should be given to the type of soil that will be on the part—especially where heavily fortified lubricants have been used in the fabricating or machining operations.

In the past it was best practice to remove oils, greases, and other shop soils, in a separate cleaning operation before placing the parts in the tumbling barrel. Most pre-tumbling cleaning operations were done in vapor degreasing units, using triclorethylene. This separate cleaning operation presented another significant cost in manufacturing a part, and also a serious "ecology" problem, since triclorethylene, for all practical purposes, has been banished from the manufacturing plant. Modern vibratory equipment systems have eliminated both of these problems with their built-in compound solution "flow-through" systems. Cleaning of the toughest oils and shop soils is accomplished very easily by constantly feeding the proper solution of water and compound through the machine during the finishing cycle. Demand for liquid compounds which can readily be put into solution with the cold water generally used in vibratory machines has led to the development of an entirely new family of cleaning compounds which are easily mixed in cold water. Most liquid compounds are mixed with water at a 1 or 2 percent concentration and fed into the vibrator with a simple pump or even by gravity feed. Some systems use aspirator type feeders, where the compound solution is made up as a concentrate at 10 to 20 percent and then reduced to the 1 to 2 percent range as it is drawn through the aspirator feeding device.

These compounds are particularly well suited to vibratory deburring operations and provide maximum operating efficiency by keeping the pores of the abrasive media open, thus allowing the media to "grind" at its maximum rate. This, of course, means that the deburring is done in a much shorter time period which not only reduces the overall cost of deburring a given part but also results in much better machine utilization—another most welcome means of reducing overall costs. The soils created by the deburring operation consist of "fines" which come from the metal being removed in the form of burrs, and from the abrasive media as it is worn down while doing the required deburring. These fines are picked up by the compound and water solution and carried out of the load through the built-in drains. At the same time fresh solution is constantly being introduced into the load so that the parts are always in a "clean" condition. The load can be inspected at any time and the machine unloaded with the very great benefit of being able to take the parts directly to the next finishing operation, with no additional rinsing or cleaning operations necessary. Since this type of finishing operation produces a very clean, active, metal surface it is possible to go directly into a plating bath, with no additional cleaning operations required.

In most systems the spent solution from the vibratory units is led directly to a settling basin where the solids settle out and the remaining liquid is allowed to go directly to the sewer. Where the neutral pH compounds are used, no further waste treatment is required. If acid or alkaline solutions are used it may become necessary to perform a pH adjustment before allowing the effluent to proceed to the sewer system. In most plants where the waste liquid is allowed to mix with other plant waste waters the pH adjustment would probably not be required at all. Compound manufacturers are very much aware of the waste treatment problem and, in most cases, can provide a suitable compound which would not require treatment.

Descaling Compounds

Another category of compounds involves those used for descaling, derusting, bleaching, and brightening of parts. These are the soluble acidic materials, either powder or liquid, with a pH range of 1.0 to 3.0 when in solution. These materials are generally known as "descalers" and are designed to be used in conjunction with abrasive media to rapidly remove heat-treatment scale, and other oxide films from parts—leaving the parts with a "whiter" color than that obtained even by acid pickling. They can also be used, at lower concentrations, for the removal of oxide films from nonferrous metals such as aluminum, brass, and zinc. Another important use is for the removal of the dark "cast" produced by long runs in aluminum-oxide media, more commonly called "bleaching." Use of this intermediate step prior to a burnishing operation produces a markedly brighter and more lustrous finish. An important point to remember about these compounds, when running ferrous metals, is that they must be neutralized immediately by an alkaline solution to prevent flash rusting and staining of the finished surface. Here again, compound manufacturers have developed compounds which will do an excellent job of removing scale, rust, and stains, but which have a pH of 6.0 and require no neutralizing operation, thus reducing the overall cost of the descaling operation.

Burnishing Compounds

A third category of compounds is the burnishing group, most of which rely on varying amounts of soaps to produce a slippery, viscous film on the parts, and to coat the media in such a manner that it can no longer act as a "cutting" material. The sliding, rubbing, or burnishing action of the media and parts produces a smooth, lustrous finish on the surface of the part. It is well to remember that the media must be thoroughly cleaned after a burnishing operation before it can be used for deburring again.

Burnishing compounds have been used to great advantage for years in tumbling barrels to produce burr-free parts with a highly lustrous finish. They have not, however, been used in vibratory machines, to any great extent, because of their high level of foaming. Most vibratory units are of the open-top design and the burnishing compound solution tends to foam over the top of the machine. This not only creates a housekeeping problem in the finishing area but, more importantly, dries out the load and "kills" the vibratory action of the parts and media. Compound manufacturers are working on new formulations for use in vibratory units which will produce acceptable burnished finishes, and much progress is being made. These compounds are divided into four basic groups—soap base, synthetic surfactant base, high alkaline inorganic chemical base, and blends of all three. The choice of the "best" one for a given job is generally determined by experimentation since the parts, media, type of machine being used, and even the water hardness vary widely.

Abrasive Compounds

The fourth category of compounds is the abrasive-containing variety, commonly called "abrasive" compounds. They are used mainly to refine surface finishes or to add a cutting action to a load of parts running without media (known as self-tumbling). Some of the abrasives used in the manufacture of these compounds are silica sand, quartzite, aluminum-oxide, silicon-carbide, emery, pumice, etc., and many combinations of these ingredients. The best abrasive compound for a given job is determined by the metal, type of finish required, and the final finish to be put on the part. Smooth finishes are not always desired; for example, in the manufacture of buttons a coarse abrasive is used to produce a scratch pattern on the button, which is then brass plated to produce a very attractive "antique" finish. Length of time cycle can be controlled by choosing a compound with the proper size abrasive grain, available from 60 grit down through the fine flour sizes. Abrasive compounds can be used to great advantage in semi or fully automated vibratory systems in which the compound is fed into the machine automatically to perform the required grinding, deburring, or radiusing. Once the desired surface finish is attained, automatic feeders flush out the load with a cleaning solution and follow up with a burnishing or corrosion inhibiting solution as required. Thus, as an extreme example, parts having a micro-inch finish of 60 rms can be automatically processed, without operator attention, to a finish as low as 2 rms by setting the feeders to introduce the proper abrasive compounds in sequence. This roughly duplicates the action of polishing a part by starting with a 60 grit belt, followed by finer grit sizes down to the last very fine grit belt. Recent experiments, using this "total systems" approach, have demonstrated that significant cost savings are attainable. An added advantage is that parts done by this method can be plated without hand buffing and still have a very attractive lustrous finish.

Summary

It is important to realize that the deburring, descaling, and cleaning of stainless steel parts in mass finishing equipment is not much more difficult than any other metal. The problem lies in choosing the right machine, media, and compound to produce a finished part successfully. The basic features of mass finishing–low cost deburring, radiusing, stress relieving, improvement in fatigue life, and surface refinement–can be applied to the stainless alloys with the right engineering approach. It is urged that any finishing engineer faced with the problem of producing quality parts at the lowest possible unit cost should call on the manufacturers of equipment, media, and compounds.

R. S. Cremisio[1]

Extrude Hone Process and Its Applications to Stainless Steel Compounds

REFERENCE: Cremisio, R. S., "Extrude Hone Process and Its Applications to Stainless Steel Components," *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 135–146.

ABSTRACT: The Extrude Hone process is a unique metal finishing technique used for polishing, deburring, sizing, radius generation, and surface removal. The paper presents the basic theory and components involved in the proprietary process. Detailed data is presented on process capability and requirements. A review of current process application is made to illustrate the versatility and cost effectiveness of the process.

KEY WORDS: stainless steels, cleaning, honing, extruding, polishing

The Extrude Hone process is a method to abrade and polish stainless steel and other metal surfaces by flowing a viscous, semisolid abrasive laden "putty" under pressure. In order to contain and specifically direct the flow of the putty-like media, the part or area of the part to be abraded is normally confined within a fixture, between the two opposed media chambers (or cylinders) of an Extrude Hone machine. Under hydraulic pressure, the media is extruded from one media chamber, through or along the part held in its fixture and into the opposite media chamber. In most applications the media is extruded back through the part into the original chamber. The amount of abrasion that is accomplished with a given media is directly proportional to the quantity of media flow. Depending upon the function to be performed, adequate flow quantities may range from a few cubic inches to several thousand cubic inches.

There are three major elements in the system: (1) an Extrude Hone machine to accomplish and control the media flow; (2) the tooling to confine and direct the flow; and (3) the Extrude Hone media. Within each of these elements there are several variables which may be altered to achieve various results.

Extrude Hone Machine

An Extrude Hone machine (Fig. 1) is an apparatus designed to force the specially formulated abrasive media through or along a work piece. The basic machine is comprised of a hydraulic power system, support frame, two directly opposed media chambers, and respective electrical controls.

The hydraulic power system produces the force required to move the media

---

[1] Consultant, Extrude Hone Corporation, Irwin, Pa. 15642

FIG. 1—*An Extrude Hone machine.*

and clamp the supporting fixture in process position between the upper and lower media chambers. Each media chamber consists of a cylinder and a piston attached to and driven by a hydraulic ram. The lower media cylinder is prefilled with specially formulated abrasive media and is attached to the stationary machine base. The upper media cylinder is attached to the vertically moving machine head assembly that lifts for loading and unloading fixtures holding the work piece. The head assembly moves down to clamp tightly on the fixture to form a closed-loop system.

During the typical process cycle, the semisolid abrasive laden media is forced from the lower media cylinder, up through the fixture and work piece, and into the upper media cylinder. Direction of media flow is then reversed and the media passes down through the fixture and work piece and into the lower media cylinder, completing one machine cycle.

The magnitude of a single cycle may be controlled by time, volume, or a number of complete cycles may be preset for applications requiring multiple cycles. The time required for a complete cycle is dependent on the cross sectional opening that the media is to flow through and on the media's viscosity. The minimum complete cycle time is 10 to 15 s when the machine is fully loaded with media.

The major parameter to be controlled with the machine is the total volume of media allowed to flow through the part. The quantity of metal removed is directly related to the quantity of media flow. Normally, media flow quantity is controlled by timing the flow with a preset media flow time, or by presetting a certain number of complete machine cycles. If precise measurement of the quantity of flow through a part is necessary, an option is available providing digital readout of the volumetric flow in cubic inches.

In the automatic mode, processing continues until the preset volume of media has been flowed through the part in both directions. Hydraulic pressure controls permit the pressure used to force the media through the part to be varied from 100 to 1600 psi. With some machines the pressure in the top and bottom cylinders may be independently controlled. Generally, the maximum available pressure is used in order to maximize flow rate and minimize the processing time. Flow control valves permit controlled media flow rates.

Tooling

The tooling performs five basic functions: (1) holds the part in position, (2) directs media flow through or along the part, (3) provides a restriction in the media flow path, (4) protects an edge or surface from media flow, and (5) aids in part loading, unloading or cleaning.

Often urethane or some other plastic material is used on contact surfaces to prevent impinging the part with loose abrasive grains in clamping. The part must be held firmly in position and sealing must be accomplished in order to separate input and exit flow paths for the media through the part.

A basic principle of Extrude Honing is that only at the greatest restriction in the media's flow path is it significantly abrasive. Depending on the configuration of a part and the function to be performed, the part may be thought of as one of three conceptual forms for the purpose of Extrude Hone flow: (1) sleeve, (2) tube, and (3) plug within a tube. Any part will fit into one or more of these categories.

Any configuration which can be made to appear as a cavity with significantly smaller intersecting passages becomes a "simple sleeve" for extrude honing purposes. This includes hydraulic valve sleeves, (Fig. 2), bearing cages, hydraulic manifolds and housings, jet engine turbine hollow vanes and tubes with air cooling holes, fuel spray nozzles, microwave tubes and waveguides, automobile transmission shafts and master brake cylinders, rocket arms, and engine cylinders, as well as a myriad of other parts (Fig. 3).

The proper flow path through this type of part (Fig. 4) is into the cavity and exiting from the smaller, intersecting passages. Normally no stock removal

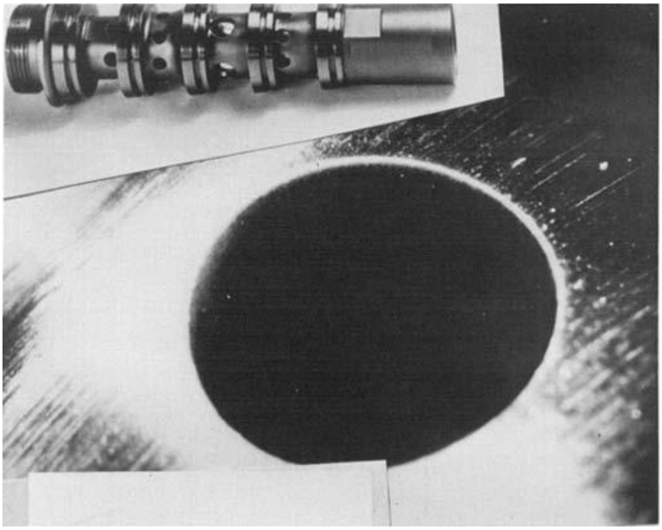


FIG. 2–*Enlargement of cross hole in hydraulic sleeve shown above following extrude hone processing.*

occurs in the cavity, for only as the media enters intersecting passages is the media flow path restricted. A comparison of the total cross sectional area of the cavity and all the intersecting passages must be made to verify this.

If the part does not have the configuration of the sleeve group, it may be processed as a "tube." This group includes rifle, shotgun and cannon barrels; extruding, compacting, cold heading, and drawing dies; glass bottle molds; sewing machine throat plates; ceramic yarn guides; internally splined gears; printed circuit boards; grid plates; wire wrapping tubes; power generating turbine multiple blade sections; and any other part whose configuration provides an enclosed flow passage.

External edges and surfaces can be processed by fitting the part within a flow passage so that media is restricted, as it passes the part, by both the surface of the part to be abraded and the wall of the fixture at that point. A hydraulic pump rotor would fit this category (Fig. 5), since in processing it is held as a plug within a tube. The external surface of nearly any part can be processed in this way.

Mandrels or plugs may be set in the tooling to provide restriction points at areas where abrasion is desired. Surfaces or edges, where no abrasion is desired, may be masked with tooling.

Media

Media is specially formulated to meet specific process and finishing requirements. The basic media formulation is composed of a media base (or vehicle), an abrasive grain, and one or more proprietary additives.

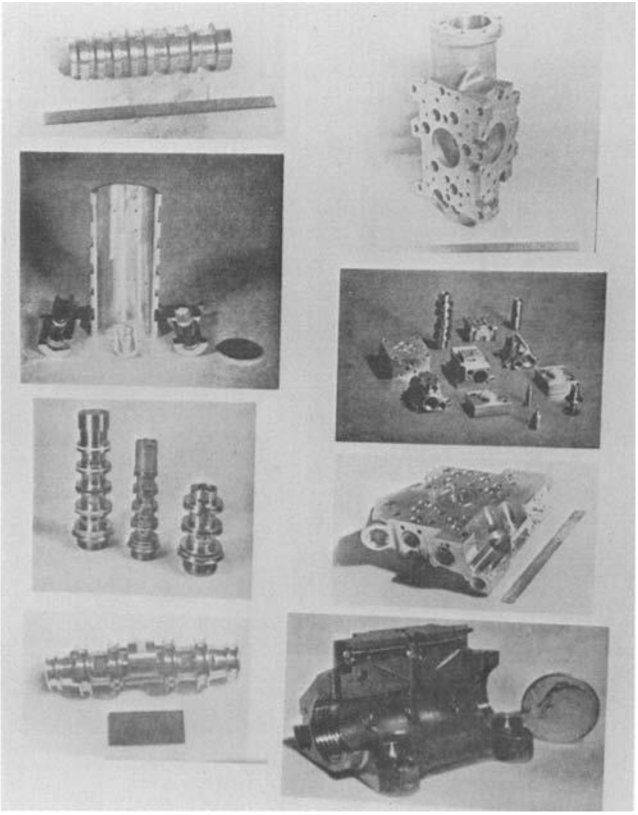


FIG. 3–*Examples of parts treated as "simple sleeves" in extrude honing range from hydraulic and pneumatic spools to complex valve bodies.*

The media base has a range of several very useful variables. Viscosity is perhaps the most important. Ideally, the media should be sufficiently viscous to flow through the restricting passage as an almost solid slug. It should also, however, flow as fast as possible to achieve maximum efficiency. Viscosity is important but need not be precisely controlled, and a given viscosity material may be suitable for a generous range of passage sizes.

Cohesion and tenacity are parameters describing the media's tendency to hold itself together; cohesion when idle, and tenacity during flow. Large or small edge radii can be generated on a work piece by altering the tenacity of the media.

Lubricity, rheology (how viscosity changes under shear), temperature stability, and solubility are other important factors which may be altered for various desirable results.

Abrasives used include aluminum oxide, silicon carbide, and boron carbide. The size of the abrasive grain is a dominant factor in determining stock removal rates and surface finish achieved. Sizes range from 8 to 500 grit, with a range between 24 and 150 the most common. Exceptionally fine surface finishes can

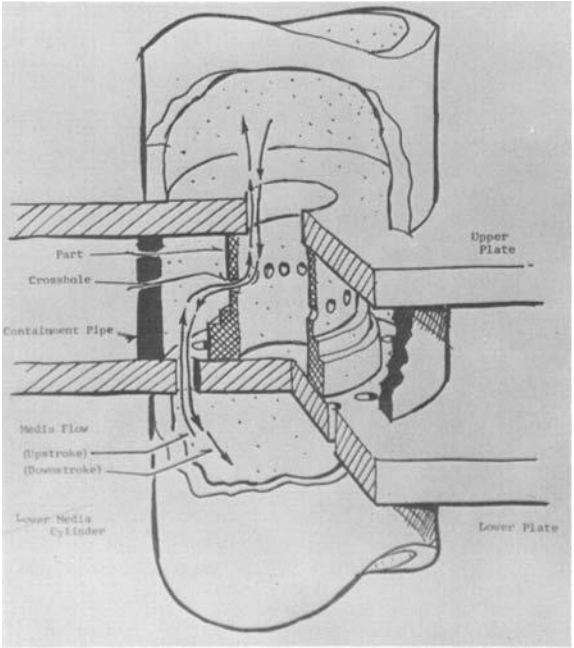


FIG. 4—*Extrude honing of a simple sleeve.*

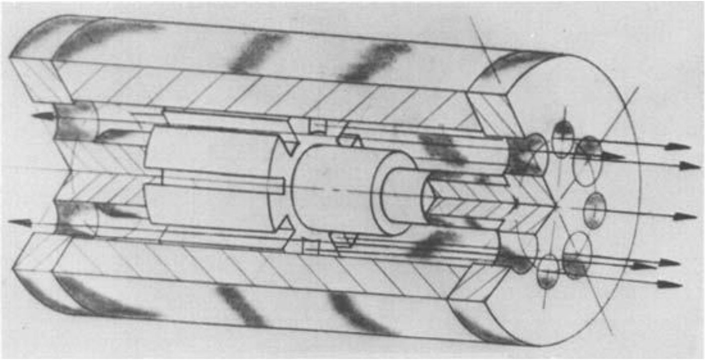


FIG. 5—*Extrude Hone media flow path to deburr, radius, and polish vane slots in rotor. Part is processed as a "plug" held in a "tube." This general tooling concept would be used to process gears, turbine disc "fir tree" slots, and an entire range of other parts.*

be achieved with relatively coarse grit sizes due to the cushioning effect of the putty-like carrier.

Deburring is normally required to prevent a burr from being dislodged during operation in hydraulic, pneumatic, or food handling equipment, for instance, and causing damage.

Radiusing may be desired to prevent cutting wire or O-rings or fingers. It also improves fatigue strength of critical parts by eliminating stress risers. Elimination of thermal fatigue and other factors may lead to the desire for the smooth true radiuses provided by this process.

Surface removal and polishing may be desired for appearance on commercial parts, improved flow characteristics on dies, or to prevent pick up, or to improve the strength of highly stressed parts. Surface integrity of parts machined by electrical discharge machining (EDM) can be significantly improved by extrude honing to remove the entire recast layer and damaged subsurface material. The improved surface finish also increases the tensile strength of parts as shown in Fig. 6.

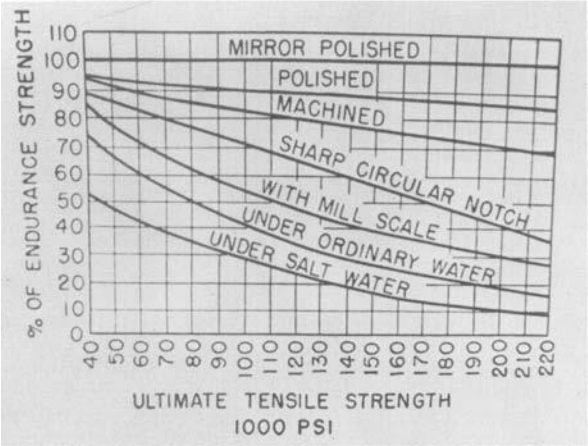


FIG. 6–*The effect of surface finish on endurance limit.*

Stainless steels are used in many critical applications in the aircraft, nuclear, and food processing fields. These applications require absolute burr removal, controlled edge radii, high surface integrity, and fine surface finishes. The Extrude Hone process is being used in many of these applications.

One example involves fuel nozzles (Fig. 7) for jet engines, diesel engines, welding tips, and similar parts that contain many small angular holes that require deburring and radiusing. The size, location, quantity, and geometry of the holes in this type of part poses a significant manufacturing problem in deburring and radiusing. Hole diameters can vary 0.005 to 0.060 in. in diameter, and the total number of holes can range from 20 holes per part for nozzles and 50 000 holes for other parts. In some cases the holes are not straight, thus complicating the problems even further. Manufacturing methods for the holes vary from drilling

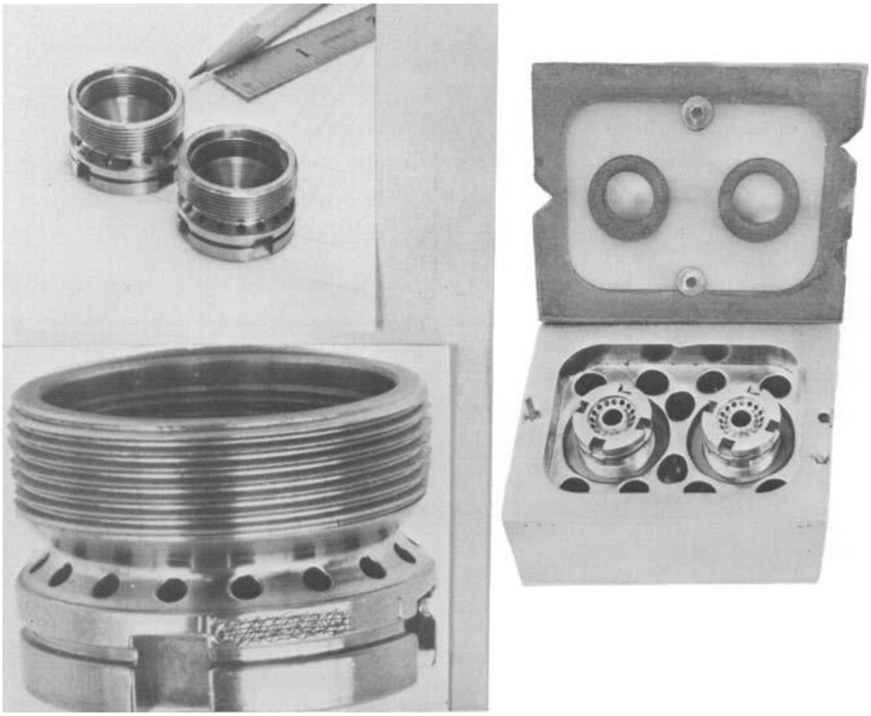


FIG. 7–*Stainless jet fuel spray nozzle and tooling. Holes to be deburred and radiused. Tooling shown at right.*

to EDM to swedging. In each case a secondary operation to deburr and radius the opening is necessary.

In this type of application, a small quantity of flow of relatively low aggressiveness media is sufficient to attain the desired results. The specially formulated media is directed along a flow path corresponding to the same flow path that the fuel will follow. Low cycle times (namely, 5 to 20 s) in conjunction with multi-part tooling produce impressive production rates.

In some applications, rejection rates have been reduced from 20 to about 5 percent. Aside from the edge radius generated, the directional surface finish is conducive to efficient flow characteristics.

Another example involves the removal of EDM recast and generating radii on coolant holes in jet engine blades, vanes, and impingement tubes (Fig. 8).

The aircraft turbine vanes and blades require accurate and consistent internal material removal. The hollow vanes and blades shown in Fig. 8 are investment cast and occasionally the hollow cores are either undersize or rough, thus failing minimum air flow requirements.

Extrude honing, along the same path that the coolant air will follow, opens and polishes the complex and inaccessible passages salvaging what would otherwise be very expensive scrap parts. The vanes at the upper left and the

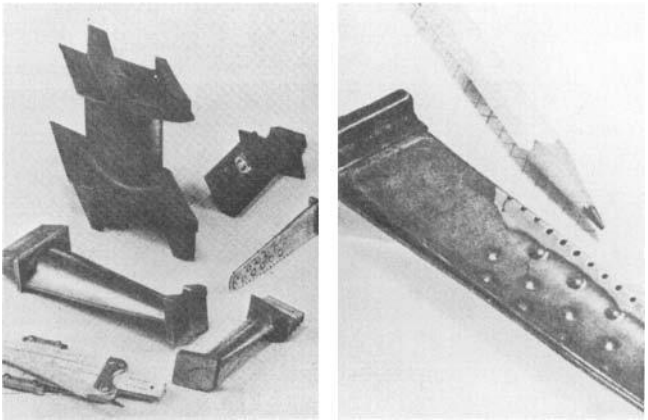


FIG. 8—*Jet engine blades, vanes, and impingement tubes.*

turbine blade cooling tube at center right have small air cooling holes electrical discharge machined (EDM) or electro-chemically machined (ECM) into the leading edges.

The EDM recast layer in the holes is entirely removed by extrude honing, eliminating the poor surface integrity produced by EDM. The holes are also radiused increasing the strength of the parts by removing stress risers caused by sharp corners. Finally, the holes are sized, sometimes opening them 20 percent to bring them accurately to the required dimension.

Another example involves EDM recast removal from steam turbine blades (Fig. 9).

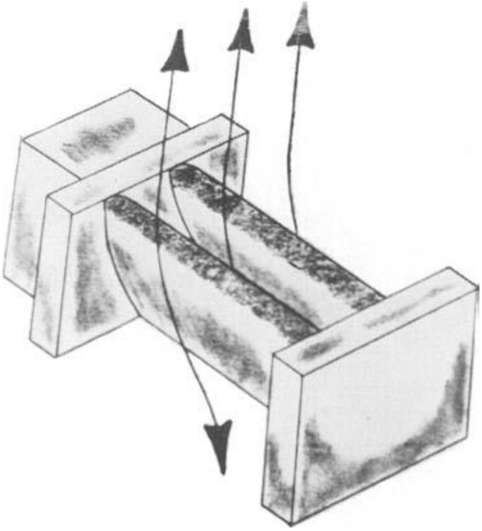


FIG. 9—*Extrude Hone media flow path to remove EDM recast layer from airfoil sections of Inconel Power Generating Turbine Blades.*

Segments known as triple impulse blades had a 250 to 350 μin. finish after EDM; complete EDM recast removal and finish improvement to 63 μin. was required. Here again, a specially formulated abrasive laden media was directed along the flow path of the medium (in this instance, steam) for which the part is designed.

Stock removal through the blade was 0.003 to 0.008 in. Cycle times of 10 to 15 s with up to 500 cycles were required. Basic time savings of 3 to 5 h per blade was achieved.

The ability of the Extrude Hone process to improve surface finish effectively and more economically than other methods is exemplified in an application involving plastic extrusion dies.

Tedious hand polishing is the common method for polishing plastic extrusion die components which require fine surface finishes. Surface finish requirements are usually based on plastic flow requirements and ease of release.

Extrude Hone polishing can automatically improve finishes as poor as 400 to 10 μin. One benefit which is especially important to this application is the directional surface finish.

Molten plastic has a tendency to pick up on surface irregularaties, and subsequent flow past a "pick-up" is greatly hampered with output severely affected. By Extrude Hone processing the die to produce a fine continuous linear surface finish with all finish marks in the direction of material flow, the opportunity for pick up is significantly diminished.

The "spider" section of a plastic tubing extrusion die is shown in Figs. 10, 11, and 12. This transition required a total of 4 h of machine time and only 1 h of

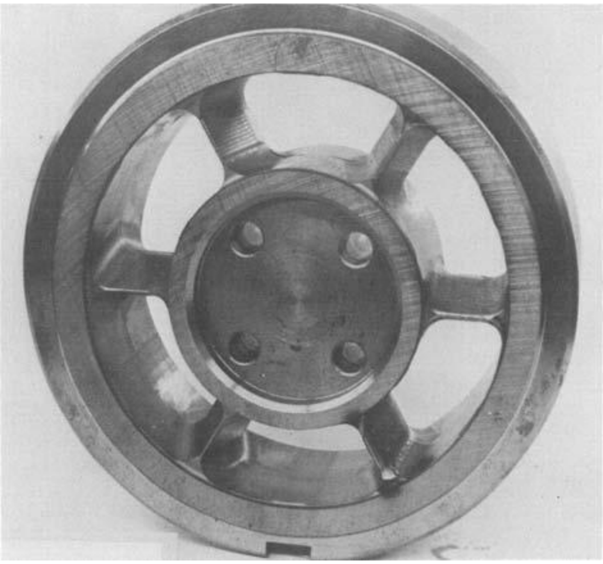


FIG. 10—*Plastic extrusion die, before.*

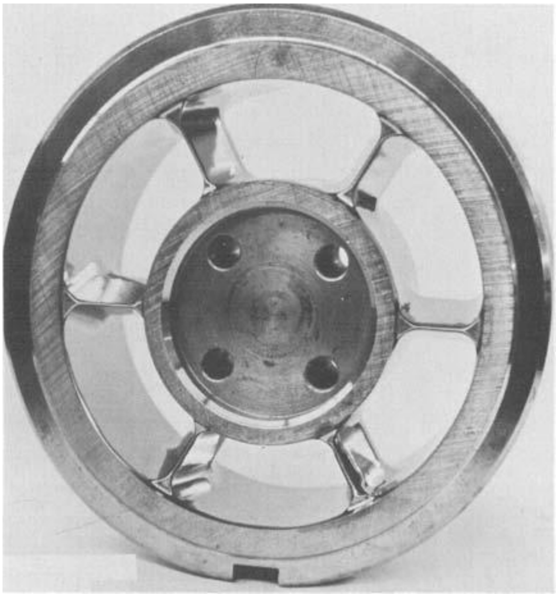


FIG. 11–*Plastic extrusion die, after.*

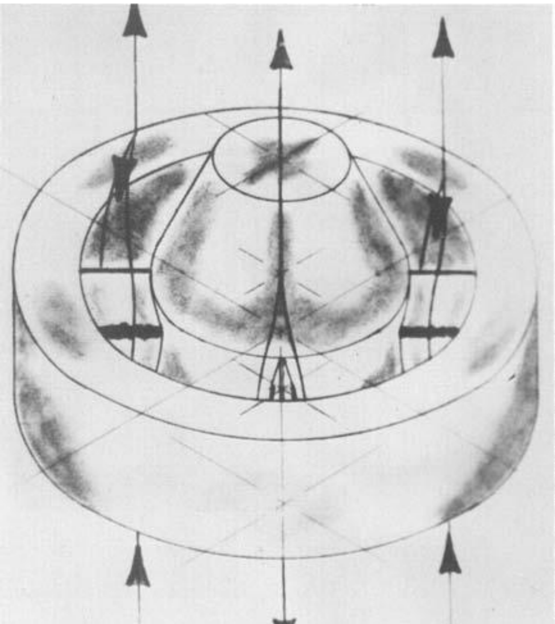


FIG. 12–*Media flow path for polishing, plastic extrusion die.*

operator time. Hand polishing, to achieve the same results, requires more than 20 h.

Conclusions

This paper briefly surveys the Extrude Hone process and its application to finishing stainless steel components. The process demonstrates its versatility while deburring, generating radii, sizing, polishing, and removing detrimental surface layers from stainless steel and other metal parts. The process is extremely cost effective since it greatly reduces direct labor costs by using unskilled labor and reducing total process time. Elimination of the hand finishing operations assures a uniform controllable finish for higher quality finished products.

W. L. Walker[1]

Pre-Service Cleaning Philosophy for Boiling Water Reactors

REFERENCE: Walker, W. L., **Pre-Service Cleaning Philosophy for Boiling Water Reactors,"** *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 147-153.

ABSTRACT: The goal of both a plant cleaning procedure and a plant cleaning philosophy is to produce a plant which is clean at the time of plant startup. The development of a preoperational cleaning procedure to be used for either a nuclear or fossil fueled power plant and the development of a cleaning philosophy related to either of the two types of plants have many common elements. However, they are distinctly different operations with potentially different consequences. Development of the philosophy incorporates all of the considerations involved in development of the procedure, plus other considerations, and a proper philosophic approach can result in greatly simplified cleaning procedural requirements. This paper presents the essential steps in the development of the philosophy, and contrasts them with the development of a procedure. The types of information required in each case are discussed, and pertinent laboratory data are presented. Some examples of plant cleaning problems are presented, with their solutions. General guidelines for the development of a cleaning philosophy are presented, and specific requirements for cleaning procedures are discussed.

KEY WORDS: cleaning, stainless steels, contaminants, boiling water reactors, nuclear reactors

The goal of pre-service cleaning in a power plant, whether nuclear or fossil fueled, or any other type of complex plant, is to provide operating systems which are clean at the time of plant startup. How clean is "clean" depends upon the function of the plant and the characteristics of the equipment and components in the systems. The cleanliness requirements of a particular plant are reflected in a large number of documents, ranging from equipment purchase specification requirements to site installation instructions. The general problem of cleanliness at the time of plant startup can be approached from two different, but related, aspects; one is a procedural approach, and the other is a philosophical approach.

Procedures Versus Philosophy

When one thinks of plant cleaning or system cleaning operations, one normally thinks in terms of cleaning *procedures,* and properly so, because a cleaning procedure represents the rules under which the cleaning operation will be

---

[1] Principal engineer, Atomic Power Equipment Department, Nuclear Energy Division, General Electric Company, San Jose, Calif. 95125.

performed. Unfortunately, thinking in terms of procedures tends to result in a rather limited viewpoint because the procedure is normally written with very specific goals in mind. This limited viewpoint can result in excessive financial costs and delays in plant startups. However, such costs and delays can be minimized or eliminated if the cleaning operation is considered from a broader viewpoint which can be thought of as a cleaning *philosophy*. While a cleaning philosophy and a cleaning procedure both have common elements, they are distinctly different. Ideally, the cleaning procedure should be written only after the development of the cleaning philosophy; and the cleaning philosophy should be developed long before construction of the plant is begun. In order to illustrate the difference between the two, they must be examined in greater detail.

The usual cleaning procedure addresses itself directly to only two questions, and indirectly to a third. They are: (1) what contaminants are present on the item to be cleaned (2) how can the necessary contaminant removal be accomplished, and indirectly, (3) what are the effects of various removal methods on the item during the cleaning operation? The third item is considered to be an indirect question because the commonly used cleaning procedures for a particular material have already taken it into consideration. For example, consider a cleaning procedure for aluminum items as they come off the end of a machining operation in a manufacturer's shop.

Generally speaking, the contaminants of concern would be organic materials from machining or buffing operations, particulates from either machining operations or from the surrounding environment, and possibly surface oxides. All of these contaminants could be readily removed in a hot 10 percent sodium hydroxide bath. This would nicely satisfy Questions 1 and 2. However, nowhere would one find such a solution recommended for the cleaning of finished aluminum items, because of Question 3. While hot caustic solutions are excellent cleaners for aluminum, they are also very corrosive and are not recommended for such operations. It is in this sense that the effects of the cleaning operation on the material being cleaned were referred to as an indirect question. It is, in a way, already taken care of by past experience in many cases.

In addition to its limited scope, the normal cleaning procedure frequently suffers from having been developed for and applied to relatively small or simple items or both. This is a natural consequence from the fact that most cleaning operations are performed in the manufacturer's shop on individual components of the finished item, and under these circumstances the effect of this feature is minimal or nonexistant. However, when one considers the size and complexity of a nuclear power plant, the effects of this feature can become formidable. How, then, does one handle these deficiencies in the cleaning procedure approach?

In order for the cleaning procedure approach to work, it must be greatly expanded beyond its normal scope. Instead of addressing itself directly to only two questions and indirectly to a third, it must address itself directly to at least six specific questions, some involving a number of sub-questions, as follows:

What Contaminants Are Tolerable?

This relates to type, size, and quantity of contaminants; their physical location; and type and metallurgical condition of the structural material upon which they are present. For example, the contaminants normally present in a main condensor coolant intake line would be intolerable in a reactor vessel recirculation loop line.

What Contaminants Are Present?

This question can rarely be answered with absolute certainty, so one must usually deal in terms of probabilities. The concern here again relates to what type, sizes, and quantities of contaminants might be present; their physical locations; and the type and metallurgic condition of the structural materials with which they are in contact. When the answers to Questions 1 and 2 are available, the contaminants which must be removed will have been defined and one can then consider methods for the actual removal.

How Can the Necessary Contaminant Removal Be Accomplished?

It is at this point that one begins to consider the actual cleaning procedures which might be used for contaminant removal. At least four different categories should be considered; mechanical cleaning, disolving in water, organic solvent dissolution, and chemical cleaning; or any combination of the foregoing. Answering this question results in a list of potential cleaning procedures for particular types of contaminants. This list must then be examined in terms of the next two questions in order to arrive at a list of acceptable cleaning procedures.

What Are the Effects of the Contaminant Removal Operation on the Materials Being Cleaned, During the Cleaning Operation Itself?

Answers to this question may eliminate a number of potential cleaning procedures arrived at in the prior question, such as hot caustic cleaning of aluminum items. In addition, one must also consider any other item which is exposed to the cleaning operation. For example, while hot caustic may be an excellent degreaser for carbon steel items, it would not be considered to be an acceptable procedure from the viewpoint of this question if it were necessary to flow the cleaning solution through an aluminum piping system in the process of cleaning the carbon steel.

What Are the Effects of the Contaminant Removal Operation on the Subsequent Behavior of the Materials Being Cleaned, or Contacted by the Cleaning Solution, in the Normal Plant Operating Environment?

This particular question has generally received a very limited amount of consideration in the past. The reason for this lack of attention appears to be a general lack of problems in this area. However, specific problems do appear to exist. For example, nitric-hydrofluoric acid pickling of welded or heat treated austenitic stainless steel is a relatively common practice in industry, and little or no concern is expressed regarding the use of this procedure. However, experience at the Savannah River Plant on operating equipment and in laboratory tests,[2] and in laboratory tests at APED,[3] indicate that pickled sensitized 304 is quite susceptible to intergranular stress corrosion cracking in high purity high temperature water. The data generated to date at APED indicate that the effect is specific to the fluoride ion, and may represent a grain boundary adsorption phenomenon. No effect was observed in samples pickled in hydrochloric acid after sensitizing.

What Are the Effects of Trapped Cleaning Solutions or Compounds on the Behavior of the Materials in the system or Component in the Normal Plant Operating Environment ?

This question represents a risk evaluation related to the consequences of incomplete removal of the cleaning solution or compound. In this event, the cleaning solution represents a contaminant and should be considered in the same light. Caustic solutions may cause stress corrosion cracking of austenitic stainless steels at elevated temperatures, and halogenated cleaning solvents which are stable at room temperature may decompose in the presence of high temperature water and metal surfaces to give chlorides and flourides which may cause stress corrosion cracking. The question should be considered in terms of the quantities of cleaning solutions which might be trapped, and the resulting concentrations of deleterious ions in the operating environment.

If one works through this series of questions completely, the result is a list of contaminant-material-cleaning procedure combinations representing as many combinations as are necessary to accommodate the contaminants and materials of concern. From this list, one can select a procedure to clean any contaminant encountered from any item in the assembled system. It is at this point that the question of system size and complexity enters the picture, although it is a factor in the last question.

Cleaning Procedure

The physical size of the system affects the costs associated with the cleaning compound itself, and the time and costs associated with the performance of the cleaning operation; particularly when elevated cleaning temperatures are required by a particular procedure. Complexity of the system affects the time and costs associated with the cleaning operation and may eliminate certain procedures for this reason alone. For example, the residual heat removal system was installed at an APED reactor site with the manufacturer's protective coatings

---

[2] Rideout, S. P., "Stress Corrosion Cracking of Type 304 Stainless Steel in High-Purity Heavy Water," Second International Congress on Metallic Corrosion, New York, March 1963.

[3] Private communication, A. E. Pickett.

still intact on the inside diameter surfaces of a number of fittings. Bench top tests showed that a hot tri-sodium phosphate (TSP) solution would soften the coatings, and a hot TSP treatment followed by high pressure water blasting was proposed for removal of the coatings. In actual practice it was discovered that by the time the TSP solution was drained from this complex system and the water blast head inserted to the first fitting, the coating rehardened to a point where water blasting would not remove it. The fittings were eventually removed from the system and the coatings were removed by abrasive blasting. If bench top tests are used to investigate or qualify a procedure, they should be conducted on the same time scale as the intended operation.

Basically, then, the development of a cleaning procedure begins with a contaminated system and moves toward an acceptable means of removing the contaminants without damaging the system material in the process, without rendering it susceptible to corrosion in subsequent operation, and without undue risk of deleterious effects of trapped quantities of the cleaning compounds on the system in subsequent operation. In what way, then, does the development of a cleaning philosophy differ from the development of a cleaning procedure, and what are the advantages of a philosophy over a procedure?

Development of a Cleaning Philosophy

Generally speaking, the development of a cleaning philosophy is the reverse of the development of a cleaning procedure. A philosophy begins with a concern for the effects of residual amounts of cleaning solutions, and subsequent effects on the operational performance of system materials. Acceptable cleaning procedures are selected which can be used on as many of the materials in the plant as it is practical, but which may be quite specific as to the type of contaminants which they will remove. Installation instructions and field housekeeping recommendations are written in a manner which minimizes the probability of introduction of other types of contaminants, and purchase specifications and storage requirements are written in a manner which assures that the system components are at the required level of cleanliness prior to installation. In effect, a cleaning philosophy is based on the assumption that contaminant introduction can be controlled during plant erection. However, cleaning procedures are an integral part of any cleaning philosophy.

The principal advantage of a cleaning philosophy approach over a cleaning procedure approach is that the philosophy constitutes a frame of reference from which consistant and systematic decisions can be made and implemented. The philosophy forms a base from which cleanliness levels can be specified on design drawings; vendor cleaning requirements can be formulated; and vendor cleaning procedures can be reviewed and approved. In the field, it forms a base for site storage and inspection requirements prior to installation; site cleaning procedure review and approval; housekeeping practices during installation; and final cleaning of the assembled plant. A cleaning procedure approach, on the other hand, simply supplies the action to be taken in a single isolated set of circumstances.

While the philosophic approach may appear more cumbersome than the procedural approach, it is not. The only additional document required by the philosophic approach is the philosophy itself. The philosophy will reflect the tone of the corporate structure in which it is formulated, and the personal attitudes of the materials personnel involved in its preparation; it may be either conservative or risky. The effect of the philosophic approach on purchase documents and site instructions should only be that of a unifying agent, since all such documents contain some expression of a cleaning philosophy in their present form. However, they are not necessarily consistent with one another. The purpose of the philosophical approach is to document the bases for cleaning decisions and to force consistency on purchase documents and site instructions.

General Electric Company's Atomic Power Equipment Department (APED) began the development of a cleaning philosophy late in 1968, and such a philosophy has been in effect since about mid-1969. Basically, the philosophy provides for only two cleaning procedures for the entire erected nuclear steam supply system; a hot alkaline phosphate degreasing treatment for the removal of light organic films, and water flushing to remove soluble inorganics and solid soils. Purchase specifications, packaging requirements, shipping and storage instructions, site housekeeping practices, and installation instructions are all written to minimize the probability of introduction of contaminants to the component or system at all times prior to plant startup. Experience with the philosophic approach at APED has been generally good. However, there have been occasional problems encountered which were not the result of that particular approach, but which have required deviations from the basic philosophy. Such problems have been treated with the conventional procedural approach for the particular situation. It should be recognized that occasional problems will arise no matter which approach is used, but the philosophic approach should minimize their number.

Two problems encountered to date have been due to simple nonconformance with instructions regarding the cleanliness level of installed components. Within this writer's experience, the cause of these incidents has been a lack of familiarity of the personnel actually involved in the installation operation with the specific requirements of the installation instructions regarding cleanliness prior to installation. Both incidents have involved the installation of pipe fittings with the manufacturer's protective coating still intact on the inside diameter surfaces. In one instance, previously mentioned in this paper, the fittings were cut out of the system, mechanically cleaned, and then reinstalled. In the other instance, it has been proposed to remove the coatings by charring them in place at a temperature of 900°F and then removing the residue by flushing. The compositions of the coatings appear amenable to this procedure. If the lead contents had been high, there would be some concern for possible deleterious effects of residual quantities on the stress corrosion cracking resistance of Inconel 600 components in other systems. If the coatings had contained appreciable quantities of halides, there might be some concern with this procedure if there were austenitic stainless steels in contact with, or in close proximity to, the coated components. While these same problems would have been encountered had the procedural approach been used, the philosophic approach offers a means of minimizing or eliminating their occurance; but only if the requirements of that approach are transmitted down through the site organization to the level of actual installation of components.

Another problem encountered was the result of conflicting specification requirements. One document dealing with site construction called for all piping buried in concrete to be coated on the inside and outside surface with a bituminous coating, while the document dealing with the particular system involved called for all piping to be metal-clean on the inside diameter. The architect-engineer cast a coated pipe section in the building wall in the early stages of construction, and then welded blast-cleaned system piping to both ends at a later date.

In this particular situation the philosophic approach offers the potential of reducing the number of such incidents, when compared to the procedural approach, but only through a thorough review of existing instructions in order to detect such inconsistencies.

Summary

In summary, then, a philosophic approach to plant cleaning offers distinct advantages over a procedural approach. These advantages consist of: (1) full consideration of all aspects of the cleaning operation, (2) documentation of the bases for decisions regarding cleaning operations, (3) formation of a consistent set of rules for the approval of vendor cleaning procedures, (4) formation of a consistent source for purchase specification cleaning requirements, (5) formation of a consistent basis for the issuance of site storage instructions, and (6) the provision of a consistent source for site housekeeping recommendations and installation instructions. The long range benefits of the philosophic approach far outweight the initial inconvenience of formal documentation of the philosophy and the subsequent review of specifications and instructions for consistency with the philosophy.

P. S. Olson[1]

Cleaning Stainless Steel Heat Transport Systems for Liquid Metal Service

---

REFERENCE: Olson, P. S., "**Cleaning Stainless Steel Heat Transport Systems for Liquid Metal Service,**" *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 154–164.

ABSTRACT: Austenitic stainless steel is maintained in a clean and dry condition during fabrication and installation of liquid metal (sodium) heat transport systems which are designed to operate at elevated temperatures. An understanding of cleaning agent actions on the metal is necessary for pumps, valves, vessels, piping, fittings, and other components comprising these systems. Control of cleaning and cleanliness operations is required, starting with the steel manufacturing and proceeding through the material forming and component fabrication to delivery and erection by field installation contractors. A variety of cleaning processes are used by manufacturers, including alkaline solutions, cleaning solvents, alcohol washes, and mechanical surface cleaning, followed by appropriate rinsing methods.

KEY WORDS: stainless steels, cleaning, liquid metals, heat transfer, nuclear reactors

Liquid metals possess high heat transfer coefficients and other properties that make them attractive as coolants for high-temperature nuclear reactors. The use of a small nuclear reactor core with a corresponding high heat transfer rate at low pressure is possible with a liquid metal coolant. Liquid metals act as the heat transfer working fluid for the evaporation of water and superheating of steam for operation of electrical power generating stations. Nuclear systems have been successfully operated with the alkali metals sodium and sodium-potassium alloy (NaK) as heat transport fluids. Sodium is the most commonly used and preferred working fluid.

At the present time considerable effort in the nuclear energy field is being concentrated on the development of the liquid metal fast breeder reactor (LMFBR) using sodium as the heat transport fluid. Figure 1 is a schematic of a typical LMFBR system. A liquid metal nuclear reactor system uses two heat transfer loops: the primary system contains radioactive sodium and transfers heat from the nuclear core; and, a secondary nonradioactive loop which transfers heat to the steam generator for steam production and turbine operation. Because sodium is a solid at room temperature, melting at 208°F, system preheating and standby heating is required to maintain sodium in the liquid state during filling and standby operations.

Favored materials for the primary and secondary heat transport loops and associated fill and drain purification systems are Types 304 and 316 austenitic

---

[1] Engineer, Liquid Metal Engineering Center, Canoga Park, Calif. 91304.

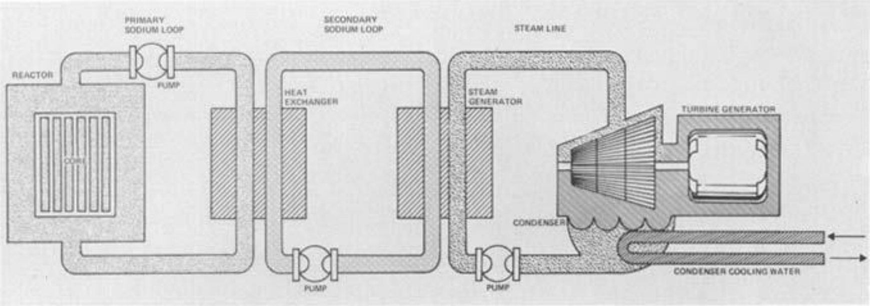


FIG. 1–*LMFBR flow diagram.*

stainless steels. One could expect to find two to three thousand tons of stainless steel in an LMFBR plant. Factors governing selection of these materials for heat transfer systems are corrosion resistance and good high temperature mechanical properties. Problems associated with their use, such as low thermal conductivity, susceptibility to sensitization, and attack by certain media are similar to those encountered in other chemical and high temperature applications. The extensive use of these materials is exemplified by current facilities under construction, such as the Hanford Engineering Development Laboratory (HEDL) Fast Flux Test Facility (FFTF), a 400-MWt nuclear test reactor designed to operate with sodium at 1050°F, and associated facilities such as the Liquid Metal Engineering Center (LMEC) 20 000-gal/min Sodium Pump Test Facility (SPTF) employing sodium at 1100°F. The construction of components for these as well as most other liquid metal facilities conforms to ASME Code Section III requirements.

Materials and components in liquid metal heat transport systems are fabricated to the highest standards and workmanship. A single class of requirements is established for cleaning of liquid metal systems with procedures developed on an individual basis to cover specific applications. Inspection and testing of components and piping for heat transport systems, including cleaning and cleanliness control, begin with the base material and are not completed until the entire system is accepted.

Characteristics of Liquid Metal Heat Transport Systems

There are several basic characteristics of liquid metal heat transport systems which require extensive engineering consideration in construction of these systems:

1. Sodium chemically combines readily with free oxygen and almost all metallic oxides, requiring that the systems be isolated from air and other sources of oxygen. By using stainless steel with appropriate cleaning after forming and heating, and by using inert gas when welding, oxide formation can be minimized in these systems.
2. The liquid metal coolant reacts vigorously wth water and many organic compounds. The sodium water reaction may form a residue which is a strong, corrosive, caustic, aqueous sodium hydroxide (time, temperature, and concentra-

tion factors must be considered). Detection of free hydrogen from sodium water reaction is the method used for rapid identification of sodium water leaks in steam generators. Dry steam, on the other hand. reacts with sodium at a relatively slow, safe rate lending itself to practical use for cleaning operations after sodium service.

3. In room temperature air, a thick coating of white oxide forms on solid sodium. In the presence of humidity, this oxide is readily converted to sodium hydroxide. Helium and argon are used as cover gases to preclude contact with air since sodium is inert to these gases.

4. Flowing sodium can cause mass transfer in stainless steel systems, dissolving metal in areas of high temperature and precipitating it in areas of low temperature. Mass transfer is accelerated by impurities, particularly oxide. This and other considerations require that the sodium heat transport fluid be constantly purified by precipitating sodium oxide from the fluid in purification systems associated with the main heat transport loops.

In the past, inadequate or improper cleaning methods and cleanliness control caused or contributed to serious problems in construction and operation of plants, often involving costly shutdown and repair. In most instances, however, it is difficult or impossible to isolate the precise effect that the cleanliness or cleaning procedure did have in causing the overall system problem. This makes it difficult to identify the deleterious features of the cleaning process and, similarly, precludes the selective elimination or quantitative restrictions of those specific features.

In a recent inspection of a Sodium Components Test Loop fill and drain tank at LMEC, both transgranular and intergranular attack were observed at nozzle inlets to tanks. No leakage had occurred, and the tanks could be repaired for continued service. Although the source of the difficulty could not be precisely established, it was generally considered that condensation, accumulation of chloride and sulfate corrodents from insulating materials, and environmental exposure factors contributed substantially to the problem. Again, this emphasizes the point of maintaining surfaces clean and dry for continued long term service. In practice this requirement cannot be completely met, and some material, for example, thermal insulation (many facilities insulate with hydrous calcium silicate) cannot be completely avoided.

A great deal of concern has arisen over chloride contamination on metal surfaces. Recent tests at LMEC of exterior surfaces of stainless steel piping, using a swabbing technique and specific ion electrode analysis of a sizeable number of samples (15 or more), have detected the presence of chloride on metal surfaces at various construction site locations (see Table 1).

These findings are in general agreement with other investigations which, for the most part, show that this level of surface contamination does not result from proper cleaning operations at the mill where less than 1 mg/ft^2 is the general level found immediately following cleaning operations.[2] There is an apparent

---

[2] Doughty, S. E., *Power Engineering,* Sept. 1966, p. 47.

TABLE 1–*Analyses for* Cl^- *Contamination*[a]

	Cl (mg/ft^2)
New pipe in closed storage area	1.2
Pipe in newly constructed system	3.5
Pipe in old system	1.4

[a] More evidence is needed to establish whether the differences in values given in the table are significant. Based on operating experiences, it is not considered that the general level of chloride contamination is detrimental.

need of an examination method for rapid, inexpensive monitoring of large stainless steel surface areas to ensure freedom from concentrations of corrodents such as chlorides. Such an industrially acceptable inspection method does not appear to be available now. Until such time as one is, a technique such as swabbing local areas to obtain specimens for analyses to some arbitrarily specified level or level based on operating experience is expected to be the general approach taken.

On occasion, inspection of newly received materials has revealed levels in excess of the values in Table 1. Materials that were rejected for this reason had to be recleaned. The contamination is suspected to result from improper cleaning and cleanliness control, possibly occurring during fabrication or after manufacture but before packaging. Residues of cleaning agents have been of particular concern in heat exchangers where tube bundles enclosed in main shells are in a cold worked and welded condition and subject to severe action from residual water or cleaning agents.

With the general lack of definition of cleaning practices designated specifically for the nuclear industry by national standards writing bodies, it has been necessary to adopt knowledge and experience available from other sources. Current practices incorporate available cleaning specifications such as the recently released ASTM Recommended Practice for Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems (A 380-72) and experiences of manufacturers, cleaning firms, and personnel involved in liquid metal systems work.

Where construction of liquid metal heat transport systems is concerned, the general tendency for an overall conservative approach is to select the more stringent and more clearly defined practices in general use outside the nuclear industry. Existing practices selected on this basis are being enhanced by a more quantitative treatment of cleaning requirements, a more specific assignment of inspection responsibilities, and more rigid requirements for documentation.

Cleaning and cleanliness control of austenitic stainless steel for liquid metal heat transport service must be observed during all stages of fabrication and installation and must be maintained during system startup, operation, and for repair or modification activities.

Fabrication Cleaning

Cleaning requirements and procedures need to be established early in the design of any system or components within that system. In the fabrication of liquid metal heat transport systems, it is necessary that containment parts be free from dirt, grease, oils, and residues and that the parts be kept in a dry, oxide-free condition. This requires that the design provides accessibility for inspection and testing for cleanness at all stages of fabrication and assembly so that available means of examination can be utilized.

It is also important that the design and fabrication methods provide for the inspection and testing of subassemblies before they are built into final assemblies and the components become inaccessible for inspection.

Once the desired degree of cleanness is established, the type of cleaning process and procedures to be used for cleaning can be formulated for all major components of the system. Cleaning operations for the most part are concentrated at the fabricator's shop and from this point extend back to the materials manufacturer's plant. Preliminary cleaning of such items as weldments, forgings, castings, and mill shapes is ordinarily performed to remove gross contaminants including scale, heavy oxide, slag, flux, and weld spatter.

Procedures using solvents, alkaline and detergent cleaners, acids, blasting, grinding, and wire brushing are frequently employed at various stages of manufacture, fabrication, and handling to provide clean metal surfaces. Preparation of degreasing, pickling, and cleaning solutions is accomplished with technical grade reagents and potable tap water.

Fabricators make extensive use of steam cleaning for components such as pipe, pipe spools, valves, pumps, vessels, and other components. Steam cleaning is also employed in conjunction with detergents to assist the cleaning process.

After cleaning with agents such as a solution of trisodium phosphate, parts are usually rinsed immediately with hot water followed by demineralized water and dried.

There has been a general restriction in the application of halogenated solvents in the cleaning of component materials for liquid metal heat transport service. The restriction is a precaution against the possible stress corrosion problems associated with the use of such solvents on austenitic stainless steels and of the potential reactions of sodium with these agents. The concern with this problem has even resulted in analysis and controls on the halogen content of cleaning agents such as detergents and alkaline solutions. Nevertheless, in recognition of the effectiveness of halogenated solvents, drainable and inspectable parts are often cleaned with trichlorotrifluorethane (TCTFE). Rarely, however, are halogenated solvents or acids used in fabricated components, particularly where crevices are present. When parts or components containing inaccessible or undrainable areas are cleaned with TCTFE, the parts or components are dried by evacuation or heated to a temperature of 120 to 140°F. They are then flushed with dry, oil-free air or inert gas until no further indication of the solvent is found, using a halogen leak detector in the effluent air or gas. Where hot-forming, heating, or welding operations are conducted, precautions are taken to prevent contamination prior to these operations. Surface inspection is conducted after degreasing and before each annealing operation.

Solution stress relieving is considered to be a desirable treatment after welding and working of parts but distortion and cleaning (particularly large components) present challenging problems.

Removal of scale generally requires a more active cleaning process such as sand blasting or grit blasting. Sand for blasting must be iron free. Acid cleaning is commonly performed after abrasive blasting; however, grinding or polishing after blasting is also used. General reluctance to use acids for descaling and cleaning in many instances derives from concern that disturbance of grain boundaries at the surface of the material may promote greater susceptibility to attack by corrodents. Where pickling or acid cleaning is performed, surfaces are throughly rinsed with water after these treatments to remove all traces of these agents. Acids and other agents, such as halogenated solvents, are not allowed on stainless steel that is sensitized and subject to intergranular attack.

Metal bellows usually contain the thinnest metal in the liquid metal system, and cleaning techniques that could remove metal are applied with care with appropriate rinsing to remove the agents. The generally preferred cleaning mode for system components is by immersion, with flushing, ultrasonic, and spraying methods following in that order.

Resin bonded aluminum oxide or silicon carbide grinding wheels and disks are suggested for grinding and polishing stainless steel. Wire brushing is performed only with austenitic stainless steel brushes. Brushes and tools used on stainless steel must not have been used on other steels. This prevents transfer of iron or other contaminating materials from those surfaces to the stainless steel surfaces. For the most part, stainless steel tools are used on stainless steel parts. Permanent markings are made using electrochemical etching techniques. Care is exercised with temporary markings to ensure that the marking materials are free of deleterious constituents.

Measures are taken during fabrication to prevent environmental contamination from normal atmospheric conditions and from shop fumes, dust, and dirt. This is accomplished by covering and capping components when they are in storage between operations and by performing mechanical cleaning operations in such a manner that loose metal particles either fall away from the components or may be removed by vacuuming. Special provisions for controlled work areas and clean rooms are often required for fabrication of components for liquid metal heat transport service, depending upon the criticality of the component being fabricated. Once internal and crevice containing surfaces become inaccessible for further cleaning or inspection, it becomes necessary to impose restrictions and controls on shop tools, materials, personnel access, and practices. Polyethylene plastic coverings are used to protect metal surfaces. Nylon slings are used to prevent damage to the metal surfaces when heavy parts or equipment must be moved. Accidental loss of personal articles and working tools to the interior of these fabricated components can result in unnecessary waste of time as well as expense for retrieval.

Generally, demineralized water, power plant condensate, or distilled water are used for engineering tests such as hydrostatic testing. The chloride and fluoride level in water is controlled with higher water grades limited to 0.1 ppm halides. Controls are also exercised on pH, turbidity, and conductivity.

Compressed air used to remove loose material from material surfaces must be clean, dry, and oil free. Normally, neither protective coatings nor inhibitors are applied to any of the austenitic stainless steel surfaces. In complex equipment where components are not readily accessible to application of cleaning fluids, each component part is cleaned before assembly and kept clean thereafter. In less complex equipment, it may be more desirable to clean the completed component after assembly. For final cleaning, demineralized water, acetone, and lower molecular weight alcohols are the more common cleaning agents. Final drying operations are performed with hot air or inert gas with cold trapping to prevent contamination by oil vapors or moisture.

Components fabricated in accordance with the above considerations are inspected visually to ensure that the surfaces are clean of mill scale, grease, oil, water, rust, dirt, flux, weld spatter, and foreign material. In addition, the cleanness of metal surfaces is verified by wiping with a clean, lint-free cloth. The cloth is unbleached and may be either dry or moistened with alcohol or acetone.

After fabrication, cleaning, and drying, component openings are tightly sealed with plugs or plastic caps. In normal practice, drying is performed immediately after cleaning and flushing, and sealing is done after drying. Fabricated piping assemblies, pumps, valves, heat exchangers, and other components are frequently shipped to the construction site with an internal inert gas atmosphere or appropriate desiccants. Controls are required when using desiccants to ensure that desiccant material is not deposited inside components and that all desiccant containers are accounted for and withdrawn. Components shipped to the site are required to be ready for installation into the system without additional cleaning.

Installation Cleanliness Requirements

Contamination introduced into the system during construction is readily translated into impurities in the liquid metal. Grease, for example, is either reduced by sodium to carbon and hydrogen, or thermally decomposed to a tarry residue. Residual water is often assumed to have been removed, yet it is difficult to verify this condition. Plugging, galling, embrittlement, and carburization are consequences of residual system impurities.

Achieving cleanliness during installation presents some unusual problems. Whereas the majority of commercial cleaning procedures employed in power plants, petrochemical plants, and other industrial facilities involve the circulation of various chemicals in a water solution through a system, water in a liquid metal system is undesirable because of the potential reactions. Any chemical used for any cleaning process certainly requires close scrutiny for compatibility with system materials and the working fluid. Liquid metal systems, therefore, are seldom cleaned with standard cleaning solutions. The possibility of reactions between residual substances and the liquid metal makes most of the commercial cleaning processes undesirable. To accomplish system cleanness, it is necessary, therefore, to thoroughly clean, dry, and seal components before delivery to the site.

Components for the liquid metal heat transport system are inspected in detail at the construction site to verify that they have not become damaged or contaminated in shipment. Construction practices range from the extreme of handling materials only in clean areas with humidity and temperature regulation, to far simpler techniques as are used in the process industries. Standards are based on allowable tolerances, material effects, and permissible contamination of the working fluid.

Coverings are installed to protect component interior surfaces, and rigid procedures are followed to preserve internal cleanliness. All grinding, cutting, and welding particles which accumulate during the work must be completely removed from inside the part. Field installation of piping is carefully executed to maintain cleanness of internal surfaces. Where physical access to the internals of components is necessary, workmen must use special protective clothing to keep the metal clean and preclude the need for recleaning. On smaller size piping where access is not possible, the root passes in welds must be skillfully placed to avoid repair operations which would probably contaminate inside surfaces.

Facility enclosures and other temporary enclosures are necessary to protect exterior metal surfaces from atmospheric contaminants such as sand, dirt, and salt air (see Figure 2). Special care must be exercised in handling materials that may be in a sensitized condition. Controlled work areas are established by using signs, gates, ropes, or other physical barriers. Special procedures and controls are exercised to ensure that restrictions on tools, materials, personal belongings, personnel access, and personnel practices are observed. Inventory control is instituted for tools, supplies, and equipment small enough to fit inside openings of the components.

Fitup of large pipe can be troublesome. Piping for sodium systems is relatively thin-walled in comparison to its diameter. Piping sections easily become out-of-round during fabrication of pipe spools and final installation. During fitup and weld preparation where some grinding or rework is required, it is necessary that a plug or device be inserted in the section to restrict the amount of extraneous material entering the system.

Welds in liquid metal system boundaries are of the full-penetration type. This type of weld leaves no cracks or crevices adjacent to the weld, and radiographs of the finished weld can readily be interpreted. Elimination of crevices is an important consideration in construction of stainless steel surfaces. Coated weld rods are frequently used for cover passes or can be used for the entire weld (root pass and cover passes) only where both sides of the weld are accessible. Flux residues and dirt must be completely removed to prevent the lodging of substances which can contribute to corrosion. These residues can be removed by

FIG. 2–*Current precautions being taken to protect stainless steel surfaces during construction of liquid metal heat transport systems.*

using steel wool, brushes, hammer and chisel, files, and grinding wheels.

Welding is an important process in the construction of any liquid metal system. Grain boundary carbide precipitation frequently occurs in the heat affected zones during welding of the austenitic stainless steels. In this heat sensitized condition, the alloys are susceptible to intergranular corrosion. This is a major consideration in the cleaning of welds and cleanliness control during installation. Hot sodium reacts with or removes carbon stringers and weld scale. Therefore, slag inclusions and fissures are regions where corrosive attack is readily initiated, particularly if the material is under stress. Propagation of defects can lead to sodium leakage.

Edges prepared by thermal cutting require removal of material by grinding (aluminum oxide grinding wheels). Cleanliness is maintained at all times. Surfaces to be welded and the adjacent surfaces for a minimum of 2 in. from the edge of the weld joint are cleaned free of oil, grinding particles, dirt, dust, scale, and rust. Preweld, interpass, and postweld cleaning of the weld groove, adjacent surfaces, and weld deposits are accomplished with stainless steel wire brushes and aluminum oxide grinding wheels followed by wiping with a clean, lint-free cloth and acetone. Internal argon purge on the underside of welding grooves is maintained for a sufficient time prior to welding to assure expulsion of any contaminating atmosphere. Welds are often ground flush with the base metal surface.

Purging or Evacuation and Sodium Filling

In the construction of heat transport systems, all components are inspected to ensure freedom from grease, dirt, oil, and foreign materials. Preparations for filling and for operation of sodium systems involve procedures which are somewhat unique. Air and moisture must be removed from the system before filling with sodium. The acceptable oxygen and moisture content will depend on the temperature of operation, purpose of the system, and the system capability for removing oxides from the sodium.

On occasion, some systems may be cleaned as a unit after installation if it is certain that there will be no difficulty in removing cleaning agents. For example, the inert gas piping system may be cleaned with a hot detergent solution followed by hot water rinsing and demineralized water flushing. Any water remaining after cleaning of this system is removed by evacuation or by the inert gas purge before the sodium charging.

The generally recommended procedure, however, is to maintain cleanness of components as they are welded into the system. Components are individually cleaned and filled with inert gas, and maintained in a clean condition until the system is to be activated. Before filling systems with sodium, the piping and components are degassed by heating and evacuation. One method is to pump the system down to several hundred microns and to apply heat with the preheating elements that are incorporated in the equipment to achieve a temperature of 250 to 500°F.

Large systems, which cannot withstand a vacuum because their components have not been designed for evacuation, are purged with hot inert gas, normally 300°F with a dew point of -40°F, until the oxygen and moisture content of the purge gas has dropped to an acceptable level.

It is possible that the sodium could be contaminated sometime between its packaging by the manufacturer and its introduction into the system. However, packaging methods have been refined to include appropriate types of valves, all welded construction, and mass-spectrometer leak testing to assure that the sodium is not contaminated during storage and shipping. The purity of sodium can now be certified for shipment to the site. It is the site's responsibility to transfer the sodium, using techniques that preclude the possibility of contamination, and following the manufacturer's recommendations on methods of transfer.

Most large systems include purification equipment which may be used to remove impurities from the sodium after charging. Regardless of the purification equipment in the system, it is good practice to filter the sodium stream during the charging operation. Filters are usually installed with bypass provisions to allow filter replacement between charging operations. Micrometallic filters saturated with sodium or NaK are highly pyrophoric and are very difficult to clean completely. Replacement is cheaper and considerably safer.

During preheating operations, care must be taken to assure that all sodium containment areas are heated above 208°F (preferably from 300 to 350°F) to prevent sodium from solidifying in small passages. Heat must be applied at a controlled rate to prevent excessive thermal stresses in components such as pumps, valves, and tubesheets during the preheating operation.

Most liquid metal systems use fill and drain tanks which are situated at the low point in the system to allow for emergency draining. Pumps are used occasionally but the most common technique is to induce flow by creating a differential pressure between the charging tank and the system fill and drain tanks.

The cleanness of the metal surface and temperature of the circulating sodium both influence the time required for wetting. The sodium is normally circulated through a 100-mesh strainer and cold trap. Cleanliness precautions are judged to have been successful when the initial sodium plugging indication temperature is about 300°F and quickly reduces to an acceptable level as the sodium is circulated and cold trapped (the solubility of oxide in sodium is temperature-dependent). Circulating sodium systems generally can be operated with less than 10 ppm oxygen. Initial wetting of the system, as determined by listening for gas entrapment and by magnetic flowmeter observations, normally occurs within a few hours. An hour at 600°F is sufficient time to promote wetting and the dissolving of most surface impurities. From these indications, one can determine how clean the system was at the time of the sodium charge. Upon removal of the strainer from the system, several grams of material may have collected–mainly stainless steel particles and grit, both probably originating from weld joint preparation and grinding operations.

Summary

System cleaning requires planning and a coordinated effort to achieve desired results. The planning includes: (1) defining what cleanness the system requires, (2) defining how this cleanness is to be obtained in the various components and systems, (3) preparing procedures for the system and components to determine how and when this is to be achieved, (4) preparing inspection and testing procedures to verify that the requirements are fulfilled, and (5) preparing inspection procedures to be assured that once the desired cleanness is achieved, it is maintained.

R. R. Borisch [1]

Theoretical Analysis of Sodium Removal from Fast Flux Test Facility Fuel Subassemblies

---

REFERENCE: Borisch, R. R., "**Theoretical Analysis of Sodium Removal from Fast Flux Test Facility Fuel Subassemblies,**" *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 165–174.

ABSTRACT: The Fast Flux Test Facility (FFTF) is a 400 MW_t, sodium cooled, nuclear fuels and materials test reactor being developed at the USAEC's Hanford Engineering Development Laboratory. The reactor fuel is clad with Type 316 stainless steel. In order to examine fuel, the sodium coolant must be removed in a manner which will not degrade the fuel cladding. Several possible processes are reviewed and a moderately detailed sizing analysis is given for the chosen process which is argon-moist argon-water rinsing.

KEY WORDS: cleaning, stainless steels, sodium, subassemblies

The Fast Flux Test Facility (FFTF) is a 400 MW_t, sodium cooled, nuclear fuels and materials test facility. It is being built at the Atomic Energy Commission's (AEC) Hanford Engineering Development Laboratory near Richland, Wash. The reactor is fueled with plutonium/uranium mixed oxide fuel. The fuel is stacked in 316 stainless steel pins which are 0.230 in. outside diameter with a 0.015 in. wall thickness. Each pin is wrapped with a 0.056 in. diameter wire. The wire equally spaces the pins and aids in mixing the sodium coolant. A fuel subassembly consists of 217 of these wrapped pins contained in a hexagonally shaped duct with end pieces. The subassembly is 12.0 ft long and 4.57 in. outside diameter across the flats of the hexagon (see Fig. 1). Each core contains 73 of these fuel subassemblies. This paper is concerned with the process selection for removing sodium from fuel subassemblies after irradiation.

In order to do a complete fuel examination, sodium must be removed by a process which will not degrade the subassembly materials. All items of the fuel subassembly exposed to sodium are made of Type 316 stainless steel. The sodium removal process must permit reinsertion of the test fuel pins in the reactor, be capable of removing sodium from highly radioactive fuel, be capable of remote operation in an argon atmosphere hot cell, and be capable of concurrent cooling during all operations since the subassemblies can be producing up to 7 kW from residual radioactive decay heating. If the subassembly temperature exceeds 800°F, there is a danger of losing valuable test data. Therefore, a maximum allowable pin temperature of 700°F during cleaning was selected. This allows approximately 3 min recovery time in case of operator

---

[1] Development engineer, Westinghouse Hanford Company, Richland, Wash. 99352.

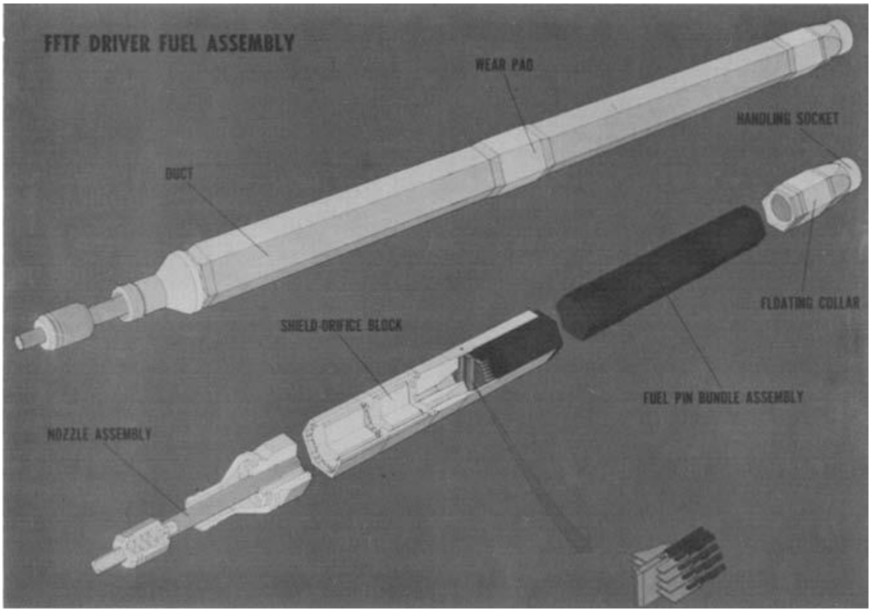


FIG. 1–*Artist's concept of FFTF subassembly, May 1972 design concept.*

error before exceeding 800°F. In addition to these primary requirements, several other requirements relating to safety, through-put, cross-contamination allowances, and degree of cleanliness were invoked on the process.

Each of the possible cleaning processes was analyzed for applicability. Temperature excursions to 1000°F were considered possible. Mechanical removal of the sodium did not appear feasible. Scraping is impossible and floating the sodium out using hot oil does not remove all traces of sodium. Also, residual oil could carburize the stainless steel fuel pins. Dissolution using ammonia was not desirable. During sodium removal the temperature could reach up to 700°F. The effectiveness of ammonia as a solvent for sodium at these high temperatures is not known. Rather high operating pressures and extensive refrigeration equipment would be necessary. Sodium removal using alcohol was eliminated because of the potential for coking and because of its fire hazard.

Vacuum evaporation was impossible because of insufficient radiant cooling. However, evaporation using a high purity forced argon flow was possible. Work at Belgonucleáire[2] and Oak Ridge National Laboratory[3] indicates that elevated temperature argon with a low sodium partial pressure will evaporate sodium. Efficient sodium removal could not be done by evaporation without increasing the maximum allowable temperature to about 1200°F. For driver fuel which is

---

[2] Van Dievoet, J., Michel, A., and Lanckman, R. (Belgonucleáire), *Sodium Evaporation in an Argon Flow,* ANL-7520 Part I, 7-9 Nov. 1968, pp. 418-425.

[3] Groenier, W. S. and Rose, J. C., "LMFBR Fuel Cycle Studies Progress Report for October 1971, No. 32," *Sodium Deactivation Studies,* ORNL-TM-3624, pp. 8-16.

to be dissolved for recyling, a 1200°F maximum temperature is acceptable. However, test fuel cannot be allowed to go to such temperatures.

The process which appeared most capable of meeting the requirements used moisture to react the sodium. For FFTF the most logical carrier gas for the moisture is argon (the process is carried out in an argon filled cell).

The process requires cooling the fuel assembly from about 700°F to about 230°F, adding moisture to the argon until sodium clinging to the fuel reacts to sodium hydroxide (NaOH), flushing with high purity water to remove all traces of NaOH, and drying. A similar process is used for removing sodium from fuel at the EBR-II reactor. However, at EBR-II the decay heat load is only 2 kW compared to 7 kW at FFTF. The total surface area of an EBR-II subassembly is less than 1/4 that of an FFTF subassembly, and the cleaning station is built out in the open at EBR-II for contact maintenance versus the completely remote operation and maintenance at FFTF. Metallurgically the 304 stainless steel EBR-II fuel cladding is normally not sensitized and mass transfer has not altered the surface metal composition. At FFTF the 316 stainless steel fuel cladding will be fully sensitized and metallic mass transfer will have altered the fueled zone and the area above the fuel pins to a ferritic surface. Therefore, direct extrapolation of data from EBR-II cleaning experience for FFTF use is not possible.

The conversion of sodium to sodium hydroxide during removal does pose a potential for caustic stress corrosion cracking. This potential hazard is also present when removing sodium from other reactor components using similar processes. A study is currently in progress which has as its purpose the better definition of operating conditions which will prevent the occurrence of caustic stress corrosion cracking. This work will be considered for a future technical paper.

Argon Flow Rates for Cooling

An experimental fuel subassembly which has gone to high burnup may have up to 7 kW of decay heating at the time of sodium removal. During the sodium removal process all of the heat which is not radiated to the surroundings must be removed by flowing argon or water. Additionally, all of the heat generated by chemical reactions during the sodium removal must be removed by the flowing argon.

Since calculation of temperature profiles across an enclosed array of heat sources is a difficult theoretical problem, I have chosen to consider the change in temperature of the argon gas passing through a subassembly (ΔT_A) as an indication of the temperature rise in the fuel section. The actual temperature rise in the fuel section must be higher than this, ΔT_A. Also, I have chosen to disregard radiation heat losses. The sodium removal chamber design which has been chosen tends to reduce radiation heat losses to insignificant levels. These simplifications make ΔT_A nonconservative for maximum pin temperatures. The actual maximum pin temperature will always be at least ΔT_A above the argon inlet temperature.

The subassembly which must have sodium removed is a hex-can 4.335 in. inside diameter across the flats with a 0.120 in. wall thickness. It contains 217 fuel pins clad with AISI 316 stainless steel. Each pin is 0.230 in. outside diameter with 0.015 in. wall and is wrapped with 0.056 in. diameter AISI 316 stainless steel wire spacers. The fuel section is 36 in. long. The cross sectional flow area is 6.72 in.^{2}.

The argon temperature change due to decay heating (ΔT_A) can be found from:

$$\Delta T_A\,{}^\circ\text{F} = \frac{\dfrac{(3413)\ \text{Btu}}{\text{kWh}} \times (\text{heat input})\ \text{kW}}{\dfrac{(\text{Cp argon})\ \text{Btu}}{\text{lb-mole-}^\circ\text{F}} \times \dfrac{(\text{Argon mass flow})\ \text{lb-mole}}{\text{h}}}$$

Additional heating from chemical reaction can be calculated if the reaction rate is known. For computational purposes I have assumed an inventory of 300 g of sodium reacting at a constant rate such that all of the sodium has formed NaOH in 60 min. This amount of sodium holdup is a reasonable, but not conservative estimate. Heats from chemical reactions are:

$$\text{Na} + \text{H}_2\text{O}_{(\text{liquid})} \rightarrow \text{NaOH}_{(\text{s})} + 1/2\ \text{H}_2$$
$$(\Delta \text{H}^\circ_{298} = -33.67\ \text{Kcal/mole})$$

If the temperature at the time of reaction were higher than recommended, the reaction

$$2\text{Na} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{O}_{(\text{s})} + \text{H}_2$$
$$(\Delta \text{H}^\circ_{298} = -31.08\ \text{Kcal/mole})$$

could occur.

However, the reaction to NaOH is the most exothermic and the most probable reaction. Calculations are therefore based on the formation of NaOH If 300 g of sodium react to NaOH at a uniform rate in 1 h, the chemical reaction produces 0.5 kWh/h of heat. Table 1 compares the argon temperature change for various mass flow rates at 2 and 7 kW decay heating. The $\Delta T_{A+\text{NaOH}}$ superimposes the chemical heat of reaction on the decay heating. The specific heat of argon is assumed to be 0.125 Btu/lb-°F or 5 Btu/(lb-mole) (°F). Argon and moist argon are assumed to obey the ideal gas laws.

Table 1 shows how much the coolant gases heat up at various gas flows during the transfer, reaction, and drying stages of sodium removal. The process is limited by the hottest point fuel pin temperature. An indication of the correlation between pin temperature and cooling gas temperature is needed. Information between pin temperatures and ΔT_A for heat inputs less than 2 kW is given in the literature.[4] Table 2 is a correlation of the data given by Bernstein et al with argon outlet temperatures as calculated by the present model. Ratios

---

[4] Bernstein, G. J., Chilenskas, A. A., and Molecha, R. F., *Interbuilding Fuel Transfer Coffin for the EBR-II Reactor*, ANL-6934, Sept. 1964.

less than one indicate that the model is nonconservative. The nonconservatism indicates that the heat transfer between pins and argon is not 100 percent effective. Conservative ratios for low heat inputs mean that radiant heat exchange with the surroundings and with outer pins is significant.

TABLE 1—*Argon outlet data for 2 and 7 kW decay heating.*

Mass Flow		Argon Velocity at Standard Temperature and Pressure, ft/s	ΔT_A °F		ΔT_A+NaOH °F		Argon Outlet Velocity for 1 atm with 100°F Inlet Temperature and ΔT_A+NaOH, ft/s 1 atm	
lb-mole, h	scfm		2 kW decay heat	7 kW decay heat	2 kW decay heat	7 kW decay heat	2 kW decay heat	7 kW decay heat
9	53.9	19.25	151	531	190	569	31	47
10	59.8	21.39	137	478	170	512	34	50
12	71.8	25.67	114	398	142	427	39	55
15	89.8	32.08	91	319	114	341	47	63
20	119.6	42.78	68	239	85	256	60	76
25	149.6	53.47	55	191	68	205	73	89
30	179.5	64.16	46	159	57	171	86	102
40	239.3	85.52	34	119	43	128	112	128
50	299.2	106.94	27	95	34	102	138	154
60	359.0	128.2	23	80	28	85	164	180
70	419.0	149.6	20	68	24	73	190	206
80	479.0	171.0	17	60	21	64	216	232

TABLE 2—*Comparison of* ΔT_A *with center line pin temperatures experimentally found at EBT-II.*

	At 20 scfm			At 30 scfm		
Heat Input kW	ΔT_A °F	C_L Pin Temperature Minus Average Inlet Temperature, °F	Ratio Calculated/ Experimental	ΔT_A °F	C_L Pin Temperature Minus Average Inlet Temperature, °F	Ratio Calculated/ Experimental
0.336	68	35	1.9	46	20	2.3
0.847	173	170	1.02	115	120	0.96
1.170	239	260	0.92	159	200	0.80
1.545	316	350	0.90	210	270	0.78

transfer between pins and argon is not 100 percent effective. Conservative ratios for low heat inputs mean that radiant heat exchange with the surroundings and with outer pins is significant.

The model predicts that the temperature rise during the $Na + H_2O \rightarrow NaOH + 1/2\ H_2$ reaction should be easily detectable for a reaction rate of 15 g per min sodium. Monitoring argon outlet and inlet temperatures and H_2 buildup rates will tell an operator if the chemical reactions are going too fast. However, they will not tell him when the reaction has gone to completion.

Since the argon flow rates give a nonconservative estimate of center pin temperature, the following conversion should obtain a conservative center pin temperature estimate from the argon ΔT_A.

1. Determine maximum permissible center pin temperature.
2. Determine argon inlet temperature.
3. Let ΔT_A = 1/2 the difference between 1 and 2.
4. Calculate mass flow rate from the equation:

$$\frac{\left(3413\ \frac{\text{Btu}}{\text{kWh}}\right)\left(\frac{\text{kWh}}{\text{h}}\ \text{heat input}\right)\left(359\ \frac{\text{scf}}{\text{lb-mole}}\right)}{\left(5\ \frac{\text{Btu}}{\text{lb-mole Ar}}\ {}^\circ\text{F}\right)\left(60\ \frac{\text{min}}{\text{h}}\right)\left(\Delta T_A\ {}^\circ\text{F}\right)} = 4084\ \left(\frac{\text{heat input in } \frac{\text{kWh}}{\text{h}}}{\Delta T_A\ {}^\circ\text{F}}\right)\ \text{scfm}$$

This should give a reasonably conservative estimate of the flow necessary to keep below any given maximum center pin temperature.

Flow rates are limited to velocities below Mach 0.4 because of excessive vibration experienced at higher velocities. Pressurization of the system to 1 to 2 atm gauge pressure eliminates the possibility of ever needing to approach coolant velocities of Mach 0.4.

Loss of Cooling

If cooling is lost the center fuel pins have a nearly adiabatic heat up rate. Assuming that the decay heat is primarily produced in the core region of a fuel assembly the heat up rate can be calculated by:

Volume of cladding in core region of one fuel pin	0.365 in.^{3}
Weight of fuel in one fuel pin	0.40 lb
Volume of wire wrap in core region of one fuel pin	0.089 in.^{3}
Heat capacity of fuel	0.0324 $\frac{\text{Btu}}{{}^\circ\text{F}}$
Specific heat of stainless steel	0.128 $\frac{\text{Btu}}{\text{lb-}{}^\circ\text{F}}$

$$\text{Heat up rate} = \frac{(\text{heat input/unit time})}{(\text{heat capacity of pin assembly})}$$

For an FFTF 1st core subassembly, this equation reduces to:

(5.42)(decay heat of subassembly in kW) = heat up rate in °F/min

Flushing with Water

After sufficient moisture has been added to the coolant argon to react all the residual sodium to solid sodium hydroxide, the sodium hydroxide residue must be washed off. This can be done using high-purity water. The quantity of water and the method of water rinsing must be determined. Water volumes are necessary to size the water feed and dump tanks. The water wash must be performed within FFTF containment. Therefore, strenuous safety precautions are necessary to prevent incidents occuring from uncontrolled sodium-water reactions. Batch processes using minimum adequate water quantities are necessary.

EBR-II uses 125 gal of water to wash sodium hydroxide from reactor fuel. FFTF fuel subassemblies have about four times the surface area of EBR-II subassemblies. Therefore, a water rinse capacity of 500 gal was deemed necessary for FFTF. A recirculation capability for the rinse water is currently being studied. This may significantly reduce the amount of water required to thoroughly rinse each fuel subassembly. The EBR-II method of determining rinse completion will be used at FFTF. This involves measuring the resistivity of the charge water and the effluent. The use of $\mu\mu$mho water for charge allows very good sensitivity. EBR-II data indicate that a factor of 2 or 3 degradation in water resistance at 5 gal/min flow rate gives satisfactory rinsing. A similar number is expected to be obtainable for FFTF. Also, sodium ion monitoring may be used.

An analysis of the effect of 7 kW decay heat load on the water rinse cycle is also necessary. If the subassembly is accidently filled with water while hot, the water will flash to steam. Since the use of hot water for rinsing seems favorable, the case of 212°F water entering a subassembly with an average temperature of 600°F was checked. At a water fill rate of 5 gal/min, 250 standard cubic feet of steam will be formed in 18 s. This would require an escape velocity from the top of the subassembly of 230 ft/s at 2 atm to avoid pressure buildup.

If a 7 kW subassembly is at 212°F when 212°F water is added at 5 gal/min, then about 0.7 percent of the water will form steam. This steam would exit the subassembly at about 2 ft/s at 2 atm if the entire cross section of the flow stream was open. Since the flow stream will be filled with water, bubble formation and vigorous boiling can be expected. If cold water entered the 7 kW subassembly at 5 gal/min, the average temperature rise of the water would be 9.3°F. This use of cold water is doubtful because of localized boiling and water hammer effects which have been observed in the past while using cold water. During startup, the rinse water temperature will be investigated. However, it presently appears that a rinse water temperature of 195 to 200°F will be best.

Drying

After rinsing, the subassembly is drained and the water is immediately replaced with argon. The argon is now acting as a coolant for high gamma heat subassemblies and as a carrier gas for drying all subassemblies. Since some of the subassemblies which must have sodium removed will produce negligible heat, heaters must be added to the system for drying these low decay heat subassemblies. The moisture content of the argon must be below 50 ppm before the sodium removal system can be opened. This prevents moisture contamination of argon cell within which the sodium removal equipment operates. After drying, the subassembly is clean and ready for disassembly and examination.

Summary

Of the currently known methods for removing sodium from FFTF test subassemblies, the argon-moist argon-water rinse process best meets all the imposed requirements. Calculations necessary for sizing argon blowers and water rinse tanks are presented. The need to maintain cooling at all times greatly increases the sodium removal difficulties. However, it is possible to perform all stages of the cleaning process without overheating a subassembly.

Discussion

J. S. Armijo[1] *(written discussion)*—This paper essentially represents a sizing effort to assess the use of the EBR-II sodium removal techniques for FFTF fuel. While there is no doubt the process described by the author will remove most of the sodium from the fuel, it still may not be suitable. First, there are relatively new data[2,3] (familiar to most AEC contractors) that show the presence of high concentrations of small (~ 1 μ diameter) holes on the surfaces of stainless steels which have been exposed to high-temperature sodium. The author should acknowledge these surface defects and discuss whether the proposed cleaning method will remove sodium from such small and deep (5 to 25 μ) holes.

Second, the author should be seriously concerned with the possibility of caustic stress corrosion cracking of stainless steel cladding by the proposed cleaning process. A serious discussion of this phenomenon is mandatory in view of (1) the deliberate formation of NaOH during cleaning, and (2) the highly susceptible sensitized and radiation hardened structure of the cladding. The sodium removal process described in this paper is potentially damaging to the items it is intended to clean.

R. R. Borisch (author's closure)—The small holes discussed in GEAP 10394 have not been confirmed to date in fuel pins being tested at the Experimental Breeder Reactor II (EBR-II) in support of FFTF fuel studies. Some preliminary surface investigations performed in May 1973 indicate that such holes may be present. If so, the current studies are actually cleaning and reinserting fuel cladding containing "tunneling" holes into EBR-II for further in-pile testing by the same process discussed here. Theorizing on the effectiveness of this process or any other process in removing sodium from these holes would be premature because of the complete lack of sodium removal data from very small diameter, deep holes. We have found, however, that this process is very effective in removing sodium from crevices as narrow as 400 μm and as long as 3 in. This data will soon be published in HEDL-TME 73-32. Other than observing the

---

[1] Manager, Plant Materials & Processes, General Electric Co., San Jose, Calif. 95114.

[2] "Summary Report—Sodium Mass Transfer Program Effects of Sodium Exposure on the Corrosion and Strength of Stainless Steels—August 1971," GEAP-10394.

[3] Sandusky, D. W., Armijo, J. S., and Wagner, W. J., *Journal of Nuclear Materials,* Vol. 46, 1973, p. 225.

effects, if any, on the cleaning and reinsertion of fuel pins in the aforementioned study, no further work in the area of cleaning very small holes is currently planned.

As stated in the text, a potential for caustic stress corrosion cracking is recognized and a study of this phenomena on sensitized stainless steel is currently underway. This work will be considered for a future published report. It should be recognized that the process described here maintains the fuel subassembly below 250°F from before the time caustic is formed until after it is washed off. Also, the entire process is to be completed within one working shift. I have *not* found anything in the literature to indicate a stress corrosion cracking problem exists when working within these parameters.

J. H. Hicks[1]

Cleaning of Fluid Systems and Associated Components During Construction Phase of Nuclear Power Plants

REFERENCE: Hicks, J. H., "Cleaning of Fluid Systems and Associated Components During Construction Phase of Nuclear Power Plants," *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 175–186.

ABSTRACT: In 1969, the American National Standards Institute's (ANSI) Committee N45 on Reactor Plants and Their Maintenance initiated a program to develop quality assurance standards for nuclear power plants. The standards are sponsored by the American Society of Mechanical Engineers (ASME). To date more than ten standards have been prepared or are in preparation. One of the standards, which is the subject of this paper, covers the cleaning of fluid systems and associated components during the construction phase of nuclear power plants. This standard emphasizes the importance of planning and establishing a cleaning program for the construction phase to maintain the required cleanness of fluid systems and components during and after installation or erection and the preoperational cleaning and lay-up requirements of fluid systems to render them ready for service. The standard also lists the requirements for the practices and procedures used to implement the cleaning program, the requirements for cleanness classifications used for the systems, and precautions that should be observed in performing the cleaning operations.

KEY WORDS: stainless steels, cleaning, nuclear power plants, construction, quality assurance, systems, components, planning, cleanness classes, cleanness control

About three years ago the American National Standards Institute's (ANSI) Committee N45 on Reactor Plants and Their Maintenance established a group of ad hoc committees to develop quality assurance standards for the construction phase of nuclear power plants. As work on these standards has progressed, the ad hoc committees have been converted to permanent working groups, and a main subcommittee, known as the ANSI N45-2 Subcommittee, has been chartered to oversee the preparation and issue of the standards. The standards include such construction phase activities as packaging, shipping, storage, and handling of items; housekeeping; installation, inspection, and testing of instrumentation and electrical equipment, installation, inspection, and testing of structural concrete and structural steel; installation, inspection, and testing of mechanical equipment; qualification of inspection, examination, and testing personnel; and cleaning of fluid systems and components, the latter of which is the subject of this paper.

This work is also sponsored by the American Society of Mechanical Engineers

---

[1] Principal engineer, Nuclear Power Generation Div., Babcock & Wilcox Co., Lynchburg, Va. 24505.

(ASME), but other appropriate technical societies' standards groups have been involved to the extent of technical support or sponsorship of working group activities in their area of competence. Examples are: Institute of Electrical and Electronic Engineers (IEEE), American Society of Civil Engineers (ASCE), and American Society for Quality Control (ASQC).

A large number of people are involved in the work of the subcommittee and the working groups; essentially all of the participants are actively engaged in quality assurance related activities in various sectors of the nuclear industry, Atomic Energy Commission (AEC), and national laboratories. Each standard issued by the subcommittee has been subject to an intensive preparation and review process and is believed to contain precise statements of acceptable current practices for commercial nuclear power plants—practices which are practical, currently available, and judged necessary to achieve required levels of quality. These standards are intended to be compatible and consistent with AEC quality assurance requirements (10 CFR Part 50 Appendix B) and ASME Boiler and Pressure Vessel Code Section III—Nuclear Components (Section NH-4000). Whereas AEC regulations and the Code are mandatory regulations establishing firm requirements for the areas they cover and, hence, include assignments for responsibilities, the standards prepared under ANSI N45-2 are not written as self-sufficient regulatory documents and are intended to be supplemented by: (*a*) a regulatory requirement prescribing its use (that is, the AEC's codes and standards rules 10 CFR Part 50), (*b*) a power plant applicant's license commitments, or (*c*) an appropriate procurement document.

The standards provide both requirements and guidelines. The requirements which almost always use the verb "shall" are expected to be followed if one intends to comply with the standards. The guidelines, which use the verbs "should" and "may" (and are sometimes introduced with the words "as a guideline"), are not intended to establish rigid requirements and generally serve to indicate the practices in the industry. This approach has been specifically applied to the cleaning standard.

Commentary on Cleaning Standard

General

The cleaning standard contains ten sections; the first of which defines the scope and applicability of the standard, identifies responsibilities, and provides definitions of some of the more important or unique terms associated with cleaning or both. A more comprehensive glossary of quality assurance terms is being supplied in another standard which is being prepared specifically for this purpose. The next section contains the general requirements that are to be fulfilled by any group or organization that is responsible for any work associated with cleaning in terms of planning for cleanness and cleanness control activities; preparation of procedures and instructions for cleanness control practices and inspections, examinations or tests to verify cleanness of items; and contents of the actual procedures and instructions to be used. The third section presents the criteria for cleaning and lists the cleanness classifications to be used. The next five sections discuss the cleanness and cleanness control related to preinstallation cleanness, installation cleaning, maintenance of installation cleanness, preoperational cleaning after installation is completed, and layup and post-layup requirements until the systems are prepared for operation.

Scope

The standard primarily covers those systems whose satisfactory performance is required for safe and reliable operation of the plant, but the requirements may also be extended to other parts of nuclear power plants when specified. The intent is to require close attention to cleanness control during erection of the plant so that only water flushing or rinsing an installed system is required to render it ready for service. Of course, it is realized that this intent cannot always be achieved and the standard presents additional requirements where these may be necessary.

The scope of the standard terminates when the systems are ready for preoperational testing because it is considered that the normal water quality specifications apply during the subsequent periods.

General Requirements

The objectives of field cleaning and a cleanness program are: (*a*) to ensure the removal of any deleterious contaminants, (*b*) to minimize recontamination of cleaned surfaces, and (*c*) to minimize the cleaning required after installation. These objectives can only be achieved by making specific plans for cleaning activities, preparing detailed procedures and instructions for such activities, and seeing that the cleaning program is followed and carried out.

The planning must start well in advance of construction phase activities to define cleaning and inspection operations to be used, the systematic, sequential progression of cleaning operations for each item or system, the responsibilities of parties concerned for each operation, and measures to be employed to preserve the cleanness of cleaned surfaces. Planning for cleaning activities includes a review of system and component design specifications and drawings and of construction work plans and schedules to ensure that provisions for cleaning have been incorporated; that they can be accomplished as specified; and that time and resources are sufficient to accomplish the required actions. The standard lists the following items as appropriate to the review.

1. Adequacy of vents and drains, inspection access points, bypass or recirculation lines.
2. Facilities for filters, and flushing or drain connections or both, in locations where dead legs are unavoidable.
3. Piping system design and installation in a manner which minimizes the necessity for installation of temporary piping during the cleaning operations.
4. Sequencing of the installation operations to provide for visual inspection (crawl through) of the inside surfaces of large diameter piping.
5. Control of the installation operations so that piping and components which

have already been installed are not subject to contamination when subsequent installation operations are performed.

6. Adequate pumping and heating capacities when these are important factors in the cleaning operations.

For the cleaning procedures the standard considers the appropriate subjects are: (1) detailed cleaning–cleanness control procedures, (2) personnel safety considerations, (3) structure or facility protection considerations, (4) inspection and test equipment requirements, (5) sequence of work activities, inspections, and tests, (6) sequential steps for a given activity, (7) acceptance criteria including methods for verifying cleanness, (8) preparatory checks, (9) approvals, (10) responsibilities, and (11) data report forms.

The standard states that the preparation of the actual working procedures or instructions should consider the following.

1. Work practices, housekeeping, access control, and prevention of contamination and recontamination.
2. Effectiveness of cleaning procedures for removal of the contaminants.
3. Corrosiveness of cleaning solutions in contact with the material of an item, particularly in the case of dissimilar metals.
4. Chemical composition, concentration, and temperature limits of cleaning solutions to avoid deleterious effects.
5. Proposed solution and metal temperatures, solution concentrations, velocity, and contact times during cleaning.
6. Methods for monitoring cleaning solution concentration and temperatures during cleaning operations.
7. Identification of the systems and subsystems with which the procedures are to be used.
8. Proposed sequence of operations and methods of filling, system circulation, draining, and flushing.
9. Proposed equipment isolation, location of temporary piping and valves, location of strainers and where possible, the location of temporary equipment.
10. Construction operations prohibited during the cleaning operations.
11. Methods for rinsing and neutralizing including number of rinses.
12. Methods for verifying cleanness.
13. Methods of drying and layup of the system.
14. Methods for protecting installed equipment which are not used in the cleaning operations.
15. Methods for disposal of cleaning solutions.

While the three preceding lists are quite extensive, it is obvious the complete lists do not apply to all construction phase cleaning situations, particularly the last tabulation on the contents of actual working procedures and instructions. For example, solvent wiping and water flushing and rinsing are normally employed if the general cleanness is properly maintained. The main point to be stressed is that there is a tendency to give cleaning and cleanness control secondary emphasis and that all of these items must be considered to assure that the cleaning is properly performed and cleanness is properly maintained in association with other construction phase activities.

Criteria for Cleaning

The degree of cleanness required is a function of the particular item under consideration. The assignment of a cleanness level to a system or item is related to the susceptibility to corrosion of the material, the consequences of malfunction or failure, and the probability of contaminants contributing to or causing such malfunction or failure. The standard does not establish the cleanness level of any specific item as the specific applications vary with the plants under consideration. However, the standard presents typical examples as a guide. The standard lists four cleanness classifications for construction phase activities, which are as follows.

Class A—A very high level of cleanness in which there is no evidence of contamination of a surface either under visual examination, with or without magnification, or with the aid of sensitive detection methods. Class A cleanness applies to special items, such as fuel elements, control rod drive mechanisms, delicate instruments, and other close tolerance or carefully controlled surfaces or assemblies. Such items should receive their required level of cleanness at the point of manufacture and cleanness must be maintained at the construction site. For these reasons the standard considers the requirements for this cleanness level to be outside the scope of the standard.

Class B—A high level of cleanness applicable to reactor coolant systems, components, and other items, such as the reactor coolant purification system, which have similar cleanness requirements.

Piping and components in systems which are designated as requiring this cleanness have the following requirements:

1. The surfaces shall appear "metal clean" when examined without magnification under a lighting level (background plus supplementary lighting) or at least 100 foot candles. Scattered areas of rust are permissible provided the aggregate area of rust does not exceed 2 in.^{2} in any 1 ft^2 area. Localized rusting may indicate pitting of the surfaces and should be evaluated metallurgically. Thin temper films resulting from welding or postweld heat treatment are acceptable.
2. The surface shall be free of particulate contaminants such as sand, metal chips, weld slag, etc.
3. The surfaces shall be free of organic films and contaminants such as oils, paints, and preservatives as determined by a visual examination or an organic solvent-dampened white cloth or an equivalent alternate method.
4. When visual inspection is not possible and the surfaces are accessible, a dry white-cloth wipe, followed by a solvent-dampened white cloth wipe may be used to evaluate the cleanness of the surface. If either cloth exhibits indications of contamination, the system shall either be recleaned or the specific contaminant shall be determined and evaluated as to its potential deleterious effect.
5. If flushing is the only means for determining system cleanness, the system shall be evaluated by examining a 20 mesh or finer filter, or the equivalent, installed on the outlet of the cleaning circuit. The system shall be flushed at its

normal velocity (or other velocity if specified) until the screen shows no more than slight particle speckling and no more than slight rust staining. There shall be no particles larger than 1/32 in. in any dimension, except fine hair-like slivers less than 1/32-in. thickness are permissible up to 1/16 in. long. There shall be no evidence of organic contamination in the effluent water or on the filter.

Class C—An intermediate level of cleanness generally applicable to closed loop service water systems that cool components containing reactor coolant, engineered safety systems, feedwater systems, and other high integrity systems. Surfaces have the same requirements as Class B cleanness, except:

1. Thin uniform rust films are acceptable on carbon steel surfaces.
2. Scattered areas of rust are permissible provided that the area of rust does not exceed 15 in.^2 in any 1 ft^2 on corrosion resistant alloys.
3. Flush-test filters may exhibit considerable rust staining.

Class D—The level of cleanness applicable to fire-protection, open service water, and similar systems requiring a nominal degree of cleanness. The following are acceptable on items which meet Class D cleanness.

1. Tightly adherent mill scale on carbon steel surfaces.
2. Paint or preservative coatings on carbon steel surfaces that will not peel or flake when exposed to cold-water flushing.
3. Rust films on carbon steel and stainless steel surfaces that resist removal by scrubbing with a bristle brush.
4. If flushing is the only practical means of determining system cleanness, the system shall be evaluated by examining a 14-mesh or finer filter, or the equivalent, installed on the outlet of the cleaning circuit. The system shall be flushed at its normal velocity until the screen shows no more than occasional particle speckling. There shall be no particles larger than 1/16-in. thickness in any dimension, except hair-like slivers of less than 1/16-in. thickness are permissible up to 1/8 in. long. There shall be no evidence of organic contamination on the screen; considerable rust is acceptable.

Preinstallation Cleanness

As indicated in the introduction of this paper, another ANSI standard has been prepared for packaging, shipping, receiving, storage, and handling of items. Of course, the desired cleanness of an item should be established at the point of manufacture and should be maintained while the item is being shipped and is being stored and handled at the construction site.

Items should not be delivered to the point of installation site sooner than necessary unless the installation location is considered to be a better storage area. Large items such as steam generators, reactor vessels, etc., are usually installed as soon as they arrive at the construction site. Inspections, examinations, and tests as appropriate shall be performed immediately prior to installation to determine the cleanness of the item. If contaminants are detected, they shall be removed if it is judged that they will not be removed in subsequent cleaning operations. Items having surfaces to which temporary paint or preservative coatings have been applied shall be identified, the composition of the coatings and methods for its removal shall be determined and removal of coatings, where required, recorded in the inspection report. Unless otherwise required by the job specifications, the temporary coatings shall be removed prior to installation of items.

Installation Cleaning

The installation process represents an opportunity for the introduction of contaminants into a cleaned item and care should be taken to minimize such contamination. Operations which generate particulate matter, such as grinding and welding, should be controlled. Local cleanup of contaminated areas is recommended as installation progresses, rather than one cleanup when installation is completed. Consideration should be given to sequencing installation and erection operations, when practical, to facilitate cleaning and cleanness control. Where visual inspection of internal surfaces of a portion of a system can be blocked, that part of the system should be fabricated as a complete unit and a visual inspection should be performed just before the access points are closed.

Openings and pipe ends shall be sealed at all times except when they must be unsealed to carry out necessary operations. Fitted and tack-welded joints (which will not be immediately sealed by welding) shall be wrapped with polyethylene or other nonhalogenated plastic film until the welds can be completed.

Precautions shall be taken to avoid contamination of crevices, blind holes, dead legs, undrainable cavities, and inaccessible areas. When grinding, sanding, chipping, or wire brushing, the item shall be so orientated that chips fall away from the openings or covers shall be provided for the openings.

Marking materials containing sulfur, lead, zinc, mercury, and other low melting alloys as a basic chemical constituent shall not be brought into contact or shall not be used on the surfaces of corrosion resistant alloys. Low sulfur, low fluorine, low chlorine compounds may be used on austenitic stainless steels. Low sulfur, low lead compounds may be used on nickel-base alloys. Paints, chalk, and other temporary marking materials shall be removed by solvent-wiping or mechanical means. Surfaces should be cleaned after completion of work on them, before proceeding to the next installation or construction step. The use of mineral acids on austenitic stainless steels and nickel alloy should be avoided except when the material is in the solution annealed condition. Pre-cleaning and post-cleaning of weld joint areas and welds shall be performed by wire brushing and scrubbing with a solvent-moistened clean cloth unless specified otherwise.

Local rusting on corrosion resistant alloys should be removed by mechanical methods. Large openings, such as the open reactor vessel, shall be protected against falling and windblown contaminants.

Maintenance of Installation Cleanness

After any isolatable system has been installed in a clean condition and cleanness control measures have been established, access control into the system is essential to minimize the introduction of contaminants between the time of system isolation and preoperational testing. Access control shall be established to exclude personnel and contaminants. Where environmental contamination could cause degradation of quality, seals must be installed which must be hermetically tight and difficult to remove. Gasketed metal seals with welded metal strap enclosures, or seal welded metal caps, are recommended for Class B systems and components. Items in this condition shall be tagged with identifications and instructions for seal removal. If access to a sealed system is required, precautions shall be taken to prevent introduction of contaminants. Prior to opening the seals, the immediate surroundings should be cleaned to remove solid contaminants which might be introduced in the system. Personnel entering the system should wear clean outer clothing and shoe covers. When the necessary work is completed, the interior surface shall be locally cleaned to its original condition and the system should be resealed.

Preparations for Preoperational Cleaning

Cleaning and flushing operations shall be scheduled so as to minimize interference from other plant operations. Areas in which cleaning operations are being performed shall be isolated to the extent that personnel performing other construction phase operations are aware that the cleaning operations are being conducted.

Personnel shall be familiarized with the intended procedure and associated hazards. Means for communicating shall be provided between the local areas in which the cleaning is performed and any remote areas (for example, control rooms) that may be related to the cleaning operations. Loose tools should be attached to either the workman or exterior of the system with a lanyard.

The actual circulating flow path shall be checked for agreement with specified requirements in regard to location, position, and status of all components. Critical valves, controls, and switches shall be tagged to prevent inadvertent actuation during the cleaning operation. The interior of all accessible components (for example, tanks) and large diameter piping shall be inspected for cleanness; all debris and contamination shall be removed.

Demineralizers, filters, instruments, valve internals, and other items that may be damaged by the cleaning process shall be blanked off, bypassed, or removed. Protective screens shall be installed on the suction side of all pumps and other components that may be subject to damage during the cleaning operations. Instrumentation (for example, pressure, temperature, and flow) shall be used where possible to monitor the cleaning operations. All other permanently installed instrumentation shall be isolated where possible. Cleaning should be completed before installation of fuel, reactor vessel internals, and control rods.

Provisions shall be made to collect leakage and to protect insulation from being wetted. Where the use of installed plant components, such as pumps, may be affected by the cleaning operations, recommendations shall be obtained from the component manufacturers regarding the use of their components. Procedures used to protect installed components which are not used in the cleaning operations but which are included in the cleaning circuit should be reviewed.

Water Flushing

If the intended level of cleanness has been maintained during erection of the plant, only water flushing will be required. The system shall be filled with water of the quality specified and flushed in accordance with approved procedures. Completion of flushing shall be determined by filter, turbidimetric, or chemical analyses. If the final flushes for removal of particulate contaminants are directed toward the reactor vessel, soluble contaminants shall be removed from the system by first flushing away from the reactor vessel until a specified water quality is achieved on the effluent from the system. At this time, high velocity flushes may be made toward the reactor vessel. This procedure is not recommended unless the reactor vessel internal surfaces are accessible for subsequent mechanical cleaning and inspection, or unless provisions are to be made to collect particulate contaminants at some accessible location within the reactor vessel by filtration or other technique.

After flushing is completed, but before system drain, all pockets and dead legs shall be flushed through their drain connections. If conditioned water (that is, water to which low concentrations of chemicals have been added to prevent precipitation of dissolved solids, inhibit corrosion, etc.) is used, particular attention should be given to assure that large volumes of solution do not remain trapped in the system. Care shall be taken to assure that organics do not remain on the surfaces. A final flush with demineralized water is desirable, but not necessarily required at this time. The system shall be sealed to prevent subsequent entry of contamination. If no further cleaning is required, system layup may be performed.

Alkaline Cleaning

Although it shall be the intent of those involved in erecting the nuclear plant to install piping systems in a clean condition, this may not be achieved. One relatively common source of organic contamination is lubricating oils from air tools. When local cleanup is not performed following grinding operations on internal surfaces of piping welds, full system cleaning to remove organic contaminants may be necessary. If required, the cleaning shall be performed according to the cleaning procedures established for the operation and the procedure shall assure that quantities of organics do not remain on the surfaces.

Alkaline cleaning should consist of the circulation of an appropriately heated solution until a selected area or coupon contaminated with the expected contamination is cleaned by the cleaning solution.

After system cleaning is completed, a flush with water of a quality consistent with the system requirements shall be performed to remove the cleaning agents. In particular, all pockets and dead legs should be flushed and attention should be given to assure that large volumes of solution do not remain in the system. The system should be sealed to prevent the subsequent entry of contamination. If no further cleaning is required, system layup may be performed.

Chelate Cleaning

Chelate cleaning is widely used to remove slightly soluble compounds, such as iron oxide, by complexing the metallic ions with organic chelating compounds such as ethylene diamine tetra-acetic acid (EDTA). It can be used to clean carbon or low-alloy steel surfaces to remove light corrosion product films although it is not a required cleaning operation by the standard.

If chelating cleaning is used, flushing with water of a quality consistent with the system requirements should be performed to remove the chelating agents. All pockets and dead legs in particular should be flushed and attention should be given to assure that large volumes of the chelating solution do not remain in the system. The system should be sealed to prevent the subsequent entry by contaminants. If no further cleaning is required, layup may be performed.

Cleaning Precautions

There are a number of precautions that should be observed during cleaning operations, and it was felt that these should be included in the standard. The ones listed for consideration as appropriate are as follows.

(*a*) The addition of a suitable chloride stress corrosion cracking inhibitor is recommended if fresh water flushing of systems containing austenitic stainless steels is planned.

(*b*) The use of alkaline cleaning compounds which contain free caustic is not recommended on components or systems in which cleaning solutions may be trapped. Cleaners based on compounds which produce hydroxyl ions by hydrolysis, such as tri-sodium phosphate, are recommended. If heavy organic contaminants are present, the addition of an emulsifier with a wetting agent may be considered.

(*c*) The use of acid-chelating agents on welded or furnace sensitized stainless steels and nickel base alloys is not recommended.

(*d*) The use of halogenated organic solvents is not recommended, except upon crevice-free, open, freely-evaporating surfaces. This recommendation is not intended to prohibit the use of solvents under other conditions, providing adequate removal is assured prior to any subsequent operations.

(*e*) Acid cleaning of installed systems is not recommended. However, if used, particular attention shall be given to:

1. avoiding the entrapment of acids in the crevices,
2. avoiding contact with either welded or furnace sensitized corrosion resistant alloys, and nonferrous materials,
3. complete removal of any residual acid solution from the system, and
4. neutralization treatment as a final operation.

Layup and Post-Layup Cleaning

Upon completion of preoperational cleaning, unless the system is to be released for the next series of operations or tests, the system should be placed in layup condition, if required, by filling with dry inert gas, the process fluid that will be used in the system during operation, water of purity equivalent to that used to make up the system, or chemically conditioned water.

Prior to the next series of operations or tests, residual cleaning solutions or layup chemicals shall be removed from the system by flushing, or draining and filling, until the effluent water from the system meets the preoperational test water quality requirements for the system.

Records

The standard states that cleaning record copies of completed procedures, reports, personnel qualification records, test equipment calibration records, test deviation or exception records, inspection and examination records shall be prepared. These shall be placed with other project records as required by code, standard, specification, or project procedures.

The preceding stresses the need for documentation of cleaning activities and one of the more common concerns expressed regarding the introduction of formal quality assurance practices in the industry has been the strong emphasis on documentation. Some have expressed the opinion that the regulations and associated standards appear to be so preoccupied with the quantity and quality of paper that the quality of the hardware and related items appear to be overlooked. A cursory reading of the ANSI standards could lead one to a similar conclusion. However, this is not the intent of these standards. The need for documentation cannot be overlooked because quality assurance demands visibility and, hence, documentation. If one is to assess the significance of documentation, it is necessary to be cognizant of the method or procedure employed to perform the inspection or test which resulted in the documentation and also to obtain some assurance that the individuals conducting and reporting the operation were capable of understanding and conducting the operation according to the prescribed requirements. It appears that it is difficult to accomplish this without written procedures, instructions, or similar documents, as well as objective evidence providing certification and data when required.

In order to help with the situation on records, the ANSI N45-2 Subcommittee has formed a working group to establish the requirements for records.

Recent Developments and Future Plans

As the work on the ANSI quality assurance standards has progressed, it has become apparent that the requirements for construction phase activities are also applicable to other activities. As a result, many of the standards are being extended to cover other activities. The working group on cleaning is looking at this for manufacture of systems and components and for modifications and repairs after the plants have been operated. The present standard is primarily related to water systems, and the needs for other fluid systems such as pneumatic and hydraulic systems are being investigated.

Acknowledgments

We wish to thank the members of the ANSI N45-2.1 Working Group, who have participated in the preparation of the cleaning standard, and the members of the ANSI N45-2 Subcommittee who have reviewed the preparation of the standard.

C. J. Veith[1]

Cleanliness Requirements in the Chemical Industry

REFERENCE: Veith, C. J., **"Cleanliness Requirements in the Chemical Industry,"** *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 187–195.

ABSTRACT: Cleanliness has been an attribute of major importance since the beginning of the chemical industry. It affects capital costs, operating costs, and product quality. The importance of cleanliness as well as the required degree of cleanliness has increased as technology has advanced to the point that some products now require expensively constructed and operated clean rooms.

When specifying cleanliness requirements, it should be remembered that the word clean, defined as freedom from extraneous matter, has a wide tolerance range and that the cost of cleaning increases exponentially with the degree of perfection specified. In order to ensure the required degree of cleaning at the proper cost level, the cleaning procedures should be specified or approved by the purchaser.

Many cleaning problems in the chemical industry have been reduced or resolved through the use of stainless steel due to the inherent property of being easily cleaned and its tendency to remain clean.

Four classes of cleaning requirements for stainless steels with the related cleaning procedures are described in this paper. In addition, comments are included relative to design considerations.

KEY WORDS: stainless steels, cleaning, contamination, chemical industry, inspection

In this paper I do not presume to speak for the entire chemical industry as I am certain that there must be almost an unlimited number of specific cleanliness requirements, cleaning procedures, and cleanliness opinions held by the various chemical manufacturers with which I am not familiar.

It is my observation, based on over 35 years of experience with the Du Pont Company, that cleanliness in the chemical industry is a matter of prime importance. It is also my observation that a comprehensive paper covering the subject is an impossible task, because there is no simple beginning or end.

Cleanliness, defined as "free of dirt or pollution" or as "free of extraneous matter," is a subjective quantity and as such it is difficult to administer. Clean means different things to different people. Clean means one thing to a mechanic operating on an automobile and something entirely different to a surgeon operating on a person. To one it means clean overalls, to the other sterilized

---

[1] Formerly, manager, Inspection Section, Construction Division, Engineering Department, E.I. du Pont de Nemours & Co., Wilmington, Del. 19898.

gowns.

It is an abstract quality which modifies, to some degree at least, nearly all chemical plant requirements. It is just about all inclusive and has to do with the cleanliness of the fuel firing the boilers and with the steam driving the turbines. It has to do with the cleanliness of the process equipment, the rest rooms, and the cafeteria kitchen. It applies to the cleanliness of the raw materials used for production as well as to the cleanliness or quality of the manufactured products, and particularly in recent years, to the cleanliness of the plant effluents. Also, it is an old subject; it was of concern to the chemical industry long before stainless steel, the subject material of this symposium, was invented.

History

In researching the subject of cleanliness in the chemical industry, I decided to start at the beginning—not the beginning of the manufacturing of chemicals, but the beginning in 1802 of the Du Pont Company for the manufacture of gunpowder.

From the very first, Du Pont has done its own engineering and construction, a policy which has been continued to the present. E. I. du Pont de Nemours, the founder of the company and its first engineer, was well acquainted with the hazardous nature in the manufacture of gunpowder, and he established the principal that safety for the worker is the number one consideration in the design, construction, and operation of a powder plant.

Safety precautions in the manufacture of gunpowder for obvious reasons, demanded the use of nonsparking tools and equipment, but one of the most important safety requirements was *cleanliness*, both in the machinery and in the general plant housekeeping—as accumulations of debris in the machines or about the premise could result in fires and explosions. Also, in reading the history of the Du Pont Company, it is noted that the early powder makers were also confronted with many other factors—corrosion, fatigue, pressure, leakage, and product quality in operating their plants.

Today, Du Pont's Engineering Department continues as the designers and constructors of the major portion of the company's manufacturing facilities. During the past ten years, the Engineering Department has completed approximately 1828 projects involving a total of over 2½ billion dollars for expansion and improvement of manufacturing facilities.

As of this date, starting with "A" blasting powder, and ending with Zytel® nylon resin, the Du Pont product book lists 1400 product lines. Manufacturing these 1400 product lines has required the use of nearly all known materials of construction incorporated into many types of chemical, mechanical, and electrical equipment.

This volume of construction and diversity of products, administered by the Engineering Department, undoubtedly presents, to some degree at least, all of the engineering and manufacturing problems experienced by the chemical industry. As a member of the Engineering Department particularly from the vantage point of being physically concerned with the inspection and testing of equipment for all of the Engineering Department construction projects, I find that many, if not all, of the old problems that earlier Du Ponters had to cope with are still with us today.

Safety is still the number one consideration in all company activities–but corrosion, pressure, fatigue, heat, cold, and *cleanliness* are still quality attributes of importance in the design, construction, and operation of chemical plants.

Cleanliness in New Chemical Plants

Cleanliness or really lack of cleanliness is of particular economic importance during the startup period of a new plant or project. Startup costs of new chemical plants can reach very significant and frequently unplanned and unexpected amounts. In some instances, more than a year has been required before a plant reaches and maintains full production. It is not infrequent, from my daily perusal of the *Wall Street Journal*, to note that reported reductions in corporate profits are often attributed to unexpected high startup costs of new facilities. Lack of cleanliness in equipment, of course, is not responsible for all startup problems; but it can and does create some expensive delays. Some examples of inadequate cleanliness which can cause startup delays are:

1. Weld slag and spatter, welding electrode stubs, bolts and nuts, small tools, and so forth, which knock out turbine and compressor blades and which damage pumps, valves, and other equipment.
2. Grit from sandblasting and from abrasive grinding wheels, chips from machining operations which score bearings, pump seals, control valve seats, and so forth.
3. Work gloves, old rags, broken light bulbs, larger tools, remains of lunches which reduce equipment capacity by plugging column downcomers and other equipment inlets or outlets.
4. Product contamination resulting from general shop dirt or from traces of iron which has not been cleaned from the system and which is picked up in the process stream.

In addition to problems at startup of new facilities, lack of proper cleanliness may result in numerous, long lasting, expensive problems in the operation of the new facility. Examples are:

1. Contamination of the manufactured product.
2. Debris left in crevices, caught behind weirs or in other dead areas which may become sites for accelerated corrosion attack.
3. Grease or small quantities of elements which may react explosively with the process stream, or which may poison a catalyst or perhaps make it impossible to obtain the necessary vacuum.
4. Some surface contaminants in trace quantities on either the internal or external surfaces or both of equipment fabricated of 300 series stainless steel may cause, under certain conditions, cracking or pitting. Such contaminants include chlorides and other halogens and molten metals particularly zinc, cadmium, copper, and their alloys.

While these problems resulting from lack of proper cleanliness are, of course, not confined to stainless steel equipment, I believe that they are relevant to this symposium on the cleaning of stainless steel because of the fact that in many instances problems which have been caused by lack of cleanliness have been eliminated or reduced by replacing the original material with stainless steel.

The relative more costly stainless steel is used as a replacement material because it is easily cleaned and tends to stay clean—analogous to the old cast iron frying pan, which in most kitchens has been replaced by one made of shiny, easy-to-clean stainless steel with a bottom clad with copper or aluminum for better heat transfer.

Stainless Steel Uses in the Chemical Industry

As you are aware, large tonnages of stainless steel are used in the chemical industry because it is highly resistant to corrosion in oxidizing environments. This high resistance to corrosion is also the reason that stainless steels are easily cleaned. Stainless steels are used:

1. To reduce corrosion of chemical process equipment to acceptable rates.

As a matter of historical interest, to the best of my knowledge, the first large scale application of stainless steel in the chemical industry was based upon its ability to resist corrosion. This plant, for the manufacture of nitric acid by the oxidation of synthetic ammonia built by Du Pont, came on stream in 1927. Its stainless steel equipment (high chrome iron in the terminology of the day) included eight 10-ft-diameter by 50-ft-high towers.

The high chrome iron, also called stainless iron, today would be classed as a Type 430 ferritic stainless steel. The alloy was originally called high chrome iron, as it could not be hardened by heat treatment and to distinguish it from the lower chrome cutlery grade alloys which were the only "stainless steel" grades commercially produced at that time. While Type 430 stainless steel is still used in the chemical industry, it has been supplanted to a large extent by the 300 series austenitic chrome-nickel stainless steels, and, unless qualified, the term stainless steel usually means one of the 300 Series.

2. To prevent contamination of materials being processed by corrosion products from the process equipment. In some cases, small amounts of corrosion products will contaminate and degrade a process stream even though the corrosion rate of a less noble material is well within acceptable rates for structural purposes.

3. To prevent contamination of the process material by providing a bright, smooth, easy-to-clean surface completely inert to both the process material and the atmosphere. Since there is no environmental corrosion, the surfaces of the equipment remain bright and easy to clean—free of rust and pitting during shutdown periods.

4. To permit acid cleaning of process equipment when processing material which adheres to or otherwise contaminates the equipment.

5. To provide a bright, clean finish which will remain bright and clean under environmental conditions—as in laboratory furniture and architectural trim and panels.

6. To enhance sanitary conditions and reduce cleaning labor in kitchens, cafeterias, first aid stations, and rest rooms.

Stainless steels in their various product forms at some point in their manufacture are clean. They have been annealed, grit blasted or pickled or both to white metal leaving the surfaces practically free of contaminants including free-iron. However, contamination frequently begins almost immediately by required additional mill operations.

As a result, contamination of the once clean and iron-free stainless steel surfaces which possibly begins before it is shipped from the producer's plant continues during shipping, interim storage, fabricating operations, and testing until the completed stainless steel object is given a final cleaning before it is placed into service.

Fortunately, this contamination for the most part is confined to the surface and is rather superficial in degree. The contaminants can be removed relatively easily by detergent washing, disc grinding, pickling, sandblasting, and so on. While it is possible that occasionally some embedded iron could occur from a hot working operation, it would be an extremely rare occurrence.

The required degree of cleanliness for the final cleaning of chemical process equipment is variable, dependent upon its service requirement; and may range from commercial clean to almost perfectly clean or maximum clean.

The final cleaning may be performed at the manufacturer's plant or it may be done after arrival at the construction site; but at either location cleaning costs can skyrocket as the required degree of cleanliness is increased from minimum to maximum. In the construction of new chemical plants, it is frequently advantageous for equipment to arrive on the site ready for installation as construction is a labor intensive activity always on a tight schedule and the elimination of site work may be of help to the project both from an economic and scheduling standpoint.

Also, it is customary for most equipment fabricators to do some cleaning of stainless steel process equipment before shipment to his customer. But the degree of cleanliness is extremely variable as each vendor's standard, or commercial standard, is the extent of cleaning which he has established for his fabrication; and it is not necessarily satisfactorily clean for installation as received.

To ensure that stainless steel process equipment arrives at our construction plant sites satisfactorily cleaned for installation and to control the cost of cleaning, we include cleanliness requirements in our specifications as follows.

Class 1–Commercial Clean

The purpose of this specification is to define our minimum essential and least costly cleaning specification for stainless steel process equipment which can be installed without further cleaning. All equipment fabricated according to this specification is to be reasonably free of weld flux, spatter, arc burns, gouges, tool marks, oil, and general shop soil, so as to provide a mutually acceptable workmanlike product. The interior is to be dried after cleaning.

In addition to the above requirements, stainless steel equipment or components of equipment which require heat treatment as the result of fabrication operations are to be sandblasted or pickled, both inside and outside to remove heat treatment scale and oxide. It is important that the pickling acid be thoroughly washed from the surface of the metal with clean water and the interior dried.

All equipment and separate components are to be closed and packaged as required to protect them and maintain their cleanliness. All vessels are to be closed immediately after having been cleaned and thoroughly dried inside. Each nozzle is to be protected by covering with an inexpensive soft full blank gasket backed up with thin metal lined cover. The cover is to be painted on both sides and held in place with a full complement of inexpensive galvanized bolts and nuts. Other openings are to be similarly closed and protected.

This specification which is satisfactory for by far the largest percentage of our stainless steel process equipment does not require: (1) the removal of heat discoloration due to welding, (2) Snag testing to determine the complete removal of weld spatter, (3) the removal of rust spots, and (4) it does not require the removal of mill markings or layout inks or the use of solvents or detergents to remove grease stains or other shop dirt.

Class 2–Free of Contamination (Not Iron-Free)

The purpose of this specification is to provide equipment which will assure minimum contamination of the process stream by more intensive cleaning requirements than necessary for Class 1, and which will be ready for process use without further cleaning. Class 2 cleaning requires, in addition to all of the requirements specified for Class 1, the following for the process side only:

1. The cleaned equipment must be completely free of weld flux, spatter, arc burns, oil, grease, shop soil, and visible rust.
2. Removal of visible rust using any means which does not bring in any iron or chloride contamination; acceptable methods are: grit blasting or sand blasting with clean new sand, stainless steel wire brushing, or nonchloride pickling.
3. Thorough cleaning using solvent, when necessary, to remove grease and followed by a steam jenny and detergent, or by scrubbing with bristle brushes using detergent or trisodiumphosphate and plenty of hot water. Detergent should be chloride free.
4. Thorough flushing with clean water and drying all inside surfaces using clean air, heat, lint-free cloth, etc.
5. Closing and packaging all equipment and separate components immediately after cleaning, as required, to protect and maintain their cleanliness.
6. Sealing all openings by taping with waterproof cloth backed tape or with a plastic film; then protecting this seal with metal cover bolted in place with a full complement of galvanized bolts and nuts.
7. Inspection by a Du Pont inspector for cleanliness and freedom from rust immediately after cleaning and drying, and the witnessing and approval of the sealings of openings immediately after for cleanliness.

This cleaning specification does not require the specific removal of free-iron, heat discoloration, or water stains.

Class 3–Clean (Iron-Free)

The purpose of this requirement is to provide equipment which will assure minimum contamination of the process stream from free-iron.

In addition to being free from iron as determined by ferroxyl testing and visual inspection, it is required that the equipment be commercially clean and packaged for shipment as described for Class 1 or cleaned free of contamination, Class 2, when specified.

The free-iron may be removed, if required, by pickling, detergent washing using bristle brushes, grit blasting, disc sanding, and so forth. Pickling for the removal of free-iron has frequently been accomplished by swabbing with a pickling solution followed by a water flush; since fabricating shop personnel generally are not accustomed to dealing with acids, many of them find it a very disagreeable job. In at least one instance, an electroplating company with personnel familiar with the handling of acids set up a pickling service for this purpose for area fabricators. The procedure used was to set the vessel on rolls partially filled with acid and rotate for a predetermined time; after recovering the acid, areas which were not submerged during rotation of the vessel are pickled by swabbing and the vessel is then flushed with clean water.

After cleaning, the equipment is visually inspected and ferroxyl tested by the Du Pont inspector to make certain that there is no embedded or concentrated iron present. Our acceptance criteria is that 95 percent of the surface must be free of iron indications, because we have found that a 100 percent free specification has been too expensive in normal shop environments.[2]

Class 4–Maximum Cleanliness

The purpose of this requirement is to provide equipment which assures virtually no contamination of the process stream by combining the requirements of iron-free Class 3 and the removal of all visible contamination.

In addition to those requirements listed in Class 2 and Class 3, Class 4 requires that all heat discoloration and water stains be removed from the process side of the equipment. The degree of cleanliness is judged by visual examination and by rubbing all surfaces with a lint-free white cloth and examining the cloth for contamination. Class 4, Maximum Cleanliness, is the most costly requirement.

These four classes of stainless steel cleaning requirements: Class 1–Commercial Clean; Class 2–Free of Contaminants (not iron-free); Class 3–Clean (iron-free); and Class 4–Maximum Clean are the basic cleaning requirements for stainless steel process equipment. However, these requirements are frequently supplemented with additional detailed procedural, design, and inspection requirements for specific types of equipment; for example, high vacuum

---

[2] Lackey, J.Q. and Streicher, M.A., *Journal of Materials*, Vol. 3, No. 2, Dec. 1968, pp. 983-995.

equipment and equipment involving major assembly operations such as bubble cap distillation columns.

It is suggested that the following points be considered for inclusion in the design or specifications of process equipment when cleanliness and cleaning are important.

1. Elimination of crevices by seal welding. Dirt which accumulates during fabrication or in service and is trapped in crevices is very difficult to remove; when free-from-iron is a requirement, it is almost impossible to pass the ferroxyl test. Crevices with their debris also provide sites for the initiation of corrosion.

2. Eliminate sharp inside corners.

3. Provide drainage. Areas which will not drain freely are more difficult to clean, particularly if flushing is required to eliminate process contaminants. Drainage slopes, holes and particularly a bottom outlet in vessels assist in cleaning.

4. Surface finish. It is self-evident that a smooth surface is easier to clean than a rough surface; it can be cleaned to a higher degree of perfection. A smooth surface will stay cleaner longer as it is easier for contaminants to stick to and build up on a rough surface. Some recent surface roughness measurements of stainless steel surfaces are shown in Table 1.

TABLE 1–*Roughness measurements of stainless steel surfaces.*

	Roughness Range
No. 1 finish stainless steel plate	150 to 300 AA
2B finish cold rolled sheet	10 to 40 AA
No. 4 polished plate	6 AA
No. 7 polished plate	2 AA
Weld, manual metal arc (MMA)	240 to 600 AA
Weld, gas tungsten-arc (GTA)	95 to 235 AA

To improve the surface finish of welds, a final wash pass by gas tungsten-arc (GTA) welding or smoothing with 150 to 180 grit wheel may be specified. Polished plate or sheet may be ordered polished from the mills or the polishing may be done by the fabricator. After fabrication, the welds are usually required to be ground flush to a finish equal to the plate finish. When a polished finish is required and the process permits, time and money can be saved by permitting the elimination of surface defects by dimpling.

5. Molten zinc, cadmium, copper, and their alloys in contact with chrome-nickel austenitic stainless steel under residual or applied stress can cause cracking. Zinc can be picked up from zinc-bearing paint or marking crayons, copper alloys, and galvanized materials or tools used in fabricating galvanized products. Contamination of stainless steels by these low melting point metals and alloys should be completely removed when the stainless is to be heated above 700°F. Copper surface contamination of stainless steel may result from rubbing contact between stainless and copper materials or components during

fabrication or in service, also by the use of copper for fixturing and as a heat sink during welding. Stainless steel suspected of having copper surface contamination should have the copper removed by disc grinding prior to welding to avoid the probability of weld cracking.

6. Chlorides or other halogens in the presence of moisture and stress can result in stress corrosion cracking and pitting. Chloride contaminants can result from brackish water and from the breakdown of chlorinated polymers and compounds such as cleaning solutions. If chloride contamination is suspected, the equipment should be flushed clean.

Summary

In summary, I would like to repeat that cleanliness requirements in the chemical industry are important and extensive. The degree of required cleanliness varies from commercial or broom clean, which probably satisfies most cleanliness requirements, to maximize clean.

The importance of the proper degree of cleanliness on new equipment is most evident at startup time. Dirt in the process stream from unclean equipment is like dropping a monkey wrench into the works and may stall a scheduled startup, causing confusion, delays, and perhaps expensive repairs.

Once the process is in operation, contaminants may cause operational and product quality problems.

Cleanliness problems in the chemical industry are not confined to stainless steel equipment, but because of a fundamental property so aptly described by its generic name, "stainless steel" has found wide acceptance in the chemical industry by eliminating or reducing the severity of cleanliness problems in many chemical plant applications by providing a stain-free, rust-free, easy-to-clean surface.

As an afterthought, I would like to point out that the very first commercial application of stainless steel was not based on its property to resist "strong water," as nitric acid has been called, but rather on the fact that it is stainless. According to "The Book of Stainless Steels" by Thum,[3]

> Harry Brearly of Sheffield, England discovered stainless steel in 1912. He was searching for a high melting point material for gun barrels, and in October 1912 published a paper recommending as the most suitable, an alloy of iron-chrome–later he reported on the unusual noncorrosive properties of the material. Nobody was impressed; perhaps the idea of producing, on a commercial scale, a steel that would not corrode sounded ridiculous.
>
> Not until June 1914 did Brearly meet Ernest Stewart, a cutler manager, . . . who realized that a rustless steel might be made into table blades. He–with Brearley's help–forged and heat treated about 125 lbs. of Firth's "aeroplane steel" as it was called, into knives. They were distributed to friends who were asked to report if they stained or rusted by contact with any foodstuff. Not a single knife failed this test.

---

[3] Thum, E.E., *The Book of Stainless Steels,* American Society for Metals.

D. A. Seiberling[1]

Design Principles and Operating Practices Affecting Clean-In-Place Procedures of Food Processing Equipment

---

REFERENCE: Seiberling, D. A., "**Design Principles and Operating Practices Affecting Clean-In-Place Procedures of Food Processing Equipment,**" *Cleaning Stainless Steel, ASTM STP 538*, American Society for Testing and Materials, 1973, pp. 196–209.

ABSTRACT: The term "cleaning" in the food processing industries refers to the treatment given all product contact surfaces following each period of use to remove all physical evidence of soil and to apply a bactericidal treatment to sanitize all surfaces. The normal period of use is less than one day and all equipment is thus cleaned at least once every 24 h.

Until recent years, cleaning of food processing equipment involved complete disassembly, manual cleaning by rinsing, brushing with solution, rinsing and sanitizing, and reassembly followed by application of sanitizing solutions just prior to processing. During the past two decades such manual cleaning procedures have been almost entirely replaced by Clean-In-Place (CIP) operations involving spray application or pressure recirculation of acid and alkaline detergent solutions under controlled conditions of time, temperature, and concentration. Such cleaning is essentially "chemical" in nature and processing equipment and CIP appurtenances are designed to permit the cleaning solution to be brought into intimate contact with all soiled surfaces and to be continuously replenished.

Stainless steel is a nearly universal material of construction for all processing and CIP equipment incorporated in such systems. It is generally possible to design and apply equipment and programs which can produce surfaces that are physically cleaned and nearly free of bacterial contamination. Experience has shown that solutions of strong alkalis, moderately strong acids, and sodium hypochlorides are highly effective in removing organic and mineral soils of almost any nature when these solutions are utilized in the proper combination or sequence.

KEY WORDS: cleaning, stainless steels, food processing, sanitation, food packaging

The term "cleaning," as related to the care and maintenance of equipment in the chemical processing industries, refers generally to the procedure of physically or chemically removing deposits in the form of a scale or sediment following prolonged use of a particular item of equipment or processing installation. By comparison, cleaning in the food processing industries (and in dairy products processing specifically) refers to the treatment given all product contact surfaces following each period of use to first remove all physical evidence of soil and to apply a bactericidal treatment to sanitize all surfaces. Non-product contact surfaces are given similar, though less rigorous, attention. The normal period of use is less than one day, and all tanks, vats, pipes, pumps,

---

[1] Assistant vice president, Equipment-Engineering Division, Economics Laboratory, Inc., Beloit, Wis. 53511.

valves, heat exchangers, and packaging equipment are thus cleaned at least once every 24 h. In some special instances, longer periods of continuous use of the piping system or certain tanks may reduce the frequency of cleaning to approximately once every third day.

Until recent years, cleaning of all milk processing equipment involved complete disassembly, manual cleaning by rinsing, brushing with solution, rinsing and sanitizing, and reassembly followed by application of sanitizing solutions just prior to processing. The labor required for these procedures frequently constituted as much as 50 percent of the total labor required to handle all phases of production operation from receiving through processing, packaging, and load-out.

The brewing industry (and other beverage processing industries) possibly applied a form of mechanical cleaning before the dairy industry, in that the nature of the equipment and products involved made it possible to apply less rigorous cleaning procedures, and piping systems in such plants frequently received nothing more than a substantial rinse followed by "solutioning," a process of pumping a cleaning solution through the system, following the product flow path, and discharging to sewer at the end of the system. However, as changes in processing and packaging have occurred, there has been increased emphasis on sanitation throughout the brewing process.

Prior to 1955, most recirculation cleaning was accomplished with existing product pumps by using existing tanks, vats, or small portable tanks as a solution tank for the recirculating procedure. Also, early applications of in-place cleaning were restricted to piping systems, and generally to only the longer piping systems. But, results achieved suggested that even greater benefits could be obtained if similar procedures could be applied to the cleaning of vessels such as tank trucks, processing vats, brew kettles, cookers, mixers, fermentation tanks, and storage tanks.

Experience has shown that Clean-In-Place (CIP) design provides the key to many other changes in technology. The ability to ensure controlled sanitation through mechanical/chemical cleaning has led to extensive development of all-welded product piping systems, application of air-operated valves, appreciable increases in the size of processing and storage tanks as compared to vessels that had to be cleaned manually, significant increases in processing flow rates and packaging machinery capacity, and approaches to plant design and arrangement not previously feasible. The total cleaning problem involves far more than pumps, tanks, sprays, and controls. The design of a modern food processing plant requires consideration of materials and methods of construction, equipment layout, specialized cleaning equipment, design of the processing equipment, and finally design of the process. The ability to clean-in-place, through application of mechanical/chemical procedures, permits design approaches which were not feasible when accessibility for manual cleaning was necessary.

Typical CIP Procedures and Recirculating Equipment

In-place cleaning as applied today is essentially chemical in nature. Processing equipment and CIP appurtenances are designed to permit the cleaning solution to be brought into intimate contact with all soiled surfaces and to be continuously replenished. Since relatively high volumes of solution must be applied to soiled surfaces for periods of time ranging from as little as 5 min to as much as 1 h (or more) recirculation of the cleaning solution is essential to maintain economic operation.

CIP systems are available in two different forms. Multi-tank recirculating units utilize the same wash solution for a large number of cleaning operations during the production day, adding to this solution as required to maintain strength and cleaning ability. Single-tank, single-use systems operate on the basis of making up smaller volumes of solution automatically to the required concentration, using it once at the lowest possible strength, and discharging it to the sewer at the end of each cycle.

The two systems are comparable with respect to program control equipment. Multi-tank systems require more space and utilize more parts in the form of tanks, valves, level controls, and temperature controls and require added attention during the operating day to check solution condition or to dump and recharge the tanks. The multi-tank systems also lack flexibility in that a single combination of temperature and concentration must be used for all equipment to be cleaned with the system. The single-tank system is smaller in size, simpler in design, lower in initial investment, and more flexible in application. All chemicals are fed automatically, and in the proper proportions, from the containers or from bulk storage (Fig. 1).

Some recent installations have incorporated systems which combine the advantages of single-use systems (flexibility and reliability) with water and solution recovery procedures which aid in reducing the total amount of water required for a given cleaning cycle (Fig. 2). These systems are designed to recover the "spent" cleaning solution and the post-rinse water from one cleaning cycle, store it temporarily, and then reuse this detergent/rinse water mixture as the pre-rinse on the subsequent cleaning cycle. This concept reduces the total water requirement for spray cleaning operations by 25 to 30 percent as compared to the alternative approaches. Steam consumption is reduced by 12 to 15 percent, and chemical consumption by 10 to 12 percent, both due to the fact that the pre-rinse with spent solution adds heat to the vessel as it effectively removes loose soil.

In addition to pumps, tanks, and valves, the CIP system will further include some type of program control equipment and chemical feed equipment. Then, a CIP supply-return system will be installed to permit the recirculation of flushing, washing, rinsing, and sanitizing solutions through various piping circuits and different items of processing equipment throughout the production period. In the dairy industry, both regulations and operating requirements have made it necessary to utilize make-break connections between cleaning supply-return piping and the various items of equipment to be cleaned in position. No valves are utilized to separate product containing circuits or vessels from solution containing piping. In some other industries, this requirement has not been

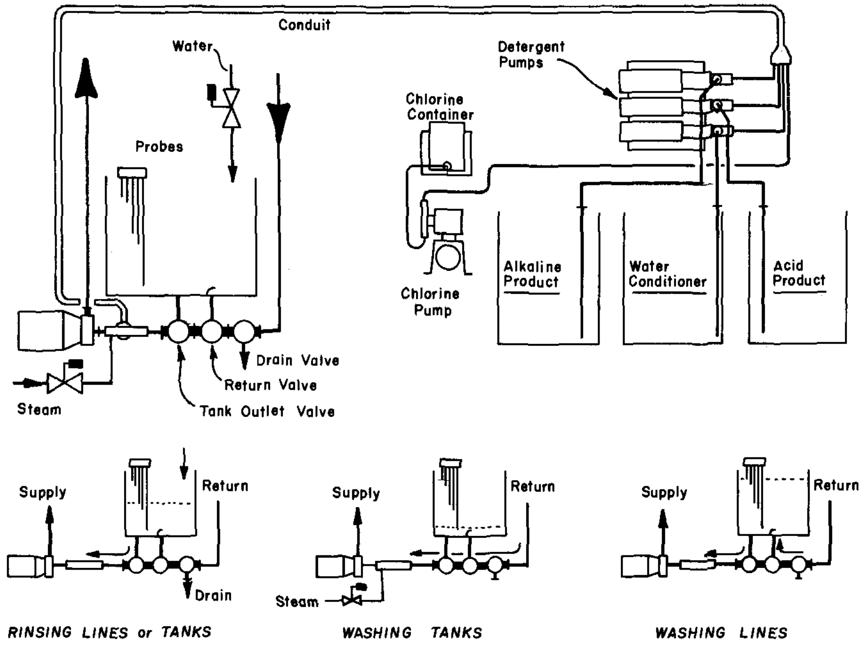


FIG. 1–*Schemetic diagram showing arrangement of recirculating unit and chemical feed equipment for single-tank single-use systems. Flow diagrams at bottom indicate water movement for rinsing tanks and lines, and solution movement for washing tanks and lines with systems of this design.*

mandatory, and, in fact, the larger sizes of lines and valves in use have made it impossible to consider such approaches. In this instance, leak protected valving is developed to prevent intermixing of product and solutions, and it is generally agreed that certain minimal portions of the piping will not be cleaned to optimum conditions.

Automated Process Piping Systems

Extensive all-welded air-valved process piping systems demand consideration of both production and cleaning problems when the system is still in the design stage. A total system (Fig. 3) must be separated into several different circuits, both with respect to variations in cleaning requirements and to schedule cleaning so as to avoid conflicts with production operations. The normal plant will generally have a minimum of three circuits including (*a*) raw product lines, (*b*) the processing system including the HTST pasteurizing unit, and (*c*) pasteurized product lines from the processing system to the fillers.

Complex piping systems of several thousand feet in length can be easily cleaned in a single operation. Pre-rinsing with cold or tempered water is continued until the effluent runs nearly clear; then recirculation of the cleaning solution is accomplished for periods of time ranging from 10 min to as much as 1 h. Temperatures may vary from 130 to 180°F or more. Chlorinated alkaline

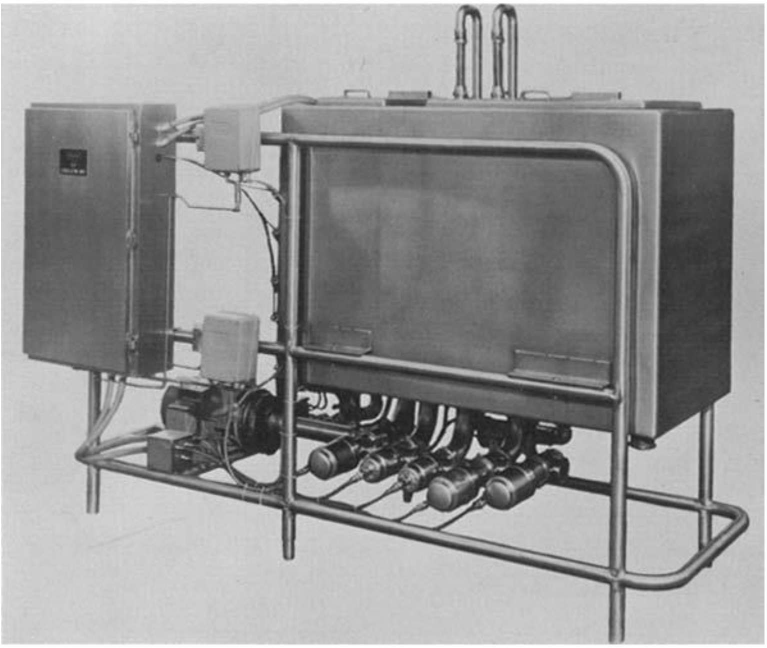


FIG. 2–*This single-use system incorporates an additional tank to recover spent solution and post-rinse water, and is programmed to utilize this water/solution mixture as the pre-rinse on the subsequent cleaning cycle.*

cleaners may be utilized alone or in the desired sequence with acid detergents. Where air-operated valving is utilized, the cleaning circuits will be developed to permit valves to be operated throughout the cleaning process so as to thoroughly clean all ports and all connecting lines. Following the solution recirculation, cold or tempered water is utilized as a post-rinse, and this is generally followed with either an acidified recirculated final rinse or a sanitizing rinse with a chlorine or iodophor based solution.

The generally accepted minimum velocity for CIP operations involving piping systems is 5 ft/s. However, satisfactory results have been achieved at velocities as low as 3 ft/s and in excess of 10 ft/s. Total circuit length must be controlled so as to achieve these velocities with the available CIP supply pump and within the pressure limitations imposed by other equipment.

Product Valves

The plug type valve of either two-way or three-way configuration is the valve most commonly used in food plant piping systems. Prior to 1969, such valves were available only with metal plugs and metal seats, generally failed to provide tight shut-off, and leaked continually when handling fluid products of low viscosity. The plug valve cannot be cleaned in position, and the plug must be removed following the pre-rinsing operation so that both the body and plug can be manually cleaned and sanitized prior to reassembly, after which the

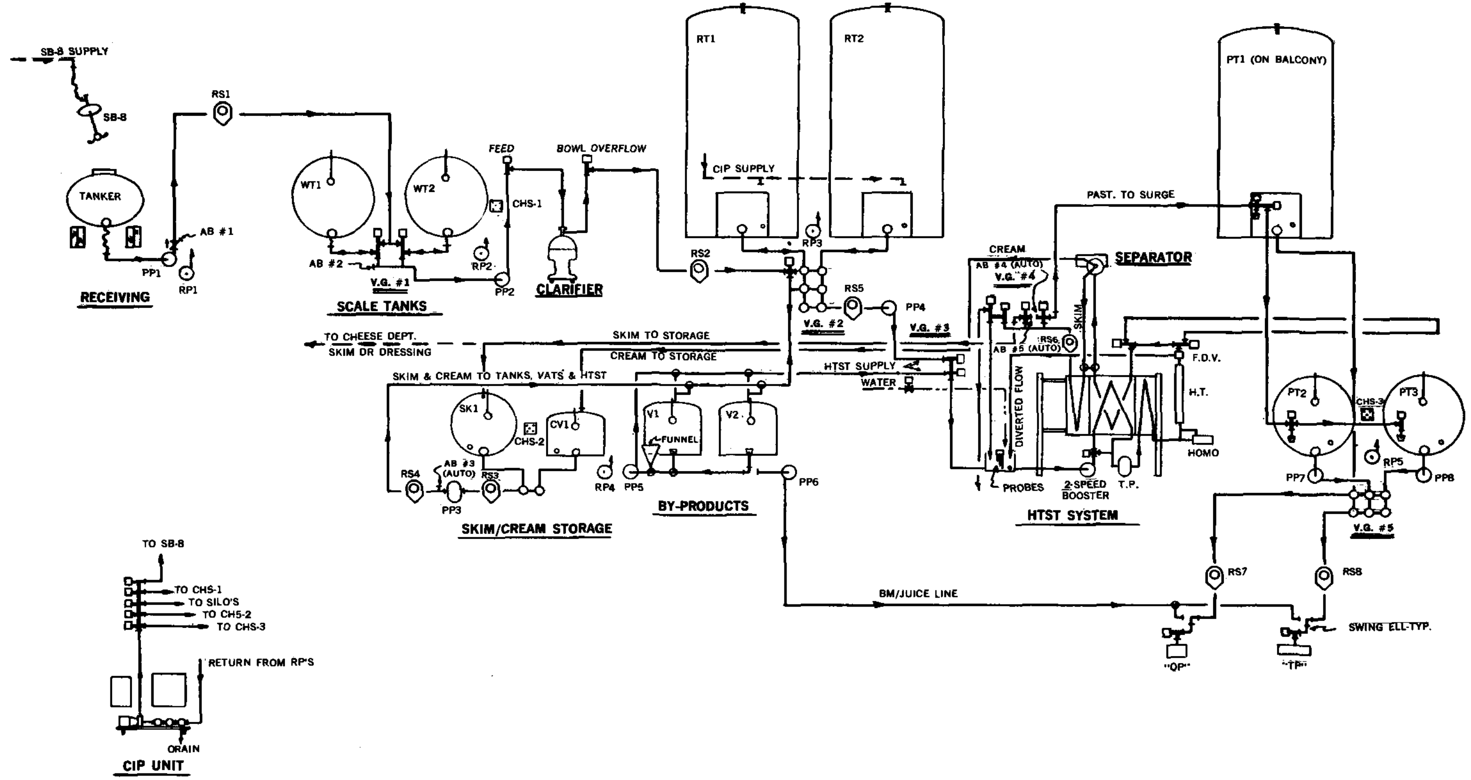


FIG. 3–*This typical schematic flow diagram of a small fluid milk processing facility illustrates the total piping and valving required for product movement from receiving to packaging. A system of this nature might be cleaned in three circuits including (a) raw processing lines from receiving pump PP1 to the HTST constant-level tank, (b) the HTST unit as a separate circuit, and (c) finished product piping from the HTST discharge valve to the fillers.*

remainder of the in-place cleaning operation is completed.

Diaphragm type valves have been used to eliminate the necessity for manual cleaning but have the disadvantage of being available only in two-way shut-off configurations. Hence, it is necessary to use three individual valves to achieve the same degree of flow control as is possible with a single three-way plug valve. And, these valves must be installed with the diaphragm in a near vertical position to achieve proper drainage of the body cavity.

Disk type valves have been used in some brewery applications. These valves can be cleaned effectively with exception of the shaft seal if left in the open position. But, they cannot be used as shut-off valves to close a port in a piping circuit which is being recirculation cleaned, for the areas beyond the valve disk will be contacted by cleaning solution.

The most satisfactory valve for CIP application is the compression type valve with a molded rubber valve disk or a Teflon O-ring seal on a stainless steel disk. O-rings are used for the valve stem seal (Fig. 4), and the piping system design provides for inclusion of all ports of the valve in the CIP circuit. Then, valve sequencing or cycling equipment is used to operate the valves in proper combinations throughout the cleaning program, causing water to first pass through the piping system in one direction, then another, in as many as six or eight different manners (Fig. 5). Every valve will be operated two or three times during the pre-rinse, four or six times during the wash, and three or four times during the post-rinse. All portions of every valve and every part of the piping

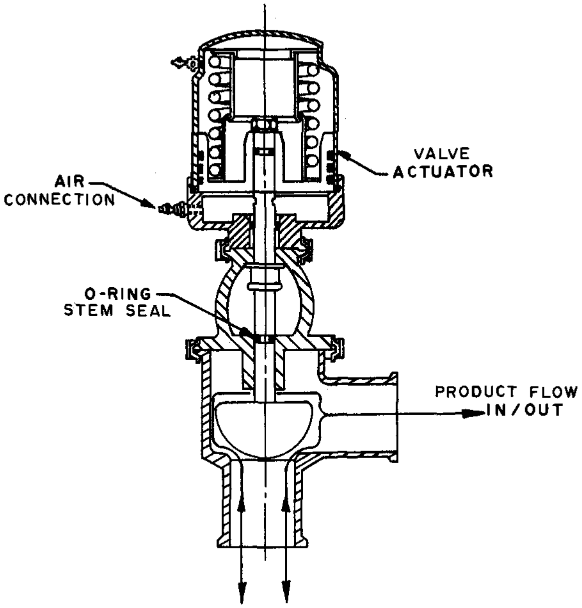


FIG. 4—*Cross-section of air-operated sanitary valve illustrates O-ring stem seal. Valve must be actuated during cleaning operations to effectively clean this seal and gland area.*

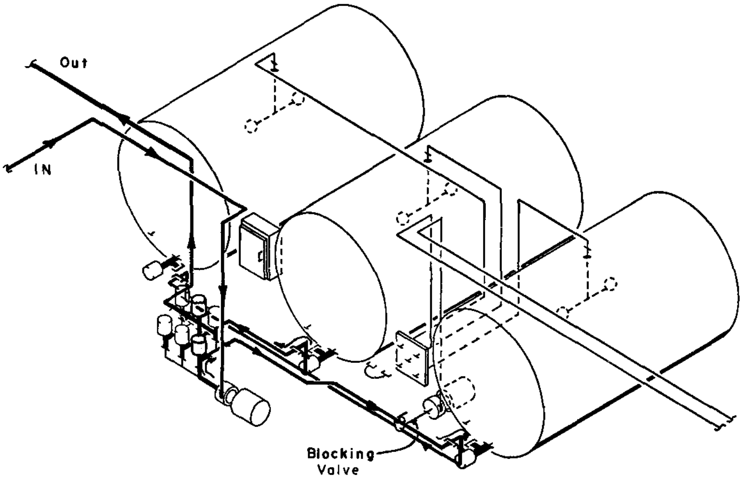


FIG. 5–*Heavy lines on piping indicate one of three typical solution flow-paths established by sequencing valves in 6-valve group, using tank CIP return line as a CIP tie line, with inlet to return pump blocked.*

system are thus exposed to equivalent mechanical/chemical treatment. The operation of the valve causes the stem O-ring to pump some cleaning and rinsing solutions into the gland area, effectively cleaning the seal, stem, and gland area.

Where air-operated valving is used in extensive food plant piping systems, the complete system or substantial portions of the system must be cleaned at one time, as some valves of a group of valves cannot be cleaned while others are being used for process operations.

Spray Cleaning of Processing and Storage Vessels

Successful spray cleaning of storage tanks and processing vats is dependent upon properly designed tanks, and properly applied spray devices.

The permanently installed fixed-ball spray has gained favor over rotating and oscillating spray devices. Its advantages include:

1. There are no moving parts.
2. It can be made completely of stainless steel.
3. Its performance is not affected greatly by minor variations in supply pressure.
4. A properly established installation will continue to provide satisfactory service.
5. It sprays all of the surface all of the time.

Fixed-ball sprays are available with a variety of characteristics in terms of flow rate, discharge pressure, and pattern of coverage (Fig. 6). Experience has indicated that cylindrical and rectangular tanks can be adequately cleaned if sprayed at 0.1 to 0.3 gal/min/ft^2 of internal surface, with patterns designed to spray the upper one third of the tank. If considerable appurtenances exist in the tank, such as heating or cooling coils and complex agitators, some special

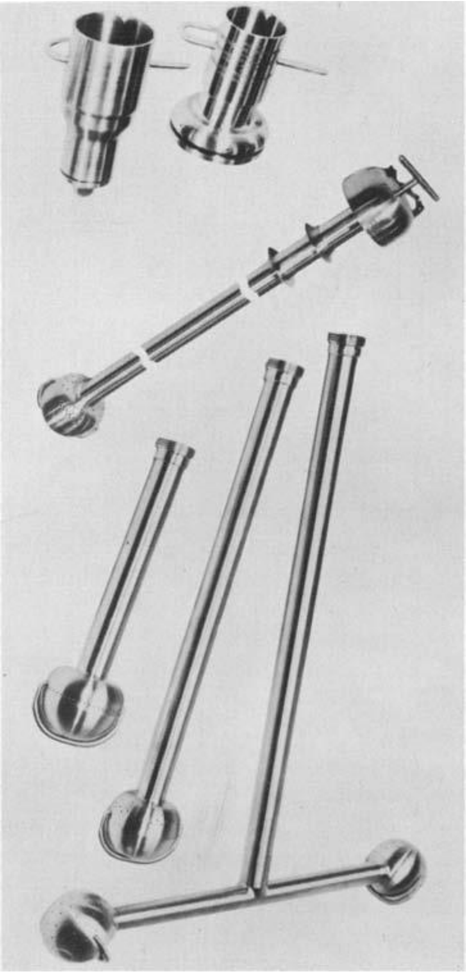


FIG. 6–*Four different types of fixed-ball sprays are shown on the bottom of this photograph, and two removable disk-type sprays are illustrated at the top.*

patterns may be required to cover these surfaces, with resultant increases in the total flow rate required.

Vertical silo-type tanks (Fig. 7) may be cleaned satisfactorily at flow rates of 2.5 to 3.0 gal/min/lineal ft of tank circumference. Nonclogging disk sprays are used in vessels of this type because of the relative difficulty in reaching the spray devices for occasional inspection and cleaning.

Whereas the major portion of all spray cleaning is conducted with relatively standard sprays, special devices in the form of ring sprays, spray sticks, and disk sprays are available for specific applications in evaporators, dryers, vacuum chambers, and other vessels having unique design characteristics to meet special processing requirements.

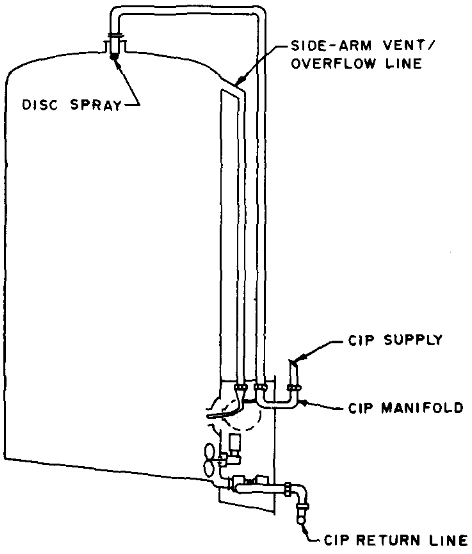


FIG. 7–*Silo-type tanks with deep-dish heads can be effectively cleaned with a disk spray device that distributes water uniformly on the tank head. Special provisions must be provided to spray into the side-arm vent/overflow line.*

Tank cleaning programs involving the use of spray devices differ from line cleaning programs in that pre-rinsing and post-rinsing are generally accomplished by using a burst technique. Water will be discharged in three or more bursts of 15 to 30 s duration, and the tank will be drained completely between successive bursts. This procedure is more effective in removing sedimentated soil and foam than is continuous rinsing and can be accomplished with much less water.

Cleaning programs for storage tanks and processing vessels are more widely varied than those utilized for piping circuits as the nature of the soil varies considerably. For lightly soiled transport and storage tanks used for milk or low-fat milk by-products, satisfactory results can be achieved by applying (*a*) a three-burst pre-rinse using cold or tempered water, (*b*) recirculating a chlorinated alkaline detergent solution for 5 to 7 min at temperatures not exceeding 130 to 135°F, (*c*) applying a two-burst post-rinse using clear cold water, and (*d*) recirculating an acidified final rinse for 1 1/2 to 2 min at tap water temperature. If the same type of vessel is used for storing or transporting cream, condensed milk, ice cream mix, or similar more viscous products with higher fat and total solids contents, concentration and recirculating time at temperature may be increased.

Vessels used for heating and cooling dairy and food products will be more heavily soiled than those used strictly for transportation or storage or both, and the soil may exist in the form of "burned-on product." In this case both concentration and temperature will be increased, and occasionally detergent solution will be recirculated at 175 to 180°F for as long as 45 to 60 min. In some instances satisfactory cleaning will require the recirculation of both a hot alkaline detergent and a hot acid detergent.

Typical detergent concentrations for use with the programs described above might include:

Storage and Transportation Tanks—Tanks used for products comparable to milk and milk by-products can be effectively cleaned at concentrations of 1500 to 2000 ppm of alkaline detergent with chlorine at a level of 30 to 50 ppm. If the same tanks are used for more viscous products such as cream, condensed milk, or ice cream mixes, the alkaline material may be increased to 2500 to 3000 ppm while maintaining the same level of chlorine.

Processing Vessels—Tanks used for moderate heat treatment of dairy and food products may be cleaned with chlorinated alkaline detergent at 4000 to 5000 ppm akalinity with a chlorine level varying from 50 to 100 ppm; it being recognized that the chlorine will be dissipated very rapidly during the cleaning process as it combines with the organic matter in the soil being removed. If heavy "burn-on" exists, chlorine may be eliminated completely and an alkaline wash at 0.75 to 1.0 percent causticity may be followed by an acid wash at pH 2.0 to 2.5.

Brewing equipment may be cleaned with approximately the same programs just described, with the more rigorous programs being applied to brew house vessels, the intermediate programs to fermentation vessels, and the lighter programs to beer storage tanks.

Heat Exchangers

Shell and tube heat exchangers equipped with return-bend connections of CIP design can be incorporated in CIP piping circuits or may be cleaned independently as a separate operation. Triple-tube heat exchangers are available only in CIP design and have a further advantage in that they can be installed so as to be completely self-draining. Plate-type heat exchangers (Fig. 8) are more widely used than either of the tubular units, however, because of ease of inspection, flexibility of design with respect to proper streaming for desired velocities and pressure losses, and ease of adaptation to new applications. Plate-type heat exchangers are being designed for increasingly higher operating pressures but in some instances are not capable of withstanding the pressures required for associated line CIP operations at flow rates required to produce adequate velocity in the piping system. Satisfactory performance can be achieved under these conditions by utilizing a booster pump downstream of the plate heat exchanger to reduce back pressure on the plate unit or by using split-flow cleaning hook-ups to reduce velocity, and hence pressure loss, through the various sections of the plate heat exchange unit.

High Temperature Short Time Pasteurizing Systems utilized in the dairy and egg processing industries, and in some food processing installations, are normally cleaned as an integral system including the plate heat exchanger, holding tube, constant-level tank, homogenizer (if utilized), and all of the associated piping (Fig. 9). A two-speed centrifugal pump may serve as a product booster pump for

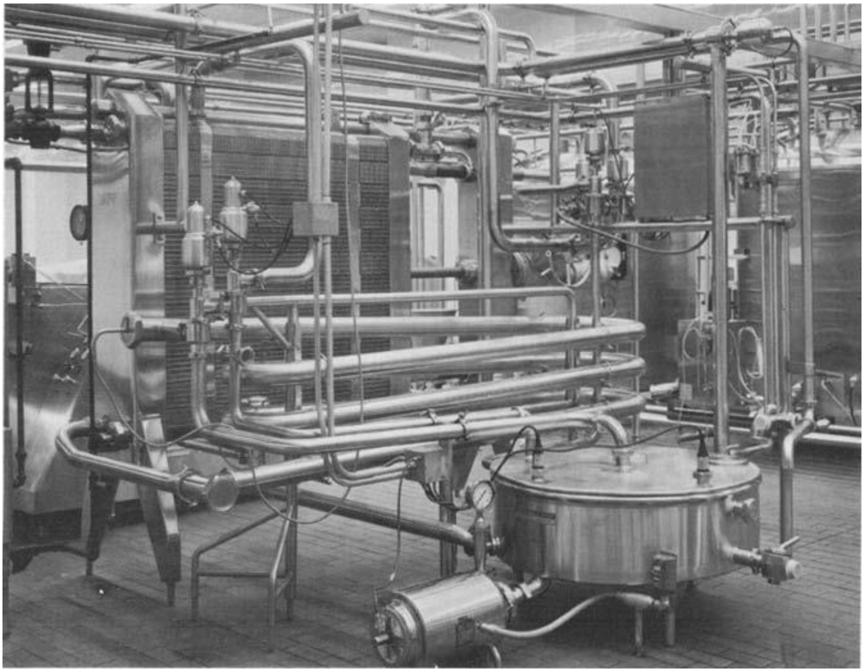


FIG. 8–*The plate-type heat exchanger in the background of this photograph is capable of heating and cooling milk at 60 000 lb per h for HTST pasteurization purposes. The constant-level tank, 2-speed booster pump, and all interconnecting piping are included in the CIP circuit developed to clean this unit.*

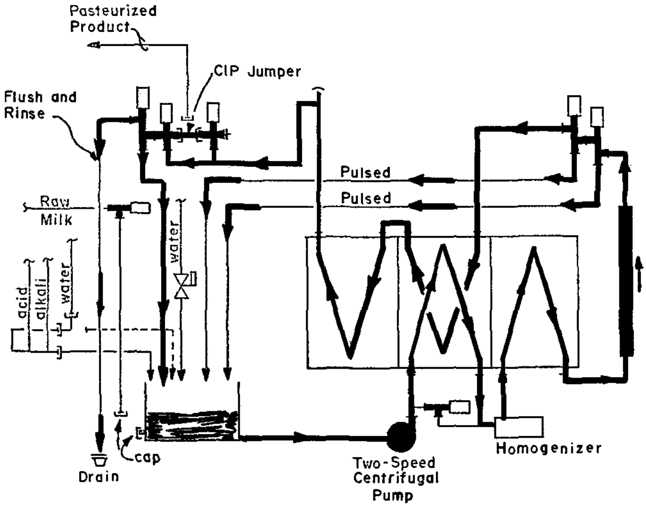


FIG. 9–*This schematic drawing shows the flow-path for cleaning an HTST system similar to that shown in Fig. 8.*

processing operations at 1750 rpm, and may produce increased pressure and flow through the system for CIP operations when operated at 3450 rpm. The cleaning program will depend upon the nature of the products processed through the system during the operating day, and some typical programs are as follows:

1. Systems used for processing milk, skim milk, and low-fat products may be effectively cleaned by recirculating an acid detergent for 20 to 30 min and then overriding this through the direct addition of a heavy alkali which is then recirculated for 45 to 60 min. Alternatively, an intermediate rinse with clear water may be used between the acid and alkaline detergent.
2. Systems used for processing primarily creams or ice cream mixes will be cleaned more effectively if the alkaline detergent is recirculated first for 30 to 45 min, followed by an intermediate rinse (absolutely necessary) and then the recirculation of the acid detergent for 20 to 30 min.

For the above operations alkaline concentrations may range from 0.5 to 1.5 percent causticity and acid will generally be added to produce a pH of 2.0 to 2.5. The cleaning temperature during the recirculating period will generally be adjusted to approximately 10°F higher than the maximum processing temperature used during the production day.

The successful mechanical/chemical cleaning of heat exchange equipment is dependent in part upon proper operation of the equipment during production processes. For instance, the use of high pressure steam and high heating rates with inadequate agitation, or turning steam on before all heat transfer surfaces are covered with product, may produce burn-on which is nearly impossible to remove through application of normal cleaning programs. As a result, time, temperature, and concentration must all be increased to cope with this problem, at extra expense for the cleaning procedure. Or, similar results may be experienced through repetitive use of equipment without cleaning between operations. In most instances food processing equipment has an optimum operating period beyond which further operation without shutdown results in reduced efficiencies and increases the cleaning problems.

Summary

The basic procedures outlined have been applied in fluid milk plants, ice cream plants, cheese plants, edible soy protein processes, brewery operations, and various other types of food processing operations with uniform success. It is generally possible to design and apply equipment and programs which can produce surfaces that are physically clean and nearly free of bacterial contamination. Standard swab tests on in-place cleaned equipment should yield sterile plates in 75 to 80 percent of the samples and plates showing not more than three to five colonies on the remaining samples when sampling is done immediately following cleaning and before sanitizing. If equipment is properly handled, there should be no positive coliform counts on any swab taken from surfaces cleaned by in-place cleaning procedures.

Mechanical cleaning utilizing spray or pressure recirculation of cleaning solutions under proper combinations of time, temperature, and detergency has gained wide acceptance in the food and beverage processing industries. Experience has shown that solutions of strong alkalies, moderately strong acids, and sodium hypochlorites are highly effective in removing organic and mineral soils of almost any nature when these solutions are utilized in the proper combination or sequence.

J. J. Wegscheider[1]

Cleaning Heat Exchanger Tubing in Industry with the M.A.N. Automatic On-Load Tube Brushing System

---

REFERENCE: Wegscheider, J. J., **"Cleaning Heat Exchanger Tubing in Industry with the M.A.N. Automatic On-Load Tube Brushing System,"** *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 210–214.

ABSTRACT: The beneficial aspects of cleaning stainless steel condenser and other heat exchanger tubing are well known. Chemical or manual cleaning, which is usually performed after tubes have become dirty, requires a complete or partial plant shutdown, and both of these methods are rather inefficient. This paper describes an automatic, in-service, mechanical tube brushing system that assures positive, uniform, daily cleaning of all tubes. For example, even 40 000 condenser tubes can be cleaned in 1 min. This cleaning system can be applied to condensers and other heat exchangers in conventional or nuclear power plants, as well as other industries such as steel mills, refineries, large central air-conditioning installations, etc., and it assures highest heat transfer rates at all times.

KEY WORDS: stainless steels, cleaning, heat exchangers, tubes, nuclear power plants, condensers

Stainless steel tubes are being used in ever increasing quantities in large power stations, particularly for today's large nuclear plants and those being equipped with cooling towers. The beneficial aspects of cleaning stainless steel condenser and heat exchanger tubes have been clearly established in the literature[2] and has been discussed in earlier papers in the symposium.

Most of these papers have dealt with chemical cleaning methods. Chemical as well as manual, mechanical cleaning of tubes usually involves a complete or at least partial shutdown of the unit to be cleaned. As the utility engineers can confirm, one does not ordinarily want to shut down a modern generating unit as the energy replacement cost for one day's outage could amount to $100 000.[3] In the past utilities have therefore divided their condensers, thus permitting only a portion of the condenser to be taken out of service during reduced load periods (usually during the night) and the tubes in this section were then

---

[1] Tube cleaning system specialist, American M. A. N. Corporation, New York, N. Y. 10036.

[2] Long, N.A., "Recent Operating Experiences with Stainless Steel Condenser Tubes," American Power Conference, Chicago, 1966.

[3] When a modern large fossil or nuclear steam generating unit having a heat rate of about 9000 Btu/kWh is shut down, this energy usually has to be generated with the least efficient small older units or gas turbines having heat rates often double that of new, big thermal stations. Furthermore, gas turbines burn much more expensive fuel.

manually cleaned by shooting brushes, scrapers, rubber plugs, or little plastic pigs through the tubes. Not only is such manual cleaning rather inefficient as the average cleanliness factor between such intermittent cleaning procedures is still relatively poor, but in these days it becomes more and more impractical. Furthermore, the power plants in the design stage today will operate between the years 1980 and 2010, and one can be sure manual cleaning will be totally unacceptable. Power plants have already reduced the number of maintenance men in the plant, and wage rates have increased considerably while the number of tubes has increased dramatically. Perhaps ten years ago the average utility condenser had 10 000 tubes–now it is more like 40 000 tubes. Another problem with manual cleaning is increased social awareness of the average worker. Nobody wants to clean condensers any more–it is a hard, hot, dirty, wet, and smelly job, besides being very inefficient. It also usually has to be done at night or on weekends with premium pay. Some utility executives have told me that men have quit because they were required to manually clean condensers.

As if these problems with manual cleaning were not enough, some nuclear units expose men who clean condensers to a very slight amount of radioactivity. And last, but perhaps, the most important consideration for the future is that many new environmental protection laws are forcing utilities to discontinue the use of chlorine. Chlorination, while not perfect, has until now been a quite effective means of minimizing fouling of tubes–and tube fouling is expensive. Just a moderate amount of fouling could easily cause the vacuum of a condenser to decrease by say 0.5 in. of mercury from the clean tube value. In a typical 700 000 kW (700 MW) unit and with today's high fuel costs, this fouling could cost the utility approximately a half a million dollars a year. These figures will only get worse with cooling towers and increasing fuel costs, and particularly when chlorine has to be discontinued. Long's 1966 American Power Conference Paper already indicated the possible increased deposit formation through insufficient chlorination and he pointed out that the lack of copper toxidity in stainless tubes may amplify the possible deposit problem.

Automatic Tube Cleaning Is the Answer

Now that we have established the need to clean tubes, and the disadvantage of manual cleaning, there must be a better way. Fortunately, at present there are two automatic tube cleaning systems available. Both can keep tubes clean at all times because they prevent fouling from getting a foothold in the first place. The older of these two systems circulates special sponge rubber balls through the tubes and this system is being described by another author in this symposium.

A few years ago another type of automatic on-load tube cleaning system was developed by this author's parent company in Germany, and has since found considerable interest worldwide.

Every Tube Has Its Own Brush

Here is how this system works. Each end of every condenser tube (and this could apply to heat exchangers in industrial plants as well) is equipped with a brush retaining basket or cage. These cages are permanently attached to the tubes. There are different types of attachment methods available, both for existing tubes and new installations. For existing units we use, what is called, male type baskets; for new units or retubings, a female type basket requiring a tube protrusion beyond the tube sheet is used. By inserting a special synthetic brush in the cage at the tube outlet end, every tube will have its own brush and these brushes remain in the condenser during operation. Only after about five years would they be changed.

For example, if we would consider a condenser with 10 000 tubes, there would be 20 000 brush retaining cages (one on each end of every tube) and 10 000 brushes. The flow of the water through the tube causes the brush to remain in the cage just outside the outlet end of every tube. The cage and brush are so designed that we have not been able to measure any increased pressure drop across the condenser under normal circumstances. The circulating water system has to be equipped with at least a reduced size reverse flow system. Such backwash arrangements are already well known in this country and were previously used primarily to flush debris off the inlet tube sheet. We use similar reverse flow valving arrangements to cause the water to flow through the tubes in the reverse direction for at least a minute or two. Usually large utility condensers are divided again so that only a portion—perhaps a quarter or half of the entire condenser—is backwashed at any one time. In large utility installations, the reverse flow is accomplished through multiple butterfly valves tied into a common control panel and the entire backwash cycle takes place fully automatically. There are literally dozens of different piping or valving arrangements available to reverse the water flow. As the cooling water flow direction is reversed, the brushes which were sitting idle just outside the normal tube outlet end are forced through the tubes by the reverse flow and thus clean them in passing through. After about a minute the water flow returns automatically to normal and the brushes pass through all the tubes a second time, completing a cycle. Since we can do this very often, say once every 8 h, dirt doesn't get a chance to form in the first place. And since every tube has its own brush, every tube is cleaned. We also tested different cleaning bodies but found that a real brush did the best cleaning job.

Even Hard Scale Formation Can Be Prevented

We have found in installations with very bad cooling tower water that this system prevents even hard scale from forming, and an ASME paper[4] was given a few years ago showing that tubes equipped with our brushing system had maintained perfect tube cleanliness for many years while previously the heat transfer rate dropped to a third of this within three months. Prior to installation

[4] McAllister, R. A., "On Stream Cleaning of Heat Exchanger Tubes—Fouling Prevented by Regular Brushing," ASME Paper 68PET-12, American Society of Mechanical Engineers, 1968.

of the automatic brushing system, the client, in this case an oil refinery in Beaumont, Tex., chemically cleaned the condenser tubes about once every three months. This has been entirely eliminated. In these small installations we normally do not use large butterfly valves to accomplish the reverse flow, but use a single four-way valve. An automatic air operator is cycled by an electric timer once every 8 h, the four-way valve disk moves 90°, and the water flow through such heat exchangers or condensers is reversed almost instantaneously. This combination of a four-way valve together with our brushes and baskets is now used highly successfully on all the central air-conditioning condensers of a large missile and space manufacturing complex on the West Coast. First, two units were equipped with the system. Then the company and the U. S. Navy bought 18 additional installations. Quite a few installations, with all the recent ones being on stainless steel tubes, have been operating for about five years at the U. S. Steel, Homestead works on the Monongahela River near Pittsburgh. And we just recently received an order for two condensers serving two 850 MW units in Pennsylvania. Each of these condensers has about 41 000 7/8 in. tubes of stainless steel Type 304. The cooling water comes from two large hyperbolic cooling towers, and we believe this will be the first of many large cooling tower condenser installations which will be equipped with our automatic tube brushing systems.

As mentioned before, on the average the tubes are cleaned once every 8 h. Each cleaning cycle involves two brush passes. Thus, normally in one day the tubes would be brushed six times. It could be done more often or even just once a day depending on water conditions. Another advantage of this system is that just prior to shutdown, such as an annual turbine inspection, all the tubes can be cleaned several times by just pushing a button. One can thus be assured that all tubes are perfectly clean during this down time period.

Automatic Cleaning System Is Available for Many Tube Sizes

The brush retaining baskets just described are injection molded and are now available for almost all tube sizes commonly found in condensers and heat exchangers. Most applications have been for round, prime surface tubes; however, this system could be applied to oval and finned tubes as well. Internally finned tubes have long intrigued engineers, but the increased heat transfer rate would usually have been lost in a very short time due to fouling. By installing the automatic tube brushing system described here, the new tube heat transfer rates could be maintained at all times.

I mentioned central air-conditioning units before and there we were faced with externally finned tubes which had a larger inside diameter at the very end than at the finned sections, and the system is cleaning these tubes perfectly. There are basket designs for every type of tube joint. In existing tubes we either have a mechanical fit (this is primarily used for copper alloy tubes) or use an especially designed male basket together with a two-part epoxy adhesive. But normally, we are talking about new tubes and here we are working with a very simple press-fit by having the user order the tubes about 1 in. longer than normal and letting them protrude 1/2 in. beyond each tube sheet. Baskets are simply pressed onto this protrusion with a special tool. They do not come off in normal service. The baskets are injection molded out of a special polypropylene material and so are the plastic caps of the brushes. The bristles are made out of a synthetic material which does not absorb water and thus they remain stiff even after years of immersion in water. A nylon toothbrush gets soft by just leaving it in a glass of water overnight. The wire that holds the bristles together can be made out of different materials—even out of titanium.

You will probably agree that this principle looks so simple that one wonders why no one has thought of it before. I can also assure you that properly applied, the system is very effective. The heat transfer rate through the tubes can be maintained at its clean tube value for years and this has been positively established and is documented in ASME Paper 68PET-12, and we guarantee tube cleaning effectiveness.

One problem that was encountered in a few installations was excessive debris in the cooling water. While power plants have changed from small 40 MW units operating at perhaps 900 psi steam pressure to 1200 MW units operating at 3500 psi, or even with a sophisticated automated nuclear steam supply system, circulating water intake screening has hardly changed at all in this country. American travelling screens are often quite inadequate and large amounts of debris such as sticks, fish, shells, beer cans and pieces of plastic can easily get past the screens. This debris can accumulate at the inlet tube sheet and can interfere with an automatic cleaning system, regardless of its design, or even the normal operation of a condenser without a cleaning system. To have an automatic tube cleaning installation function perfectly for many years without maintenance, better intake screening is a must. Greatly improved screens are available from Europe. Of course, with the increasing trend to cooling towers, the debris problem is eliminated and the automatic brushing system works perfectly.

Conclusion

The automatic, in-service tube brushing system described here is a great improvement over manual or chemical cleaning methods. We have found its addition to be economically justified in almost every case and believe more and more designers and operators will specify and use it in the future.

D. M. Harbaugh[1]

Experiences with Cleaning Stainless Steel Condensers on Allegheny Power System Stations

---

REFERENCE: Harbaugh, D. M., "**Experiences with Cleaning Stainless Steel Condensers on Allegheny Power System Stations,**" *Cleaning Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 215–219.

ABSTRACT: The history of keeping stainless steel condensers clean on Allegheny Power System power generating facilities is presented. The acid mine drainage waters in Pennsylvania and West Virginia dictated the use of stainless steel for condensing steam turbine exhaust. With the stainless steel condensers, continuous, on-line tube cleaning systems were installed. These systems, in general, have maintained condenser cleanliness at levels equal to or better than design. The cost of the system could be recovered in a few years with the savings from the improved performance.

KEY WORDS: stainless steels, cleaning, condensers (electric), electric power generation

Allegheny Power System consists of three separate operating companies and a central service group. The operating companies serve portions of southwestern, north, and south central Pennsylvania, northern West Virginia, and western Maryland. The bulk of the power generating facilities are located along the Monongahela River and its tributaries. All of the units with completely stainless steel tubed condensers are located along this river system.

Many of the tributaries of this river are contaminated by drainage from coal mines in the area. This drainage is normally acidic, and as a result, the pH of the cooling water ranges from 3 to 7 at the various plants. This situation dictated the use of stainless steel for condenser applications. The early history of use of stainless for condenser applications has been well documented.

History of Stainless and Continuous Cleaning

A brief summary of these early findings will reveal some reasons that led to our use of continuous on-line cleaning systems. The first unit in the system to use stainless was Rivesville No. 6. This unit went into service in 1951 with a copper alloy tube condenser. In less than seven years, the average tube wall thickness had diminished to the point where a retubing was required. For the first time, serious consideration was given to stainless steel. The detrimental factors of poor heat transfer and high initial cost were outweighed by the expected 30 year life. The results of this retubing revealed some significant

---

[1] Power engineer, Allegheny Power Service Corporation, Greensburg, Pa. 15601.

misconceptions about the thermal properties of stainless steel tubing, which greatly enhanced its position in succeeding retubing considerations at other plants. The two most significant areas of better performance were a result of higher fluid velocities and cleanliness factors.

This unit was operated for several years with periodic cleanings made in the same manner as with the copper tubes. Studies there indicated that the copper alloy tubes could not be returned to the 85 percent cleanliness factor when cleaned. From a corrosion standpoint, it was even undesirable to have them this clean. Cleanliness factors with the stainless after a mechanical cleaning were as high as 124 percent, based on original Heat Exchange Institute (HEI) data. With this degree of cleaning possible and now desirable, a continuous cleaning system could be justified.

The first continuous cleaning system in Allegheny Power was installed on the Rivesville No. 6 unit in June 1964. The equipment was justified on the basis that it would be able to maintain cleanliness at a level equal to that found after a conventional cleaning. However, initial data showed an approximate 25 percent better than anticipated cleanliness factor.

At the same time the Rivesville studies were being made, No. 3 unit at the Mitchell Station was being built. From the results of using stainless at Rivesville and the studies made on existing units at Mitchell, stainless steel was chosen for use in the condenser. Consideration was also being given to installing a continous cleaning system. However, at this time, there is a lack of information available on the effectiveness and reliability of a continuous cleaning system. As a result, the system was not installed for the initial startup of the unit. After approximately one year of operational data, along with the results of the Rivesville installation, the economics looked favorable and the system was installed.

Since these two initial stainless steel condensers with continuous cleaning systems were installed, Allegheny Power now has a total of 14 units in operation with stainless steel condensers, eight of which have continuous cleaning systems. Some of these systems were incorporated into the design of new units while others were added to existing units. Those units without cleaning systems have not had them installed either because of the physical limitations of the circulating water system or heavy amounts of debris in the water.

Performance of Cleaning Systems

Our experiences with continuous cleaning on nearly every unit have been highly successful. Those plants where cleaning systems have been added to existing units have provided a basis for comparison of the effects of continuous cleaning on performance. Since each unit has its own design characteristics, it is difficult to compare the effects of continuous cleaning on a new unit to an older unit which did not have a system. Where circulating water temperatures vary greatly, it is even beneficial to make performance comparisons during the same seasons of the year.

The studies made at Rivesville and Mitchell have clearly shown the benefits of continuous cleaning. On later installations, the results have been similar, but not as well documented. Typical results before a system was added would show the difference between actual turbine exhaust pressure and expected pressure increasing to a point where the loss in efficiency was great enough to justify a manual cleaning with either high pressure water or brushes. This type of cleaning would generally increase the cleanliness factor to an acceptable 85 percent level or better. After the cleaning, the condenser would again begin to foul. The time between cleanings varied, but was generally from one to two months.

Upon installation of a continuous cleaning system, the back pressure would nearly always be at design or better, design being based upon 85 percent clean tubes. In terms of efficiency, this represented a significant improvement in turbine heat rate. If the operating and maintenance costs of the cleaning system could be maintained at a reasonable level, then the cost of equipment and installation could be recovered within a few years.

At the present time, all of the cleaning systems that we have purchased for use on main turbine condensers have been the sponge rubber recirculating ball type manufactured by Amertap. Initially, this was the only one available and since we have obtained satisfactory operation with them, we have continued to buy Amertap systems.

As more and more experience is gained with using Amertap, both from within the company and from other users, we anticipate further reductions in operating costs. Recently some standardization has taken place regarding the proper size and consistency of the balls to be used based on tube size and differential pressures available. This has enabled us to do a more effective job of cleaning the tubes and yet attain maximum ball life.

An area that we are presently studying is the economics of 24-h operation of the system. Previous studies had shown us that we could maintain our desired cleanliness with intermittent circulation. It was felt that this would reduce ball wear and loss. Many operating schedules were tried at the various plants to determine the minimum number of hours circulation required to maintain the desired back pressure. Once the minimum was attained, the balls were taken out of circulation, in some cases for several days, until the cleanliness factor deteriorated to a predetermined level. In a sense, the schedules were set up in the same manner as was the conventional condenser cleaning schedules, except the periods between cleaning were much shorter.

Amertap personnel have recently pointed out to us that continuous circulation may offer cost reductions that are overlooked with intermittent operation. With periodic operation, hard deposits will sometimes form on the tubes which cannot be removed with the usual sponge rubber balls. An abrasive type ball must be used, or if the deposits are exceptionally heavy, the condensers must be taken out of service and manually cleaned. The abrasive balls are a higher cost item, and, of course, the manual cleaning represents a considerable expense, especially on the larger units. Also, the tubes are subjected to a higher attrition rate with these two alternatives and the cost of the cleaning, the loss of generation, and the decrease in efficiency until the condenser can be cleaned must be absorbed.

Several cost advantages present themselves with continuous operation. The maximum level of cleanliness possible with the use of the system can be achieved at all times. This results in a slight increase in efficiency over intermittent operations. When looking at the cost of operating the Amertap, loss of balls and power consumption, this increase in efficiency alone is usually not enough to balance the increased operating expenses.

An area where continuous operation has a hidden advantage is with the attrition rate of the balls. Much of the normal ball wear is caused by the thin layer of deposits on the tubes. With continuous operation, these deposits are not given a chance to form, and as a result there is a reduction in ball wear. However, since the balls will be circulating continuously, even the reduced attrition rate may not reduce ball consumption from wear and this must be determined.

Because the balls are circulating continuously, the chances for any one tube being cleaned in a given period of time are greater. This fact enables us to reduce the number of balls circulating from the normal quantity equal to approximately 10 percent of the number of condenser tubes, to a value of 7 or 8 percent, depending upon the particular station. Since ball consumption through wear and loss represents the largest cost of operation, any reduction in ball usage represents a significant cost savings.

Although we have never experienced any corrosion problems with stainless, isolated instances of attack have been reported elsewhere. Studies of these cases have revealed that tube deposits were partly responsible for this attack. Continuous operation of an Amertap system would have reduced, if not eliminated, this problem.

Although continuous operation appears to be the most efficient way to utilize the Amertap system, it is still under investigation at some of our plants. At present, the results look quite favorable. However, as to the exact level to which we can reduce the number of balls in circulation and still maintain desired cleanliness factors remains to be determined. Much time and data are necessary to determine the long range benefits of this type of operation.

Each unit has its own operating peculiarities and requires individual attention to determine the exact method in which the Amertap will be used. Probably the most radically different is the Albright No. 3 unit, located along the Cheat River. During about nine months of the year, there are extremely heavy amounts of leaves and debris in the river. This buildup required frequent backwashing to remove the bulk of the debris and eventually requires that either the tube sheet be picked clean or the tubes manually cleaned. This situation prevents us from using the Amertap system during these periods when the river is exceptionally dirty.

Most of our new units have closed cooling cycles with natural draft cooling towers. These systems require special consideration in terms of protection against condenser corrosion. With once through cooling, our prime concern was protection against attack by the acid waters. However, with cooling tower operation, high concentration of dissolved solids coupled with air-borne bacteria were thought to be a major fouling problem for condensers. Our experience to date, however, has shown us that these problems have not been as severe as expected. At one of our plants, there are units of the same size and design, one of which has a closed cycle and another with once through fresh water cooling. Results to date have shown that we can maintain a higher degree of cleanliness with the unit operating on the tower than with the unit on the river.

Summary

Allegheny Power has used stainless steel quite extensively for turbine condenser applications. Our early experiences with its use showed us that it was practical to use a continuous cleaning system with stainless. Many of our installations now have Amertap systems on stainless steel condensers. These systems are the only means used to keep the tubes clean and have yielded highly satisfactory results.

E. W. Leschber[1]

Premature Failure of Type 316 Stainless Steel Condenser Tubing in Brackish Water

---

REFERENCE: Leschber, E. W., **"Premature Failure of Type 316 Stainless Steel Condenser Tubing in Brackish Water,"** *Cleaning of Stainless Steel, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 220–223.

ABSTRACT: In 1964, a Worthington single pass condenser with twin tandem shell and common inlet divided water boxes was shut down after one month operation because of perforated Type 316 stainless steel tubing. In 1965, stainless steel tubing in the periphery and air removal section of a condenser in a sister unit failed after three months operation, and again 4040 tubes were replaced. The condensers are at the Potomac Electric Power Company's Chalk Point Generating Station in Prince George's County, Md., where they draw brackish cooling water from the Patuxent River. This paper discusses the operating conditions and probable causes of these failures, and how they might have been minimized or avoided.

KEY WORDS: cleaning, stainless steels, condenser tubes, tubes, brackish water

The Chalk Point Station is equipped with two 355 MW generators served by two universal pressure (UP) boilers. The condensers on each unit are single pass, twin tandem shell units requiring 261 000 gal/min of cooling water. Each is designed with a common inlet divided water box.

Discussion

Each condenser has 162 000 ft^2 of effective condensing surface. The tubes were Type 316 stainless steel in the air removal section and around the periphery of each shell. The remainder of the tubes in the condenser were arsenical aluminum brass. In each quarter of the condenser there were 1010 stainless tubes and 5300 brass tubes for a total of 4040 stainless and 21 200 brass tubes.

The cooling water for the condensers is Patuxent River water. This is a brackish water that has approximately 5000 to 6000 ppm chlorides. An average analysis of the river water is included in Table 1.

The stainless steel condenser tubes failed completely in a little over two months of service (start-up of the circulating water pumps), and one month of operation on unit number one. Time for failure on unit number two was slightly longer, approximately three months of operational service. The similarity of the two units is such that the remainder of this paper will be limited to unit number one. Table 2 includes data for both units.

---

[1] Chief chemist, Potmac Electric Power Company, Washington, D.C. 20006.

TABLE 1–*Patuxent River water.*

	Typical	Range	
		High	Low
pH	7.6	8.0	7.5
Conductivity, mmho	14 000	20 000	9 000
Total solids, ppm	10 500	14 000	7 000
Dissolved solids, ppm	9 500	13 000	6 300
Hardness, ppm as $CaCO_3$	2 100	2 400	1 000
Chlorides, ppm	5 000	6 500	3 500
Iron, ppm as Fe	0.15	0.20	0.10
Manganese, ppm as Mn	0.20	0.25	0.15
Chloride Demand, ppm	0.85	0.91	0.71

TABLE 2–*Significant operational dates.*

	Unit I	Unit II
Circulating pumps in service	25 June 1964	8 February 1965
Chlorination system in service	1 July 1964	February 1965
First synchronization	23 August 1964	25 March 1965
First condenser leak	10 September 1964	April 1965
Unit removed for re-tubing of stainless steel tubes	18 September 1964	15 June 1965
Re-tubing complete unit returned to service	2 October 1964	June 1965

The circulating water pumps were first operated on 25 June 1964. The chlorine system was put in operation on 1 July 1964. Chlorination was at a negligible rate until 6 Aug. 1964, when gross fouling was discovered in the outlet water boxes. The chlorine feed was raised to 0.7 ppm residual chlorine at outlet water box and was continued for three days at this level, which showed a residual at the circulating pumps of 2 ppm. The outlet water boxes were inspected again and found to be much cleaner, though still partly fouled. The chlorine residual at the outlet water box was then decreased to 0.1 to 0.3 ppm and maintained until the unit was synchronized on 23 Aug. 1964. On 10 Sept. 1964 the unit was removed from service for a condenser leak in the secondary condenser. On 18 Sept. 1964 the unit was again removed from service for another condenser leak. On the 19th the shift supervisor reported that the leaks in the condenser were too numerous to plug.

Up until September 18, there had been 15 starts since the first synchronization. Many of these restarts were due to control problems and the circulators had been left running. The unit was kept out of service at this time pending arrival of new 90-10 copper nickel condenser tubes.

The stainless tubes that failed were examined by the tube supplier, water consultants, and by the Potomac Electric Power Company Laboratory. Consensus of those examining various tube samples was that the failure was due to pitting corrosion initiated by permanganate cation in the presence of a halide.

The stainless tubes were examined and found to be AISI Type 316 of the following composition:

% chromium	17.44
% nickel	13.62
% molybdenum	2.79
% manganese	1.37
% copper	0.03
% silicone	0.33

Metallographic examination of the microstructure showed the tubes to be fully annealed and the weld completely recrystallized.

Examination of the inside diameter surfaces of the tubes revealed many pits; however, the inlet and outlet ends of the tubes were clean and free of pits for a distance of 4 to 6 in. The pits on the inside diameter surface were covered with a deposit of material that ranged in color from light brown or tan to dark purple. Penetration of the tube wall in some areas was as high as 10 pits per inch. Analysis of the deposit in and around the pits showed a very high concentration of manganese. Deposit analysis showed the purple colored areas to be permanganate and the dark brown areas to be hydrated manganese dioxide. The pits also showed a high concentration of ferric ion, and chloride ion was very positive in some of the pits. The deposit itself contained very little chloride ion. Table 3 lists the elements that were detected by X-ray fluorescence.

Conclusions

It is concluded that the pitting corrosion in these tubes was caused by a depolarizing cathodic reaction. To have this reaction the iron and manganese in

TABLE 3–*Deposit analysis by X-ray fluorescence.*

Iron–ferric and ferrous
Manganese–
Nickel–
Copper–
Chromium–
Zinc–
Molybdenum–
Lead–
Cobalt–
Silicon–
Calcium–
Strontium–
Aluminum–(trace)
Bromine–
Chlorine–(trace)

the river water had to be converted to reducible metal cations, such as ferric chloride or bromide, or a permanganate. Chlorination of the river water provided the impetus for oxidation of the metal cations. Low flow or minimal flow allowed the deposition to take place in the tube. As soon as the permanganate deposit formed, a crust of stable manganese dioxide formed over it, sealing the highly reducible metal cations beneath the deposit. The areas under the deposit then became corrosion cells of such magnitude that rapid pitting corrosion caused massive failures in the tubes.

The design velocity through the condenser tubes was 6.93 ft/s. Flow much of the time was low due to only one circulator running, and for short periods of time nonexistent. This condition, coupled with an environment conducive to rapid pitting, resulted in the failure of these condenser tubes.

Recommendations

First, a thorough examination of the cooling water is mandatory. Recognizing those elements in a cooling water or those conditions, however remote, that could cause trouble should be done well in advance of selecting the tube material for any particular condenser.

Secondly, cleanliness is of prime importance when using stainless steel. Fouling or deposition must be controlled to such a degree that is is practically nil.

Finally, in a brackish or sea water installation, stainless steel tubes must be flushed with fresh water each time the circulators are shut down to prevent stagnation. The velocity through the tubes should also be kept up so that the tubes are continually swept clean.

Additional research into the subject indicates that the problem is not just limited to the presence of manganese, but can occur with a variety of elements. Deposits are, in general, detrimental to stainless steels (316) in brackish or sea water service. Deposits in fresh water applications may or may not cause problems. Efforts to date have not been successful in predicting the eventual failure of a tube based on a prior study of the environmental conditions. Continued efforts to relate prior study with tube performance are necessary.

It is agreed that other elements can and will cause similar type failures. Hopefully, someday we will be able to predict the best tube material for specific water conditions that will prevent the type of failure described in this paper.

D. S. Detwiler[1]

Improving Condenser Performance with Continuous In-Service Cleaning of Tubes

REFERENCE: Detwiler, D. S., **"Improving Condenser Performance with Continuous In-Service Cleaning of Tubes,"** *Cleaning of Stainless Steels, ASTM STP 538,* American Society for Testing and Materials, 1973, pp. 224–228.

ABSTRACT: Continuously clean condenser and heat exchanger tubes result in many operating economies. Several methods of tube cleaning exist, among which the continuous system utilizing a constant recirculation of sponge rubber balls has proven to be the most effective.

Improved heat transfer, reduction of chemical additions, and corrosion and scaling protection significantly reduce condenser maintenance and offer significant cost savings.

KEY WORDS: stainless steels, cleaning, condenser tubes, corrosion

What is required for the waterside surface of a condenser or heat exchanger tube to be considered clean? According to Webster, "clean" means "to be maintained free from dirt or pollution" or "in a non-fouled condition." This definition implies that for the waterside surface of a stainless steel tube to be clean, it must only be kept free of organic or inorganic matter or both. However, for condenser tubing the effect of the waterside laminar layer on heat transfer also must be considered. This will be discussed in more detail later.

Methods of Tube Cleaning

Presently, three cleaning techniques are available for the cleaning of condenser or heat exchange tubes; manual, chemical, or mechanical. Chemicals include biocides, fungicides, and corrosion inhibitors, among others. Manual approaches utilize high pressure water or air or various types of plugs, scrapers, or brushes or both. Mechanical systems incorporate one of two basic approaches—intermittent or continuous cleaning. The intermittent system uses brushes and cages in conjunction with a condenser back-washing system. The continuous system uses the sponge rubber cleaning balls. The continuous system will be the subject of this paper.

A continuous tube cleaning system circulates sponge rubber cleaning balls of a size slightly larger than the tube inner diameter to wipe the waterside tube surface free of deposits, scale, or bacterial growth. The fact that the cleaning ball

---

[1] Formerly, regional sales manager, Amertap Corporation, Mineola, N. Y. 11501.

is larger than the tube inner diameter forces it to compress against the tube wall, thereby wiping the interior surface clean. The continuous cleaning action is accomplished by passing at least one cleaning ball through each tube on an average of once every 5 minutes. Sponge rubber balls are forced through the condenser tubes by the pressure drop between the tube inlet and outlet with the ball recirculating system operating on a closed cycle around the condenser or heat exchanger.

The cleaning balls are injected at the inlet of the condenser or heat exchanger and after passing through the tubes are collected at the outlet by the installation of a special strainer section. This strainer section separates the balls from the circulating water and directs them to a common point where they are extracted by the recirculating pump suction. The balls are then pumped back to the condenser inlet where they begin another cycle.

Mechanical Cleaning versus Other Methods

Why should mechanical cleaning be considered instead of either chemical or manual cleaning? The basic reasons are discussed in the following.

Increased Heat Transfer Efficiency

Approximately 70 percent of the total resistance to heat transfer through a tube wall is directly attributable to tube waterside fouling [*1*].[2] This fouling has two distinct components or layers: one is the water laminar film; the other a scaling or sedimentary buildup commonly referred to as "fouling."

The laminar layer isolates the turbulent water flow within the tube from the fouling buildup on the tube surface. Thus, if the laminar layer is continually disrupted, the tendency for waterside fouling is greatly reduced. Continuous mechanical cleaning does just this.

The laminar layer also has a significant effect on heat transfer as it accounts for almost 55 percent of the total long term waterside heat transfer resistance [*1*]. However, the isolating effect of the laminar layer is even more dramatic in the short term as the initial waterside deposit buildup accounts for a decrease in the heat transfer of as much as 10 percent within 4 h and up to 15 to 20 percent in 12 h [*2*].

After about 12 h of unit operation, the rate of heat transfer loss decreases significantly because the initial deposit buildup is complete. Additional losses in heat transfer are the result of sedimentary deposition or scale buildup on the tube surface (see Fig 1).

Advantages of Improved Heat Transfer

What can the improved heat transfer provided through continuous mechanical cleaning mean to the user? There are two distinct advantages. First, through the utilization of higher cleanliness factors in the condenser design, reduced heat

---

[2] The italic numbers in brackets refer to the list of references appended to this paper.

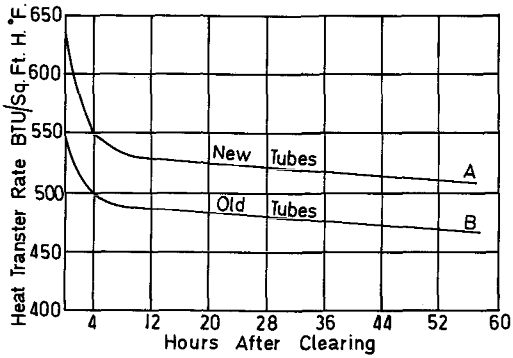


FIG. 1–*Decrease in heat transfer rate versus time [2].*

transfer surface will be required resulting in initial capital savings. A second and more important advantage is the improvement in turbine heat rate. This heat rate improvement can result in both increased generation capability and reduced fuel requirements. For a midrange turbine, a 0.2 in. Hg improvement in condenser backpressure can equal a 0.5 percent increase in the turbine heat rate. Through a mathematical calculation it can be shown this 0.5 percent increase in the heat rate is equal to almost three additional megawatts of generation capacity for a 600-MW generating unit.

In addition to the increase in generation capacity, the improved turbine heat rate results in significant fuel savings. Considering fuel costs of \$0.40/10^6 Btu and a 60 percent loading factor, savings of over \$60 000 per year can be realized. At one installation, a major utility was able to record an improvement in the heat transfer rate from approximately 310 Btu/h ft^2°F to 595 Btu/ft^2°F after only three days operation with a continuous mechanical system [*3*].

Reduction of Chemical Additions for Organic Control

Continuous mechanical cleaning usually allows a reduction in the amount and type of chemicals required for control of water quality. The necessity for biocides, antifoulants, antinucleants, and other chemicals is greatly reduced because the action of the cleaning ball provides as much or more tube protection. This has been proven by several utilities where chlorine additions have either been reduced or completely eliminated as the result of inclusion of continuous mechanical cleaning.

At one plant, the installation of the sponge rubber ball system not only eliminated chlorine, but also improved the heat transfer rate almost 80 percent. At another location continuous mechanical cleaning equipment has been purchased for a plant operating on a closed cycle where all corrosion inhibitors will be eliminated. The plant will operate with the circulating water in a scaling condition (pH 8.2) using continuous mechanical cleaning to keep both the stainless steel tubed condenser and auxiliary heat exchanger free of scale buildup. The circulating water system will then be acid-treated (pH 5.5) to remove scale from the tower and auxiliary piping. It is presently anticipated that an 8-h acid treatment will be required every week, but it is hoped the time period between treatments can be extended. This operation is anticipated to reduce yearly chemical costs by over $70 000.

Reduced Cleaning Costs

A third area where mechanical cleaning more than returns its investment is in the elimination of manual cleanings of the condenser or heat exchanger. This is especially true when labor availability and power replacement costs are considered as well as the direct costs. One nuclear plant recently incurred ten days of lost production for a single cleaning. Based on the present daily cost of $40 000 to $50 000 for this type of outage, it is possible to project the cost of this condenser cleaning at close to half a million dollars. This is a single example, but it is typical of the costs which many utilities experience in manually cleaning condensers.

Corrosion or Scaling Protection

As far as stainless steel tubed condensers are concerned, probably the most important advantage of continuous mechanical cleaning is the superior level of corrosion protection which it provides. Stainless steel tubes are highly susceptible to oxygen-excluding underdeposit corrosion attack. Continuous cleaning keeps deposits from accumulating on the tube surface, thereby eliminating the main cause of most stainless steel tube corrosion failures [*4*].

At one generating plant two unit condensers were tubed with admiralty but without mechanical cleaning while the third unit has a stainless steel tubed condenser complete with a mechanical cleaning system. These units operate on a closed cycle with the makeup water being secondary treated sewage effluent. After three years of operation of the third unit, sample tubes were removed from Units 1 and 3 and compared for corrosion. Severe pitting of the admiralty tube was noted even though heavy chlorination was employed. The tube from the stainless steel tubed condenser showed absolutely no signs of corrosion and chlorination had not been used except for periodic additions for tunnel and tower algae control. This excellent condition was attributed entirely to the ability of mechanical cleaning to maintain a corrosion-free tube surface in a severe environment.

As a result of this comparison, mechanical cleaning systems were installed on Units 1 and 2. Within six weeks after startup of these cleaning systems, the tube surface was not only returned to a relatively corrosion free condition, but condenser back-pressure was also improved by 0.7 in. Hg. In addition, chlorine usage has been reduced over 80 percent. Therefore, not only has the probability of a condenser retubing been eliminated but the operational economics are sufficient for the system payback period to be less than two years.

Tube Restoration as Well as Maintenance

A corrosion-free tube can be kept in that condition by the use of a good continuous mechanical cleaning system—but more than that—this system can arrest or reduce pitting which has already occurred through the circulation of cleaning balls coated with an abrasive material [*5*]. In a number of tests, severely fouled tubes have been removed from condensers and installed in separate circuits parallel to the condensers [*3*]. In each of these parallel circuits the normal circulating water was used, however, an abrasive cleaning ball was circulated through the tube every 5 min. In each test, the tube was removed at predetermined intervals and examined. In all cases the tube surface was improved as a result of the corrosive particles being removed by the scouring action of the abrasive cleaning ball. This not only stopped the propagation of the pitting but also returned the tube surface to a more uniform condition. This capability of continuous mechanical cleaning to restore as well as maintain tube surfaces has more than doubled tube life in many instances.

Conclusion

Mechanical cleaning can do more to eliminate tube cleanliness problems than any other single approach in use today, and in a more economical manner. However, because each application is different, it is not possible to give an exhaustive commentary of all the reasons for consideration of a good mechanical cleaning system. Some of the more pertinent considerations include greater heat transfer efficiency, reduction in chemical usage, elimination of manual cleanings, and improved corrosion protection.

References

[*1*] Schwer, R. E., "Experience with Stainless Steel Tubes in Utility Condensers," *Nickel Topics,* Vol. 24, No. 5, 1971.

[*2*] Bulletin No. 250, Prime Movers Committee, National Electric Light Association, USA.

[*3*] Heidrich, Arthur, Jr., Roosen, J. J., and Kunkle, R. G., "Calorimetric Evaluation of Heat Transference by Admiralty Condenser Tubes," ASME Publication 65-WA/CT-2, presented at the Winter Annual Meeting of the American Society of Mechanical Engineers, Chicago, 7-11 Nov. 1965.

[*4*] Long, N. A., "Recent Operating Experiences with Stainless Steel Condenser Tubes," American Power Conference, 1966.

[*5*] Kuester, C. K. and Lynch, C. E., "Amertap at English Station," ASME Publication 66-WA/CT-1, presented at the Winter Annual Meeting and Energy Systems Exposition, American Society of Mechanical Engineers, New York, 27 Nov. through 1 Dec. 1966.