

CLEANING AND DESCALING STAINLESS STEELS

A DESIGNERS' HANDBOOK SERIES
Nº 9001



Produced by
AMERICAN IRON
AND STEEL INSTITUTE

Distributed by
NICKEL
INSTITUTE



CLEANING AND DESCALING STAINLESS STEELS

A DESIGNERS' HANDBOOK SERIES
Nº 9001

Originally, this handbook was published in 1982 by the Committee of Stainless Steel Producers, American Iron and Steel Institute. The Nickel Institute republished the handbook in 2020. Despite the age of this publication the information herein is considered to be generally valid.

Material presented in the handbook has been prepared for the general information of the reader and should not be used or relied on for specific applications without first securing competent advice. The Nickel Institute, the American Iron and Steel Institute, their members, staff and consultants do not represent or warrant its suitability for any general or specific use and assume no liability or responsibility of any kind in connection with the information herein.

Nickel Institute

communications@nickelinstitute.org
www.nickelinstitute.org

CONTENTS

INTRODUCTION	2
Keeping Stainless Steels Clean.....	2
DESCALING STAINLESS STEELS	4
Acid Pickling	4
Commonly Used Acids	4
Pickling Chromium-Nickel Stainless Steels	6
Pickling Straight-Chromium Stainless Steels	9
Pickling at Room Temperature	11
Pickling Light Scale and Weld Discoloration.....	12
Pickling Tanks.....	12
Control of Pickling Baths.....	13
Caustic Descaling	14
Sand Blasting.....	15
CLEANING STAINLESS STEELS.....	17
Shop Soils.....	17
Conversion Soils	17
Lubricant Oxide Mixtures	17
Simple Cleaning	17
Finger Marks	18
Ink Stencil Marks	18
Drawing Lubricants and Machining Oils.....	18
Chemical Cleaning	19
Alkaline Cleaning.....	19
Electrolytic Cleaning.....	21
Solvent Degreasing	21
Vapor Blasting	23
PASSIVATION.....	24
FUTURE TRENDS.....	26
CONSUMER AND INDUSTRIAL/COMMERCIAL CLEANING METHODS	27

The material presented in this booklet has been prepared for general information only. It should not be used without first securing competent advice with respect to its suitability for any given application. Neither the American Iron and Steel Institute, its Committee of Stainless Steel Producers nor the companies represented on the Committee warrant its suitability for any general or particular use.

INTRODUCTION

Cleanliness and stainless steels are closely related and, in many applications, each is dependent upon the other. In the handling of food, chemicals, and pharmaceuticals, for example, stainless steels provide the degree of resistance to attack that is necessary to prevent product contamination. On the other hand, stainless steels perform best when clean—cleanliness is essential for maximum resistance to corrosion.

This publication will describe for designers, manufacturers and consumers various practices for cleaning stainless steel before, during, and after fabrication. This includes methods for removing oxide scales resulting from hot-forming operations, thermal treatment, and welding and brazing; for removing free-iron contamination on stainless steel surfaces that may have been picked up from metalworking tools; for removing metal-forming lubricants and coolants; and for removing the general accumulation of dirt, grime, and surface stains that occur during normal storage, handling and fabrication.

When reading this booklet, it should be kept in mind that there are few specific rules for establishing descaling (pickling) or cleaning procedures, and that approaches to the problem vary considerably according to manufacturing capabilities, production volume, and part configuration. Accordingly, the methods discussed in this publication should be received as suggestions, and each manufacturer, after obtaining competent advice with respect to its individual requirements, should select methods appropriate to those requirements.

Passivation Defined

The term “passivation” has different meanings according to the principal interest of the individual. Corrosion engineers, for example, define passivation as the loss of electrochemical reactivity experienced by certain metals and alloys (including stainless steels) under particular environmental conditions. That is, certain metals and alloys may become “passive” in the environment and corrode at very low rates.

Passivation has also come to mean a surface cleaning operation with nitric acid, especially to dissolve iron contamination from the surface of stainless steels.

Complete separation of these two meanings of passivation is not possible, for both occur in the nitric acid cleaning solutions.

For the purposes of this booklet, passivation will mean cleaning, unless the term passivation is indicated to denote passivation in the corrosion sense.

Readers are referred to ASTM A 380-78, a Standard Recommended Practice for “Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems.” and to ASTM Special Technical Publication 538, “Cleaning Stainless Steels,” which discusses practical, up-to-date information on well-established methods and procedures.

KEEPING STAINLESS STEELS CLEAN

The cleaner stainless steels can be kept while in storage or while progressing through the shop, the greater the assurance for optimum corrosion resistance in the finished product. It goes without saying that prevention costs less than the cure.

Among the preventive measures normally observed in manufacturing

stainless steel products are the following:

1. Hold stainless steels in original containers or wrappings until the start of fabrication, and keep protective wraps in place during fabrication whenever possible.
2. Provide clean indoor storage places such as racks, shelves and platforms, and use covers where necessary.
3. Provide storage places well removed from sources of shop dirt and other contamination. Fumes from pickling operations should be avoided in order to guard against possible condensation of acidified moisture on clean surfaces. Fine particles of scale from carbon steel fabrication or fragments of other metals undergoing work should be prevented from collecting on exposed metal.
4. Maintain clean work areas so that work in progress will stay clean. Locations under lubricating lines from which oils and grease may fall should be avoided.
5. Remove residues of other materials from fabricating equipment before starting a new job on stainless.
6. Avoid walking over stainless steels with dirty shoes or hobnail boots.
7. Handle stainless steels with clean gloves or cloths to guard against perspiration stains or finger marks, which can burn in during subsequent annealing operations.
8. Use easily removed identification markers.
9. Use paper or other protective coverings to protect stainless steel surfaces during and after fabrication. (See "Caution" below.)
10. Avoid use of oily compressed air to blow away chips, dirt, or welding flux or slag.

These ten suggestions are all basic good housekeeping measures that are typical of what may be considered essential fabricating procedures with stainless steels.

CAUTION: Many adhesive-backed papers and plastic sheets applied to stainless steel for protection age in fairly short periods of time (several weeks to a few months) and become extremely difficult to remove. Manufacturers should obtain from suppliers information as to how long protective films or papers can be left in place. It is also good public relations to pass this information to customers so they can avoid expensive and time-consuming cleaning procedures.

DESCALING STAINLESS STEELS

Descaling, and/or pickling, is the removal of heavy, tightly adhering oxide films resulting from hot-forming operations, thermal treatments (such as annealing or hardening), or welding. Because most stainless steel products received from the producing mill have been pickled, descaling is required only as a result of subsequent manufacturing operations.

In evaluating the different methods for removing scale, it is well to keep in mind that scale on stainless steel is far more complex than scale formed on plain mild steel. The scale on stainless steel consists of oxides of chromium, nickel and/or other alloying elements—in addition to iron, and the ease by which it can be removed depends on base metal composition and the thermal treatment to which it is exposed. The problem may be further complicated by the presence of lubricants. Lubricants and other contamination should be removed before thermal treatment.

When the metal is exposed to hot gases containing oxygen, a heavy scale is formed. A heavy scale, because it is readily exposed to the oxygen only near the surface, may be oxygen-rich at the surface and metal-rich near the base metal. Most oxygen-rich scale is readily soluble in common pickling acids, but the metal-rich scale may require acids aggressive to the base metal itself. For this reason, pickling is sometimes preceded by a preconditioning step, such as an alkaline salt bath, or scale removal by mechanical means, such as shot blasting.

The final step, however, nearly always involves nitric acid, either alone in solution or combined with another acid. Nitric acid, generally, is not aggressive to stainless steel, and it serves to speed optimum corrosion resistance—or passivation.

A word of caution is appropriate for chemical cleaning and pickling: The acids used present numerous hazards to both personnel and facilities. It is recommended that Manufacturing Chemists Association data sheets be consulted to determine the hazards of handling these chemicals. Proper protective gear, such as face shields, rubber gloves, and rubber clothing, must be provided, adequate ventilation must be maintained, and personnel access restrictions must be applied and enforced.

ACID PICKLING

When planning an acid pickling operation, it is necessary to know the type of stainless steel and its metallurgical and physical condition. Because the various stainless steels have different alloy compositions, they can be expected to behave differently when exposed to pickling acids. Also, stainless steel parts that have been sensitized by welding or thermal treatment, or parts in a highly stressed condition, may be more susceptible to corrosive attack and thus require special attention.

Because of the inherent differences in the material, or in the way the part is fabricated, care must be exercised in the selection of acid solutions and pickling procedures. There is no single acid solution or process that is effective for all situations.

COMMONLY USED ACIDS

The acids most commonly used for pickling stainless steels are

nitric (HNO_3), hydrofluoric (HF), sulphuric (H_2SO_4) and hydrochloric (HCl).

Nitric acid is oxidizing in character, whereas the others are reducing. Nitric acid tends to promote and preserve the corrosion-resistant qualities (passivity) of stainless steels; i.e., it does not act to destroy the microscopically thin oxide surface film that gives stainless steels their corrosion resistance (except under unusually severe conditions not generally encountered in pickling). Its oxidizing behavior accounts for the fact that when alone or in solution with water, nitric acid will not dissolve and remove oxide scale from stainless steels.

The other pickling acids—hydrofluoric, sulfuric, and hydrochloric—are reducing in character. Their strength as reducing agents depends upon the amount present in water solution and upon the solution temperature. They accomplish descaling by reducing the oxides of which scale is composed. At the same time, they also reduce the protective oxide film on stainless steel and thus lay the underlying metal open to corrosive attack.

Because of the inherent characteristics of oxidizing and reducing acids, mixtures of the two acid types are used for pickling stainless steels—the most frequently used solution being a combination of nitric and hydrofluoric acids. They combine the scale-removing feature of the reducing acid constituent and the base metal protecting or passivating action of the nitric. By changing the relative proportions of these two acids in an aqueous solution, a wide range of strengths is obtainable, which can still further be manipulated by varying temperatures.

Solutions of sulphuric acid find their main use as a preliminary step in descaling. Sulfuric acid provides a quick initial attack on scale deposits, and it is always followed by the much more controllable nitric/hydrofluoric treatment.

Hydrochloric acid solutions behave similarly to sulphuric acid mixtures. Because the action of hydrochloric acid on both oxide scale and base metal is exceedingly rapid, it must be used with extreme caution. Unlike sulphuric acid, however, hydrochloric acid produces ferric chloride which is a strong pitting agent. As the salt content builds up in the bath, pitting becomes quite rapid. For that reason, solutions can be used but for a short time and should be discarded as soon as any tendency toward pitting attack becomes apparent.

Hydrochloric acid may be substituted for hydrofluoric in nitric/hydrofluoric pickling solutions under conditions later described when the use of hydrofluoric is not feasible. In such cases, great care should be exercised to guard against the effects of ferric chloride as previously noted.

Hydrofluoric acid is never used alone. Because of the hazards connected with its handling, users should observe strict safety precautions.

Organic Acids

Organic acid chelates can be used to clean light oxides or scales and free iron particles from stainless steel surfaces.

The organic compounds combine acid solution activity with sequestrant and buffering properties. Light scale residues can be solubilized with dilute solutions of ammoniated citric acid. Treatments

of this type are satisfactory for final cleaning of fabrications for the food and chemical industry. A concentration of 3 to 5 percent citric acid is preferred, and this solution is adjusted with ammonium hydroxide to a pH of between 3 and 4. An operating temperature of 170°F will produce good cleaning within acceptable time cycles.

Embedded iron particles may contaminate stainless steel surfaces as a result of shot blasting or machining. This free iron produces unacceptable corrosion resistant properties. Formulated cleaning compositions with dibasic ammonium citrate combined with anionic or non-ionic wetting agents are effective in removing these iron particles. An operating temperature of 170°F and concentrations of 2 to 5 percent are preferred.

Citric acid, glycolic acid, and formic acid are used in many equipment cleaning operations including pharmaceutical processing equipment, whiskey storage tanks, steam generators, and nuclear reactors. In addition to their ability to combine with many other chemical compounds, the advantages of using acids of this type for these applications include the low corrosion rate experienced, ability to hold iron in solution, and safe handling properties. A number of manufacturers of these compounds have detailed descriptive literature of specific formulations which may be employed for cleaning stainless steel surfaces.

PICKLING CHROMIUM-NICKEL STAINLESS STEELS

Nitric/Hydrofluoric Acid Treatment

Mixtures of nitric and hydrofluoric acids in water are the most effective and most widely used solutions for pickling the chromium-nickel stainless steels. Properly handled, they are entirely satisfactory.

The strength of these mixed acid solutions can be adjusted within very wide limits by varying the proportions and by adjusting bath temperatures. The extent of their action can be governed by controlling the time of exposure in the bath.

Nitric/hydrofluoric acid solutions are corrosive to unoxidized stainless steel surfaces (without scale). The corrosive action is that of general overall attack. This form of surface attack is controllable and is usually not of great importance in normal pickling operations provided the metal is in a condition that enables it to exhibit its maximum ability to resist corrosion. Metal that is in a sensitized condition (that is, subject to intergranular corrosion due to the presence of precipitated carbides along grain boundaries) is definitely susceptible to intergranular attack at zones in which carbides are present, such as heat affected zones adjacent to welds.

Intergranular Corrosion. When austenitic stainless steels are heated or cooled through the temperature range of about 800-1650°F (427-899°C), the chromium along grain boundaries tends to combine with carbon to form chromium carbides. Called carbide precipitation, or sensitization, the effect is a depletion of chromium and the lowering of corrosion resistance in areas adjacent to the grain boundary. This is a time-temperature dependent phenomenon.

Sensitization may result from slow cooling from annealing

temperatures, stress-relieving in the sensitization range, or welding. Due to the longer time at temperature of annealing or stress-relieving, it is possible that the entire piece of material will be sensitized, whereas the shorter time at temperature characteristic of welding can result in sensitization of a band, usually $\frac{1}{8}$ to $\frac{1}{4}$ inch wide, adjacent to but slightly removed from the weld. This region is known as the heat-affected-zone or HAZ.

Intergranular corrosion depends upon the magnitude of the sensitization and the aggressiveness of the environment to which the sensitized material is exposed. Many environments do not cause intergranular corrosion in sensitized austenitic stainless steels. For example, glacial acetic acid at room temperature or fresh clean water does not; strong nitric acids do.

Carbide precipitation and subsequent intergranular corrosion in austenitic stainless steels have been thoroughly investigated; the causes are understood and methods of prevention have been devised. These methods include:

1. Use of stainless steel in the annealed condition.
2. Selection of the low-carbon (0.030 percent maximum) stainless steels for weld fabrication. Low-carbon grades are Types 304L, 316L, and 317L. The less carbon available to combine with the chromium, the less likely is carbon precipitation to occur. However, the low-carbon grades may become sensitized at extremely long exposures to temperatures in the sensitization range.
3. Selection of a stabilized grade, such as Type 321 (titanium stabilized) or Type 347 (columbium stabilized), for service in the 800-1650°F (427-899°C) range. The protection obtained with these grades is based upon the greater affinity of titanium and columbium for carbon as compared to chromium.

Columbium stabilization is preferred because its carbides are more readily retained in welds and it is easier to add in the steelmaking process. However, the use of columbium stabilized steel requires additional care in welding.

4. Redissolving carbides by annealing parts after fabrication, although this is not always practical.

In addition, the presence of heavy stress concentrations may tend to accelerate attack on the base metal. For these reasons, the use of nitric/hydrofluoric acid pickling solutions should be confined to descaling the chromium-nickel grades only when the base metal is in its best condition to resist corrosion, that is, free of precipitated chromium carbides and preferably in a condition of minimum stress (annealed condition).

Percentage contents of the two acids in water solution are always best determined by actual test. Their adjustment to specific jobs is governed by the amount and kind of oxide scale present and by the condition of the base metal. The solutions can vary from 5 percent up to 25 percent of nitric and from $\frac{1}{2}$ percent to 3 percent of hydrofluoric (both by volume).

For light scales, 12 to 15 percent nitric and 1 percent hydrofluoric is usually satisfactory; but for heavier oxides the percentage of hydrofluoric may have to be increased, say to 2 or 3 percent depending

upon results. The more nitric acid (oxidizing) present with respect to hydrofluoric (reducing), the less rapid the action will be. Conversely, the higher the percentage of hydrofluoric in proportion to the nitric, the more rapid the pickling will be. Nitric acid acts to inhibit the action of the hydrofluoric acid.

Bath temperatures are normally set at from 120 to 140°F. Holding them below 120°F reduces the speed of intergranular attack in sensitized areas, such as localized weld zones in workpieces that have not been annealed after welding. With low temperature, it is frequently possible to obtain complete scale removal before any pronounced attack develops on chromium depleted areas. Increasing temperatures within the 120-140°F range results in faster descaling. Higher temperatures are normally avoided to minimize loss of hydrofluoric acid due to evaporation.

The length of exposure time in the bath is determined by examination of test results. Time beyond that required for thorough descaling results in excessive surface attack, as evidenced by etching. Holding workpieces in the pickling bath for no more time than necessary for optimum scale removal avoids the unnecessary expense for subsequent finishing operations, such as polishing.

With proper solution concentration, temperature, and time, nitric/hydrofluoric pickling readily produces clean, white, scale-free surfaces on all chromium-nickel grades provided they have been thoroughly pre-cleaned and are in fully annealed condition free of precipitated chromium carbides.

Thorough rinsing in clean, warm water should always follow pickling to remove any acid residues. And rinsing should be followed by drying. Scrubbing prior to and during rinsing is sometimes necessary to aid in the removal of sludge.

TYPICAL PROCEDURES

For all chromium-nickel stainless steels in a fully annealed condition, or the low-carbon or stabilized grades, typical procedures are as follows:

1. Use a solution consisting of from 5 to 25 percent nitric acid (65 percent strength) and from 1 to 3 percent hydrofluoric acid (50 percent strength), both by volume, in water at a bath temperature of 120-140°F.
2. Immerse for 10 to 15 minutes, as determined by test.
3. Scrub as may be required.
4. Immediate final thorough rinse in clean hot water and let dry.

Exact proportions of acid are determined by test. A frequently used solution is 15 percent nitric and either 2 or 3 percent hydrofluoric acids.

Temperature is determined by observation. When oxide scale is heavy and tenacious, the above sequence may be preceded by a preliminary pickling in sulphuric acid. The advantage of such treatment is twofold: Sulphuric acid softens and speeds the loosening of scale and, being a cheaper material, helps to reduce the cost of pickling supplies.

A typical procedure for a preliminary sulfuric acid bath is as follows:

1. Use 8 to 10 percent solution of concentrated sulphuric acid (by weight) in water at 150-160°F.
2. Immerse the work for approximately 5 minutes and observe results.

3. Scrub as required to remove sludge.
4. Rinse quickly and thoroughly in clean hot water.
5. Transfer to the nitric/hydrofluoric bath and then proceed as previously described.

To avoid loss of strength in the acid bath, adequate controls should be established and replenishment made as required.

Nitric/Hydrochloric Acid Treatment

To avoid the hazards associated with handling hydrofluoric acid, it may be replaced by hydrochloric acid to make up a nitric/hydrochloric acid solution. Because hydrochloric acid is extremely corrosive to all grades of stainless steels, even when they are in a fully annealed condition, care must be exercised to provide sufficient nitric acid in excess. Experience indicates that the ratio of nitric acid to hydrochloric acid should be not less than 10 of the former to 1 of the latter.

Because hydrochloric acid promotes the formation of ferric chloride in the bath, such solutions must usually be limited to short time use if pitting attack is to be avoided. Nitric/hydrochloric acid pickling solutions are satisfactory for one-time-use jobs that can be descaled before ferric chloride can develop to a harmful extent. An example of this is cleaning a single tank containing welds from which it is necessary to remove oxide scale by flushing.

Other Pickling Solutions for the Chromium-Nickel Stainless Steels

1. An 8 to 12 percent solution of concentrated sulphuric acid plus 2 percent rock salt (NaCl), both by weight, at 140-150°F can be used. Immersion time may range from 5 to 20 minutes, with scrubbing as necessary. (This solution will generate ferric chloride after continued use, the effect of which is pitting attack.) A thorough water rinse to remove all traces of solution should be followed by immersion in a 10 to 15 percent nitric acid solution in water at 140-160°F from 5 to 10 minutes prior to a final wash in clean hot water.
2. A 10 to 15 percent solution of concentrated hydrochloric acid may be substituted for the sulphuric acid/rock salt combination previously described. This solution does not preferentially attack precipitated carbides and cause intergranular corrosion, but it is objectionable in that it quickly generates ferric chloride with resultant accelerated overall pitting attack.

Both No. 1 and No. 2 solutions result in much more general overall surface attack on all stainless steels than do the standard nitric/hydrofluoric acid solutions. To sum up, they are more corrosive to begin with, and in addition, they promote pitting attack as they become charged with ferric chloride. They have to be watched very carefully and discarded as soon as they begin to show any tendency to pit.

PICKLING STRAIGHT-CHROMIUM STAINLESS STEELS

As a general rule, the removal of oxide scale from the straight-chromium stainless steels, in an annealed condition, by acid pickling is more difficult to accomplish than in the case of the

chromium-nickel grades. Scale characteristics are subject to considerable variation from one grade to another because of chromium and carbon content. They are greatly influenced also by the conditions existing in the furnaces at the time of scale formation. For example, Type 430 given a sub-critical anneal at 1450°F will show a lighter scale than if annealed above its critical temperature at 1550°F. The first named temperature is below that of its progressive oxidation limit, while the latter is slightly above it. Consequently, there is usually more need for experimentation to determine the best procedures.

The heat-treatable grades in a hardened condition should never be placed in pickling solutions because they are susceptible to cracking. Tempering treatments in the range of 1100 to 1200°F may help render them less susceptible to cracking because of the strain relieving action at this temperature range; but the only safe procedure to follow is to conduct preliminary tests. Tempering at lower temperatures cannot be relied upon to reduce the tendency to crack. Descaling by other methods, as by light blasting, tumbling and grinding, is, therefore, frequently employed. Bright hardening and bright annealing procedures are particularly helpful because they minimize scaling to begin with.

All of the straight-chromium stainless steels in the annealed condition can be pickled in the nitric/hydrofluoric acid solutions previously described for the chromium-nickel types. These solutions are corrosive, and modification in concentration is usually necessary. Time, acid content and temperature of the solution have to be based on the alloy composition and upon the character and extent of the scale, which are best determined by actual testing.

Tightly adhering scales such as those frequently encountered on Types 403, 410, 416 and 430 after slow cooling from around 1550°F can be removed in either of two ways:

1. By sandblasting with clean silica sand as the initial step and then following with normal nitric/hydrofluoric acid pickling treatment to remove residual scale.
2. By fast pickling in 8 to 10 percent sulphuric acid solution containing 2 percent rock salt, both by weight, at 140 to 160°F in order to loosen scale. The time in bath should be determined by observation. After a thorough water wash, a normal nitric/hydrofluoric acid treatment should be applied.

An alternate pickling sequence for Type 430 is:

1. Immerse in 10 percent to 12 percent sulphuric acid containing 2 percent rock salt in water, both by weight, at 140 to 160°F for 10 to 20 minutes, depending upon observed results. Scrub as necessary to remove sludge.
2. Thorough water wash with additional scrubbing as required.
3. Dip in a 10 to 20 percent nitric acid solution by volume at 160 to 180°F for 5 to 10 minutes.
4. Thorough water wash in clean hot water and allow to dry.

In this alternate sulfuric acid treatment, the sulphuric acid quickly softens and loosens the scale, and the final nitric acid serves to brighten the metal. If the initial sulphuric acid treatment leaves any residue of scale, the addition of ½ percent to 1 percent hydrofluoric acid to the nitric solution will completely remove it. If this addition is made, it is not

necessary to follow with additional treatment in a straight nitric acid solution.

Type 446 may be descaled by using substantially the same treatment as described for Type 430, with the exception that a preliminary sandblast may be applied to loosen the scale.

Discoloration of Straight-Chromium Stainless Steels in Nitric Acid Solution

The straight-chromium stainless steels may occasionally discolor when immersed in nitric acid solution. Possible causes may be some surface condition associated with mild stress or the presence of foreign material. The condition is frequently observed with the free-machining grades.

An addition of 2 percent copper sulphate crystals (by weight) to the nitric acid solution will eliminate the condition without harming the effectiveness of the nitric acid.

PICKLING AT ROOM TEMPERATURE

Pickling stainless steels at the elevated temperatures previously discussed may sometimes prove objectionable. While most solutions of the types in use can be operated at room temperature, certain other changes have to be made in order to offset the slower chemical action that results.

The changes for pickling chromium-nickel stainless steels at room temperature may be summarized as follows:

A. In the case of the nitric/hydrofluoric acid solutions:

1. The time of immersion should be increased.
2. The solution may be made more active by changing the relative proportions of the two acids. For example, a 15 percent nitric-2 percent hydrofluoric acid solution as used at high temperature may be altered by dropping the nitric to 10 or 12 percent and increasing the hydrofluoric to 3 percent or 4 percent.
3. The agitation of the work in the bath should be increased or forced movement of the solution should be created in order to profit by the mechanical action of the scouring.

B. The employment of stronger acid solutions such as a 15 to 25 percent (by volume) solution of hydrochloric acid. Because such a medium is very corrosive and fast acting, time in the bath would have to be watched very carefully to avoid undesirable surface attack (excessive etching). Such a bath would quickly generate ferric chloride and become unusable on account of its strong pitting tendency; so it will have to be monitored and replaced as necessary.

In the case of both modifications, the usual subsequent operations of thorough washing in clean hot water would be applicable. The hydrochloric acid bath also requires the usual final nitric acid immersion. If this is performed at room temperature, the time in the bath would have to be lengthened or the acid content increased, or both. One important advantage of holding nitric/hydrofluoric acid below 120°F, as previously mentioned, is that of greatly curtailing intergranular attack where precipitated carbides may be present.

PICKLING LIGHT SCALE AND WELD DISCOLORATION

Pickling is also used for the removal of light scales or heat tint discoloration of the sort produced by flux-free inert gas arc, atomic hydrogen, or resistance welding.

The nitric/hydrofluoric acid mixtures previously described are satisfactory for most light-scale removal, but it is always good practice to choose by test. A typical solution is one with the nitric acid in the range of 10 percent to 20 percent and the hydrofluoric acid at 1 percent to 2 percent, followed by a thorough water wash. Temperatures should be in the low side of the range, preferably under 120°F if there is danger of etching or of severe attack where precipitated carbides are present.

An alternate procedure for pickling sensitized chromium-nickel stainless steels consists of immersing the work in a 10 percent solution of sulphuric acid plus rock salt, both by weight, under 120°F for 10 to 20 minutes, followed by a thorough water wash. This is followed by dipping in 10-20 percent nitric acid under 120°F, followed by a final thorough water wash. This treatment will avoid the preferential attack of carbide precipitated areas.

When it is not convenient to immerse a welded fabrication in a pickle tank, or if it is necessary to restrict pickling to the immediate area of the weld zone, the acid mixture may be applied as a paste with a brush or a glass rod. Such a paste can be made up with lamp black, graphite, diatomaceous earth, or any material that is completely inert to the acids used. Commercial pastes are also available. Pastes containing ferric chloride should be avoided because any traces of ferric chloride left on the surface are likely to cause pitting. The pickling solution may be a nitric/hydrofluoric acid solution or one of straight hydrochloric at room temperature. For a light scale, 5 minutes contact is usually sufficient. Heavier scale may require two or three applications. Testing will quickly determine best procedures. A final thorough water wash should be immediately applied.

It is important to keep in mind that (a) nitric/hydrofluoric mixtures can result in rapid preferential attack of carbide precipitated areas and that (b) hydrochloric acid solutions do not, although they will produce quite rapid overall attack.

These paste treatments are not intended for removal of flux deposits. If used on weld zones that have been made with flux-employing methods, residual deposits thereof should first be removed by other means.

PICKLING TANKS

For straight nitric acid solutions operating at the temperatures described, welded tanks constructed of Types 304L or 347 are satisfactory, widely used, and do not require annealing after welding to remove precipitated carbides.

For nitric/hydrofluoric acid solutions, carbon brick linings installed with acid-proof cement are satisfactory. Rubber lined tanks may also be used.

For sulphuric acid solutions, the carbon brick acid-proof cement type of construction is satisfactory. Also used is wood protected with lead lining or asphalt, or concrete lined with asphalt.

Heating Equipment

Pickling solutions are usually heated by use of the following methods:

1. Steam introduced into the bath through open pipes. The disadvantage of this is dilution of the baths with the condensate and the danger of introduction of scale from piping.
2. Steam heating utilizing immersion heaters.

Heater parts in contact with the acid solutions should be constructed of corrosion resistant materials. Type 310 stainless steel tubing is frequently used for heating nitric/hydrofluoric acid solutions. Its low resistance to corrosion is offset by the relative ease in replacement.

For the racks, Type 316L is generally satisfactory although racks of Type 347 are frequently used in nitric/hydrofluoric and straight nitric acid solutions. Even greater corrosion resistance is obtained in nitric/hydrofluoric acid solutions with a proprietary nickel-chromium alloy known as INCONEL* alloy 600.

Agitation of baths is desirable for the following reasons:

1. Agitation facilitates contact between acids and scale.
2. It helps free loosened scale by flushing action.
3. It promotes uniformity of acid mixtures and of bath temperatures.

Agitation may be accomplished by the following methods:

1. Oscillating the racks which carry the work.
2. Open-end steam pipes.
3. Jets of clean compressed air.
4. Forced circulation of solutions.

CONTROL OF PICKLING BATHS

Overpickling, underpickling, and pitting usually are the direct results of lack of control over process variables in pickling stainless steel. This can cause permanent damage to the surface of the product, necessitating reprocessing or scrapping. A control program is justified on the basis of the value of the product involved and the inherent hazards of pickling.

The immersion time required to pickle a particular product can best be determined by trial. After immersion time has been determined, it should be maintained for product uniformity.

The influence of temperature on pickling time and on iron solution is pronounced. In 15 percent sulfuric acid, for example, each increase in temperature of 15-20°F within the range of 70-200°F doubles the pickling rate, and the rate of solution of iron at 180°F is about five times that at 140°F and about 100 times greater at boiling than at room temperature. Automatic control therefore is required for maintaining temperature within specified limits.

The control of concentration of pickling baths is important because the rate of pickling increases in proportion to the concentration of the acid from zero to 25 percent by weight. The frequency of analysis of solutions is usually determined by the size of the pickling installation and the volume of material being processed. For pickling tanks of 3000- to 4000-gallon capacity operating 16 hours per day, analysis of the

*Trademark: The Inco family of companies.

solutions at the beginning of each day is usually adequate for normal handling. However, periodic titration of samples taken from the acid bath throughout the day is recommended to maintain a closer control over acid concentration.

The useful life of a pickling solution is determined by the amount of contamination, and a solution is discarded or diverted to other uses after specific limits are reached. Solutions containing sulfuric acid and salt may either be diverted to the pickling of other material or be discarded, when the iron content reaches 1.5 percent by weight. The nitric/hydrofluoric acid solution is discarded when the iron content reaches 5 percent by weight; the nitric acid solution, 2 percent.

The analytical procedures and sampling of these solutions are the same as those described in most standard methods of chemical analysis. Simplified methods using standard solutions are available so that tests can be made by personnel with very little training.

In most installations, rinse tanks are of the overflowing variety. These require little or no attention, because there is a constant flow of fresh water into the tanks. However, when the rinse tanks are not of the overflowing type, frequent sampling of the rinse water and testing with pH paper is required, to indicate if an appreciable buildup of acid is occurring. Thus, it can be determined how frequently the rinse water should be discarded.

CAUSTIC DESCALING

As previously stated, the scale formed on stainless steel is complex, and in heavy scale exposed to atmosphere the surface is oxygen-rich while scale close to metal surface is metal-rich. The former is soluble in pickling acids, the latter generally is not. A salt bath conditioning either oxidizes the scale so all of it is oxygen-rich and soluble, or it reduces the scale.

Primarily proprietary processes, one uses sodium hydride, and the other uses sodium nitrate. Each can be adapted for use with straight-chromium and chromium-nickel stainless steels. Among the advantages they afford are the following:

1. By acting only on the scale, they avoid metal loss and resultant etching.
2. They do not preferentially attack areas in which intergranular carbides may be present.
3. They are particularly helpful for descaling the straight-chromium grades in that they avoid the need for preliminary sandblasting, which is frequently required prior to descaling by acids.

Sodium hydride, a strong reducing agent, is produced in an anhydrous sodium hydroxide bath by the introduction of metallic sodium and hydrogen. It is maintained at a content of approximately 1.5 to 2 percent, and the bath operates at 700°F. Parts, which must be thoroughly dry, are introduced via racks or baskets, and they are held for periods determined by test, usually 15 to 20 minutes. The action of the bath stops when reduction of oxide scale is complete, at which time the parts are withdrawn, preferably in such a manner as to insure minimum carryout of solution. They are then immersed in a water quench, in which the thermal shock serves to free reduced scale residues. Following this, acid treatment (as previously described) is provided to

neutralize any residual caustic and to whiten the parts.

On the other hand, sodium nitrate is oxidizing, and its action is that of disintegrating (rotting) the scale which is then removed by a water quench and subsequent acid treatment. Typical baths operate at approximately 850-900°F, although there is a low-temperature process that operates at approximately 400°F.

The acid treatment following the water quench is usually a 10 percent solution of sulphuric acid, which is less expensive than nitric acid. This is followed by water washing (and scrubbing if needed) and by immersion in approximately 10 percent nitric acid solution at 120-140°F which whitens and passivates the stainless steels. A final thorough hot water wash and subsequent drying complete the treatment.

In the case of the chromium-nickel grades, approximately 1 percent of hydrofluoric acid may be added to the nitric acid bath, if desired, for maximum insurance of scale removal.

There is a third basic class of molten conditioning salts that are neither oxidizing nor reducing but are used in conjunction with electrical current. When the workpiece is positive, these baths are oxidizing and convert metal-rich scale to oxide-rich scale. When the workpiece is negative, the baths are reducing in nature. Typical baths operate at 875°F, although a low-temperature process (400°F) is available. Its principal operation, however, is oxidation only. As previously stated, the scale is removed by water quench and subsequent acid treatment.

SAND BLASTING

Sandblasting is an effective method for the rapid removal of heavy or tightly adhering scale, and it is usually employed as a preliminary step to acid pickling. Blasting cannot be considered as a complete cleaning procedure in itself. Typical examples of where sand or grit blasting is used include heavily scaled plate sections, forgings and castings, and parts made of straight-chromium stainless steels that have been annealed in a manner so as to produce a tightly adhering scale. It is fast, and its use in conjunction with a final pickling treatment may result in significant economies.

Clean silica sand should be used. If it is iron-bearing or becomes contaminated with scale, minute particles thereof can become imbedded in the metal. Since blasting does not always result in uniform and complete cleaning, it is usually followed by pickling in a nitric/hydrofluoric acid bath. Nitric acid alone is not effective as it will not remove oxide scale. A solution of 10 percent nitric and 1-2 percent hydrofluoric concentration at 140°F (maximum) is suggested.

Dipping in a pickling solution may not be feasible for large parts, such as tanks, in which case it may be possible to pour the pickling solution into the tank, and rotate the tank slowly. If it is necessary to pickle by swabbing, it is better to use a nitric/hydrochloric acid solution of the following approximate composition by volume:

Nitric Acid	20 percent
Hydrochloric Acid	2 percent
Water	78 percent

Immersion in or swabbing by the nitric/hydrochloric acid solution should be followed by (a) a thorough scrubbing and water wash, (b) a treatment with 20 percent nitric acid solution at 120-140°F and (c) a final

rinse with clean hot water. The nitric/hydrochloric acid solution should be watched carefully and discarded before its ferric chloride content increases to an extent that may lead to pitting of the chromium-nickel grades.

Obviously, sandblasting should not be employed on materials too light to stand the blast pressure. Distortion is bound to result in such cases unless the work is supported. Also, the blast should be kept moving to avoid excessive cutting at localized points.

The use of carbon steel shot or iron grit blasting is open to the definite objection that iron particles may become imbedded in the surface and seriously detract from the corrosion resistance of the stainless steel. Unless this contamination is removed, it will start rusting and ultimately may lead to pitting. The way to remove embedded iron particles is to pickle the surfaces thoroughly. Straight nitric acid solutions of 15 to 20 percent strength at 100-120°F will remove iron particles but not residual oxide scale. For that reason, it is preferable to use a 10 percent nitric-½ percent hydrofluoric solution and then a thorough water wash. This solution maybe strengthened to 15 percent to 1 percent proportions if necessary. A nitric/hydrochloric solution may also be used.

The use of stainless steel shot or grit reduces the danger of rusting; but it cannot assure total elimination of oxide scale residue. Final pickling remains necessary for maximum corrosion resistance.

CLEANING STAINLESS STEELS

To properly clean stainless steel during or after fabrication it is necessary first to know what has to be removed and then it is possible to select the appropriate cleaning procedure. How to proceed is influenced by the size and shape of the fabrications and the number of parts involved.

Approaches to cleaning vary considerably: from those jobs that involve simple removal of dirt or smudges that collect on surfaces, to the more complex operations for removing free-iron contamination that may have been picked up from tooling. Following is a discussion of typical procedures appropriate for most cleaning problems.

Surface Contaminants:

Shop Soils Stainless steel, like any processed metal, is subject to different surface contaminations and each of these requires specialized cleaning. Shop soils, including grease, oil, grit and metal chips, resulting from machining and fabrication processes, require a combination of dissolution and flotation for their removal. Lubricant residues, including both saponifiable and unsaponifiable oils, graphite, molybdenum disulfide, and silica type materials, also require some solution of the binding material and suspension of solid residues.

Conversion Soils A different classification of soils requiring a very specialized approach is the conversion coating types which are actually integral with the surface. This category would include the short time anneal oxides, which could be formed as a continuous layer on the product during a few minutes' dwell time at 1200-1500°F, and all the intermediate possibilities up to the long time box anneal scales formed on 430 grades of stainless steels. These variations alone suggest numerous approaches to the problem of obtaining a clean metal surface following heat treatment.

Lubricant Oxide Mixtures Another group of conversion coatings which can be even more complex than those resulting from in-process annealing are those formed during hot working, forging and casting. These scales not only include the multiple oxide combinations which are possible in all heat treated stainless steels, but also may incorporate the elevated temperature lubricants or mold and core treating materials which can be combined with oxides to produce some extremely complex scales.

The removal of anneal and hot work scales requires cleaning processes which either mechanically abrade and attack the surface or chemically react and dissolve the surface or possibly a combination of both processes.

SIMPLE CLEANING

Dirt deposits on stainless steel, which include accumulated dust and dirt, finger marks, and identification markings, are easily removed. Frequently, warm water with or without detergent is sufficient. Next in order are mild nonscratching abrasive powders such as typical household cleaners. These can be used with warm water, bristle brushes, stainless steel brushes, sponges, or clean cloths. Ordinary carbon steel brushes or steel wool should be avoided as they may leave particles embedded on surfaces which can lead to rusting. For slightly

more aggressive cleaning, a small amount of vinegar can be added to the scouring powder. Cleaning should always be followed by rinsing in clean hot water. When water is known to contain mineral solids, which leave water spots, it is well to wipe the surfaces completely with dry towels. Some companies use oil-impregnated cloths to remove water spots and enhance appearance.

Commercial metal cleaners may also be considered, but it is important to make certain that they can be used on stainless steels.

FINGER MARKS

Finger marks are probably the most troublesome of unwanted marks on stainless steel. They not only detract from overall appearance of smoothly polished or bright finishes, but they also can “burn in” quite deeply during annealing or other thermal treatments, leaving permanent marks. Fortunately, they can be easily prevented through the use of clean gloves, or they can be removed by gentle rubbing with a paste of soda ash (sodium carbonate) and water applied with a soft rag. Again, this should be followed by a thorough warm water rinse. On the other hand, burned-in marks can be removed only by grinding and polishing; so prevention is worth the effort.

INK STENCIL MARKS

Most inspection stamps and identification marks applied by the mill are ink, which can be removed by applying a solvent on a rag and rubbing. Examples of solvents are:

1. Grain alcohol.
2. A mixture of equal volumes of oleic acid, xylene and triethanolamine combined in the order named.

Selection of solvent is determined by the type of ink used. Solvents should be rinsed from the stainless steel with warm water, repeating the treatment if necessary.

DRAWING LUBRICANTS AND MACHINING OILS

Drawing lubricants and machining oils in common use for stainless fabrication differ very widely in composition and, therefore, in characteristics. Lubricant selection is based on manufacturing requirements, and there is usually a problem of complete removal. Like finger marks, lubricant residues remaining on stainless steel surfaces can burn in upon subsequent annealing and heat treating operations, the result of which may be unwanted carburization and loss of good surface finish. Lubricants should also be removed before welding, because oil in the weld zone can result in weld porosity or cracking.

Determining the nature of the lubricant to be removed is obviously the first step in planning a cleaning procedure. In the case of cold drawn parts, for example, consideration should be given to the fact that the heat of drawing may cause a certain amount of drying.

Some lubricants are made up of mineral oils, while others are derived from animal and vegetable oils and other chemical ingredients, such as inert pigments. Therefore, it is best policy to tailor the cleaning procedure according to the type lubricant used. There is no one cleaning method that is satisfactory for all situations.

CHEMICAL CLEANING

Cleaning methods for the removal of drawing compounds and machining lubricants from stainless steel workpieces may be grouped as follows:

1. Those employing hot alkaline solutions along with auxiliary hot water rinsing and drying operations.
2. Those using chemical solvents for degreasing.

Information as to methods of lubricant removal obtained from suppliers of lubricants together with technical advice and assistance from firms producing cleaning materials are always most helpful in deciding what method to use. In addition, there are many firms that specialize in the design and manufacture of cleaning equipment for the volume processing of all manner of workpieces.

ALKALINE CLEANING

Alkaline solutions are used for the removal of water soluble materials, and the methods of applying them are determined by the contour of workpieces and by the volume of production to be handled. Parts may be placed in tubs and hand scrubbed, rinsed and dried; or they may be mechanically carried by conveyors through immersion tanks or through a series of high-pressure sprays and scrubbers for cleaning, then through a similar system for rinsing, and finally through drying chambers.

Each one of these steps, cleaning, rinsing and drying, should be considered as a separate operation and be properly adjusted and controlled in order to obtain uniformly satisfactory results. Each step is discussed separately in the following text.

The Cleaning Cycle

To repeat, the selection of cleaning compounds, of which there are many commercially available, should first be determined by experimental testing, or on the basis of experience with similar work, or with the advice of technicians experienced in the field of metal cleaning. Typical materials are soda ash, tri-sodium phosphate and sodium metasilicate. Actual strengths of solutions are best determined by test. Detergents and/or wetting agents may also be added to reduce surface tension. Solution temperatures range from warm to boiling. Having once determined the most satisfactory strength of an alkaline solution, it is necessary to establish process controls for maintaining proper conditions and uniform results.

As production proceeds, the bath gradually becomes weakened and contaminated with accumulations of material removed from the parts. In batch operations with immersion tanks, this calls for shutdown periods for removing the solution, cleaning the tank and introducing fresh solution. In continuous mechanized operation through immersion tanks or through a series of sprays pumped from a reservoir tank, necessary controls are readily maintained.

Regardless of method, good work depends on maintaining uniform conditions with respect to the following factors:

1. Solutions should be maintained at proper strength.
2. Solutions should be at proper temperature.

3. Solutions should be relatively free of accumulations of removed material.
4. In the case of spray jet cleaning, proper direction of pressure sprays is necessary to insure uniform and thorough coverage of all part surfaces.

The maintaining of proper conditions calls for close supervision and adequate controls.

Since the action of cleaning is that of removing material from a workpiece, its effectiveness can be increased by speeding up the movement of the solution over part surfaces. In immersion tanks, this can be accomplished by agitating the solution by mechanical means, by open-end steam heating pipes, by sprays, or by rapidly traversing the work. It can also be aided by brushing. In spray cleaning, impingement of the cleaning solution brings about the same result. Pressure sprays reduce the danger of blind spots.

Mechanized movement of workpieces on hooks or conveyor belts through agitated solutions or under pressurized sprays or between rotating scrubbers constitutes an effective means of removing finely divided pigment material from metal surfaces. Workpieces should be held in such a position as to insure thorough drainage of cleaning solution.

Parts coming out of a deep drawing die are frequently warm enough to change the consistency of drawing compounds that adhere to them. Lighter ingredients may be evaporated and the heavier portions remain as thick, tightly adhering coatings, which may or may not include pigment material. Under intense heat conditions, these residues may become much more difficult to remove than their parent material in original condition. The extent of such heating action on the lubricant can be minimized by speeding the transfer of workpieces into the cleaning operations.

When a situation of this kind cannot be avoided, preliminary testing to determine required solution strength and manner of cleaning should be based on the condition in which the drawing compound actually reaches the cleaning operation, not on its condition as originally applied to the draw blank.

Rinsing When parts have progressed to the point where all lubricant residues have been removed, they are ready for rinsing. The purpose of this operation is to remove any residues of cleaning solution together with any residual particles of foreign materials that may tend to cling on the work surfaces. The operation must be conducted with diligence and care. It should be regarded as a separate sub-operation that follows actual cleaning and not as a part thereof. Copious quantities of clean hot water are called for. High pressure sprays, manual or mechanized brushing and bath agitation are means frequently employed to insure effective results.

Final Drying Stage At this stage of the process, parts should be completely free of anything but rinse water. The removal of this carryout water, that is, the final drying operation, can be accomplished by evaporation in a hot air chamber or by wiping off to dryness by using either wiping rags, an absorbent material like sawdust, or by compressed air jets (oil-free).

Rinse water high in solid content (high hardness) will leave

objectionable water marks on evaporation. If these marks cannot be eliminated through the use of rinse waters that are low in solids content, steps should be taken to prevent the evaporation of droplets on the work. This may require the use of wetting agents which prevent water collecting in droplets.

When parts intended for annealing have been cleaned and dried, they should be handled with clean gloves or cloths and stored under the cleanest possible conditions.

ELECTROLYTIC CLEANING

An electric current of very low amperage is sometimes used to assist the cleaning action of alkaline solutions. By arranging the parts as the cathode, gas bubbles collect upon their surfaces. In freeing themselves, the bubbles accelerate the removal of adhering material. This process appears to have only limited use in the fabrication of stainless steel parts. Bath temperatures of alkaline solutions may be reduced to 160-180°F when aided by current.

Electrolytic polishing may be employed as a means of surface cleaning in isolated cases and on small work. In this process, parts are set up as anodes in an acid type bath. Cleaning consists of actual metal removal to expose fresh surfaces, during the course of which any surface contamination originally present is automatically removed.

SOLVENT DEGREASING

The removal of oil and grease from stainless steel parts by solution in chemical solvents is frequently used because it is a very satisfactory cleaning method. It is used mostly with cold-formed or machined parts that are laden with lubricants. As its name implies, the cleaning action is one of direct solution of the lubricants, which are soluble in the solvents employed.

This process, in its simplest form, consists of bringing liquid solvent into contact with a surface to be cleaned and allowing solution to take place. Examples are (a) washing a surface with trichloroethylene or similar liquid and (b) stirring a batch of small parts in a container of solvent. Such procedures amount to direct immersion in liquid.

As commonly used in production sequences, the process makes use of solvents which vaporize at low temperature. Equipment is usually designed so vapors will condense on the parts. This condensate dissolves the dirt and runs off by gravity into a reservoir. As the solvent evaporates, it results in a continuous supply of clean vaporized solvent.

Typical halogenated solvents (containing halogens chlorine or fluorine) are methylene chloride, trichlorotrifluoroethane, chloroform, methyl chloroform ethylene dichloride, trichloroethylene, and perchloroethylene. (Carbon tetrachloride, once widely used, has been almost completely phased out because of its toxicity.) Generally speaking, the chlorinated solvents are more toxic, but less costly, than the fluorinated compounds.

Typical nonhalogenated solvents are acetone, methyl alcohol, ethyl alcohol, methyl ethyl ketone, benzene, isopropyl alcohol, toluene, mineral spirits, and turpentine. These work well but have the drawback of being flammable.

Many of the above-mentioned solvents are widely used as individual

cleaners, but there are many thousands of blended or compounded cleaners available under a wide variety of names. Good advice is to contact suppliers of solvents.

Liquid Solvents

Cleaning by direct immersion in liquid solvent appears to be limited generally to the more or less occasional handling of relatively small batches of parts. The use of solvents of low vaporization rate reduces the hazards of fuming, a typical example of which is carbon tetrachloride which vaporizes at a much lower rate than solvents used in vapor degreasing. Parts immersed in a liquid solvent carry out some of the solution on withdrawal and must, therefore, be given further cleaning. Rinsing and scrubbing in hot water followed by nitric acid treatment, as described later under vapor degreasing, are recommended for this purpose.

Another disadvantage of the full immersion treatment is the constant buildup of dissolved material in the bath. As a result, the cleaning effectiveness of the solution is gradually diminished. As production proceeds, the bath becomes weaker and also depleted, its content of removed material increases, and the cleanliness of treated work diminishes.

Vapor Degreasing

This process uses solvents of low boiling points, which vaporize rapidly at comparatively moderate temperatures and condense on cool parts immersed in the vapor. As the condensate builds, it dissolves the soluble components on the parts being cleaned. Vapor degreasing can be precisely controlled, and the process is relatively fast.

Equipment may be of relatively simple design. It consists basically of a tank for the solvent, which may be heated to stimulate vaporization. Above this is a chamber to confine and cool the vapors, and above this vapor zone is an opening through which parts are introduced.

Equipment of various designs are commercially available, and manufacturers should be consulted as to design and capacity.

An important feature of the vapor degreasing, as compared with the liquid solvent process, is that only clean solvent comes in contact with the work. As the condensate runs off, it collects in the lower reservoir from which it is continuously vaporized. The material which it removes from the work remains behind in the bath.

The solvents in general use are trichlorethylene and perchlorethylene, the former being the more popular. Trichlorethylene operates at low temperatures, and finished parts are easier to handle. Perchlorethylene has a higher boiling point, resulting in parts having a higher temperature as they leave the operation. Inhibited trichlorethylene is also used. The selection of one or the other should be based on discussions with degreasing equipment suppliers.

Parts can either be suspended in baskets or conveyed continuously through the vapor zone, so there is considerable versatility.

Following vapor degreasing, a hot water rinse with scrubbing will help assure complete removal of residual solvent or undissolved material (like inert pigment in a drawing compound). Such treatment

removes the possibility of the formation of hydrochloric acid and ferric chloride, which can develop from hydrolized chloride-containing solvents. Hydrochloric acid will attack all grades of stainless steels, and ferric chloride is particularly harmful. Complete freedom from this danger can be obtained by following the hot water rinse with immersion in a 15 to 20 percent water solution (by volume) of nitric acid at 120-140°F and then finishing with a thorough wash in clean hot water.

It is important to realize that solvent degreasing removes only material that dissolves in the solvent, and that it may be necessary to employ additional cleaning steps to assure positive results. Such steps can include high pressure sprays, mechanical scrubbing and acid treatments.

Modifications of Solvent Degreasing

The two solvent processes (liquid and vapor) may be combined for better cleaning efficiency. For example, parts can be first positioned in liquid solvent for first-stage cleaning and then withdrawn into the vapor zone for final cleaning; or, while being held in the vapor zone, they can be subjected to pressure sprays of liquid solvent.

VAPOR BLASTING

A proprietary process known as vapor blasting is adaptable to use with stainless steels. Various abrasives conveyed in liquid carriers are discharged at the parts to be cleaned by compressed air. A variety of finishes can be obtained through selection of abrasives and adjustment of pressures. Finishes much smoother than those resulting from dry sand and similar in appearance to a Tampico No. 6 finish* may be obtained with this process. As in the case of sandblasting, a final treatment in nitric acid followed by water washing is required.

Testing Prior to Annealing

Because of the extreme importance of having stainless steel surfaces thoroughly clean prior to annealing, it is suggested that test samples be processed and annealed before starting full-scale production. When exposed to annealing temperatures, unclean parts can be severely damaged, and the remedy is generally expensive. Testing will reveal, in advance, the cleanliness of the parts.

*Note: A No. 6 Finish is a dull satin finish having lower reflectivity than No. 4 Finish. It is produced by Tampico brushing No. 4 Finish sheets in a medium of abrasive and oil.

PASSIVATION

Passivation of stainless steels, as defined here, is essentially a surface cleaning operation conducted with solutions of nitric acid in water, which has the effect of eliminating surface contamination that may cause discoloration or superficial corrosive attack in service. Typical contamination includes iron from cutting tools and contaminated sandblast materials.

The removal of these residues from stainless steel surfaces promotes the complete formation of the invisible oxide film that gives these alloys their corrosion-resistant properties.

Protective oxide films form on clean stainless surfaces in the presence of oxygen in normal air. Their effect is to render the material passive, which is to say that the material is placed in a condition of maximum corrosion resistance. Experience indicates that the speed of oxide formation is accelerated by the oxidizing behavior of nitric acid. For example, a 30 percent solution of that acid is known to produce more rapid passivation than normal air.

The reason for removing foreign materials is to allow complete formation of the protective oxide film. Areas in which oxygen is denied tend to remain active, which is another way of saying that the material lacks corrosion resistance in those areas.

Nitric acid, by virtue of its dissolving of iron particles, removes sources of possible rusting. While rusting of this kind persists only as long as there is anything remaining to rust, it may also lead to pitting of surfaces beneath it.

Passivating Solutions

In general, there is considerable latitude in solution strengths, operating temperatures, and immersion time in acid baths. However, no one solution is applicable to all grades. Solutions and operating procedures that may be satisfactory for one type of stainless steel may not be appropriate for other types.

For all chromium-nickel stainless steels including the precipitation hardening alloys, but with the exception of the free-machining compositions (such as Type 303), nitric acid passivating solutions usually contain from 20 percent to 40 percent nitric acid (by volume). Temperatures range from room temperature up to 140°F for periods of 30 to 60 minutes. They must be followed by thorough washing in clean hot water. For the straight-chromium stainless steels containing 17 percent or more chromium, the above treatment is also satisfactory.

The free-machining Types (416, 430F, and 303) and the high-carbon, heat-treatable, straight-chromium Types 410, 420 and 440 may show etching under the aforementioned treatment. This can be avoided through the use of solutions containing 20 percent (by volume) of nitric acid and 4 to 6 percent (by weight) of sodium dichromate at room temperature up to 110-130°F for 30 minutes.

Considerable latitude is permissible in adjusting temperatures, solutions and times. However, accurate controls may be necessary to avoid impairment of finish or loss of dimensional tolerances. It should be kept in mind that the free-machining and high-carbon types, especially the straight-chromium analyses, maybe etched or dulled by hot solutions of nitric acid, such as under 5 percent (by volume) boiling, and by 20 to 40 percent (by volume) solutions at 140-160°F.

Attention is also called to the fact that concentrated nitric acid at atmospheric temperatures may passivate free iron (in the corrosion sense) and prevent its desired removal by solution. Also, parts partially immersed in solutions may show etching above the liquid level.

Passivation with straight nitric acid solutions generally is not necessary on parts that have been pickled in nitric/hydrofluoric solutions. These acid solutions, which are widely used for pickling stainless steels, also passivate the parts; so nothing would be gained by an additional nitric acid dip.

However, if pickling was done by straight solutions of hydrochloric or sulphuric acids followed only by washing in water, it is important to add a final nitric acid passivating treatment and thorough water wash.

The passivating value of electro-polishing methods is frequently a subject of inquiry. These processes actually remove metal of uniform thickness; and in doing so, they also dislodge foreign materials. They are excellent cleaning processes. After final water rinsing and drying, the electropolished stainless steel surfaces will passivate themselves in normal air.

FUTURE TRENDS

Future investigations to improve the present methods of cleaning and descaling stainless steel will be directed toward minimizing acid consumption and disposal problems. This can be accomplished through increased application of electrical energy to cleaning systems, whether continuous or batch operations. Electrolytic acid pickling can also reduce the concentration of acids required and the metal attack.

Combinations of mechanical finishing, including abrasive cleaning, flapper type wheels, and even slurry finishing, will be used with salt bath conditioning. It is quite feasible that the proper combinations will effectively minimize or possibly eliminate acid requirements.

One area of investigation that has been seriously neglected in recent years but which is expected to grow in the future is the control of furnace atmospheres to reduce the amount of scale formed in heat treating operations with a consequent reduction in conditioning and pickling requirements. New scientific equipment which permits exact analyses of molecular surface films will aid in determining the direction of furnace atmosphere control.

Development in the knowledge of chelating systems, along with the introduction of new metal chelates, hold strong promise for the eventual elimination of acid in pickling systems. At the present time, it is quite feasible, with lighter oxide scales, to completely clean heat treated parts in a caustic base chelated solution.

CONSUMER AND INDUSTRIAL/ COMMERCIAL CLEANING METHODS

Quick Reference Cleaning Tables For Consumer and Commercial Users

Both consumer and industrial/commercial users of stainless steel products have occasional need for spot cleaning to remove light dirt and debris. The following tables, one for consumers and the other for industrial/commercial users, suggest several methods for spot removing dirt and light soils. The table also identifies several commercially available cleaning products—from plain water to more effective detergents and solvents.

The use of brand names serves only to identify categories of cleaners, and others not listed may be equally serviceable. Most products are available through local supermarkets, hardware stores, and department stores.

METHODS FOR CLEANING STAINLESS STEEL

	<i>CLEANING AGENT*</i>	<i>METHOD OF APPLICATION**</i>	<i>EFFECT ON FINISH</i>
Routine Cleaning	Soap, ammonia, or detergent and water	Sponge with cloth, then rinse with clear water and wipe dry.	Satisfactory for use on all finishes.
Stubborn Spots and Stains, Baked-on Splatter, and Other Light Discolorations	Revere Ware Cleaner, Twin- kle, or Cameo Stainless Steel Cleaner	Apply with damp sponge or cloth. Rub with damp cloth.	Satisfactory for use on all finishes. Satisfactory for use on all finishes if rubbing is light. Use in direction of polish lines.
	Goddard's Stainless Steel Care, Revere Ware Stainless Steel Cleaner, Soft-Scrub	Apply with damp sponge or cloth.	
	Household cleansers, such as Old Dutch, Bon Ami, Ajax, Comet	Rub with a damp cloth. May contain chlorine bleaches. Rinse thoroughly after use.	Use in direction of polish lines. May scratch or dull highly-polished finishes.
	Zud	Rub with a damp cloth.	
Heat Tint or Heavy Discol- oration	Revere Ware Stainless Steel Cleaner, God- dard's Stain- less Steel Care	Apply with damp sponge or cloth.	
Burnt-On Foods and Grease, Fatty Acids, Milk stone (where swabbing or rubbing is not practical)	Easy-Off Oven Cleaner	Apply generous coating. Allow to stand for 10 to 15 minutes. Rinse. Repeated application may be necessary.	Excellent removal. Satisfactory for use on all finishes.

	<i>CLEANING AGENT*</i>	<i>METHOD OF APPLICATION**</i>	<i>EFFECT ON FINISH</i>
Hard Water Spots and Scale	Vinegar	Swab or wipe with cloth. Rinse with water and dry.	Satisfactory for all finishes.

*Use of brand names is intended only to indicate a type of cleaner. This does not constitute an endorsement. Nor does the omission of any brand name cleaner imply its inadequacy. Many products named are regional in distribution, and can be found in local supermarkets, department and hardware stores.

**It is emphasized that all products should be used in strict accordance with instructions on package.

1. Use the mildest cleaning procedure that will do the job efficiently and effectively.
2. Always rub in the direction of polish lines for maximum effectiveness, to avoid marring the surface.
3. Use only soft cloth, sponge, fibrous brushes, plastic or stainless steel pads for cleaning and scouring.
4. Rinse thoroughly with fresh water after every cleaning operation.
5. Always wipe dry to avoid water marks.

REMOVAL OF SOILS FROM STAINLESS STEEL FOR THE INDUSTRIAL OR COMMERCIAL USER

NOTE: Mention of products by name in this table should not be construed to indicate their sole suitability for solving the specific problem—others in the same product type classification may prove to be equally effective.

OBSERVE THESE PRECAUTIONS!

ABRASIVES—Even the finest cleaning powders can scratch or burnish a mill-rolled finish like Nos. 2B and 2D. On polished finishes like Nos. 3 and 4, rubbing or wiping should be done in the direction of the polish lines, not across them.

ACIDS—*Acids are dangerous* and for on-the-job cleaning should be used only as a last resort. Synthetic rubber gloves should be used by the operator, and goggles and aprons are advisable even though the solution is relatively nonhazardous. Acid cleaners may possibly harm paint, wood or fabrics and stain concrete, galvanized steel and other metals. Therefore, provision should be made to avoid contact with such materials when using them on stainless. Before an acid cleaner is wiped on a stainless steel surface, the surface should always be rinsed with an ample amount of clean water, preferably hot. This is done to wash away chlorides which, if present, would cause etching and white spotting. This precaution is generally not necessary when the item can be immersed in a large volume of acid.

SOLVENTS—Do not use solvents in closed places or while smoking. Keep them out of contact with hands and skin. All solvents should be used only in well-ventilated places as their vapors are toxic to breathe for extended periods or in high concentrations. Also, wear rubber gloves when working with these cleaners.

<i>SOILS</i>	<i>CLEANING MEDIA</i>	<i>COMMENT</i>
Chlorides (before rusting starts)	Water, an ample amount, preferably warm or hot and from a hose.	Water is most useful when hot and from a hose for: 1. Washing away flux immediately after soldering. 2. Washing away chlorides prior to use of acid cleaners such as phosphoric acid. 3. Washing away excessive amounts of soils from the surface.
De-icing salts	Water, an ample amount, preferably warm or hot and from a hose.	
Dirt	1. Soap or detergent and	Household soaps and

<i>SOILS</i>	<i>CLEANING MEDIA</i>	<i>COMMENT</i>
Accumulations	water, or	detergents are sometimes overlooked for use on metal surfaces. They can be very effective.
	2. Mild abrasive cleaners	Some mild abrasive cleaners are pumice and household cleaning powders such as: Ajax, Bon Ami, Comet, Twinkle, Cameo Stainless Steel Cleaner, or Soft Scrub. Household abrasive cleaning powders may have additives that leave smears. Many also have chlorine bleaches, which if left on a surface might lead to corrosion. Thorough rinsing is necessary. SEE PRECAUTIONS ON ABRASIVES.
Fingerprints	1. Soap or detergent and water, or	Some solvents are: acetone, alcohol, benzene, gasoline, kerosene, lacquer thinner, methyl-ethyl-ketone, mineral spirits, naphtha, perchlorethylene, or trichlorethylene. PRECAUTIONS ARE REQUIRED, SEE TOP OF TABLE.
	2. Solvent, or	
	3. Detergent and water plus a solvent, or	While solvents are very effective for removing oils, greases and various other soils, they leave surface smears. These can be eliminated by using a combination of a solvent with a mild detergent and water and agitating the mixture before each application. A water rinse and wiping

<i>SOILS</i>	<i>CLEANING MEDIA</i>	<i>COMMENT</i>
		with a soft cloth completes the operation.
	4. Mild abrasive cleaner, or	(See previous comments on mild abrasive cleaners.)
	5. Oily or waxy cleaner.	Some oily or waxy cleaners are: Lac-O-Nu ⁽¹⁾ , Vista ⁽²⁾ or Paste Wax ^(2,3) . These remove light soil and also provide a barrier film that minimizes fingerprints.
	NOTE: Methods 1 and 2 clean off fingerprints but do not prevent their reregistering. Method 5 minimizes re-registering, but is not a cure-all.	Paste waxes are more difficult to apply, but are more effective than liquid, oily or waxy cleaners.
Grease, oil	1. Soap or detergent and water, or 2. Solvent, or 3. Detergent and water plus a solvent, or 4. Mild abrasive cleaner, or 5. Oily or waxy cleaner, if soil is light.	
Grease pencil markings	1. Soap or detergent and water, or 2. Solvent or 3. Detergent and water plus a solvent, or 4. Phosphoric acid cleaner, but pre-rinse with ample amount of water.	Some proprietary phosphoric acid cleaners are: Dilac ⁽⁴⁾ , Oakite Composition No. 33 ⁽⁵⁾ and Texo 12 ⁽⁶⁾ . PRECAUTIONS ARE REQUIRED, SEE TOP OF TABLE.
Iron contamination—not yet rusted	Nitric acid or nitric acid plus dichromate passivating solution as described in the text.	Nitric acid removes embedded iron or iron lying in the surface, <i>but does not remove the rust</i> . Swabbing is dangerous and requires extreme care. Immerse, if possible.

<i>SOILS</i>	<i>CLEANING MEDIA</i>	<i>COMMENT</i>
		OTHER PRECAUTIONS ARE REQUIRED, SEE TOP OF TABLE.
Lead pencil markings	1. Oily cleaner, or 2. Mild abrasive cleaner, or 3. Phosphoric acid cleaner, but pre-rinse with ample amount of water.	NOTE: All of these remove the marks, but any scratching of the metal surface by the pencil point will not be removed. PRECAUTIONS ARE REQUIRED, SEE TOP OF TABLE.
Plaster	Stronger abrasives	Stronger abrasives include: chipping tools, grinding wheels, stainless steel wool and stainless steel wire brushes. These, however, will scratch the surface. Steel wool made from carbon steel, when applied <i>by hand</i>, can be used on stainless <i>if</i> all loose particles are washed away afterwards; otherwise these particles will rust. <i>Stainless wool is preferred.</i> Ordinary steel wire brushes or wire brush wheels should <i>never</i> be used because steel from these tools can easily deposit, work into the surface, and rust later.
Rust and other corrosion products	1. Mild abrasive cleaners, or 2. Phosphoric acid cleaner (a pre-rinse with an ample amount of water and long-time contact with the acid is required), or 3. Oxalic acid (a pre-	Proprietary cleaners containing phosphoric, oxalic or sulfamic acids remove rust, but require considerable time to do so. Thus, the acid must contact the surface for a period of time. These proprietary acid

<i>SOILS</i>	<i>CLEANING MEDIA</i>	<i>COMMENT</i>
	rinse with an ample amount of water and long-time contact with the acid is required), or	cleaners will remove dirt, grease, heat tint, light and heavy discoloration rust and other bad stains. When properly used, they do not mar or harm stainless steel.
	4. Sulfamic acid (a pre-rinse with an ample amount of water and long-time contact with the acid is required).	With respect to proprietary cleaners, here is how Oakite No. 33 might be used. Make a solution of one part cleaner and two parts water. Use a stainless steel, glass, porcelain enameled, or wood container. Wash the item to be cleaned with plenty of clean water first, then simply swab the solution over the area to be cleaned, using a small clean cloth or sponge. Allow to stand 15 to 20 minutes, rinse with clean water and dry with a soft cloth. If the surface still isn't clean and bright, repeat. It is sometimes advisable to let the solution stand on stubborn stains for several hours or more. Always rinse afterwards with water and dry with a soft cloth. FOLLOW PRECAUTIONS REGARDING ACID CLEANERS AT TOP OF TABLE.
Scratches	1. On bright annealed 2B and 2D finishes scratches cannot be removed successfully. 2. On No. 3 and 4 polish finishes use a Scotch-Brite pad in direction of polish lines.	

<i>SOILS</i>	<i>CLEANING MEDIA</i>	<i>COMMENT</i>
Soldering flux (<i>before</i> rusting starts)	Water, an ample amount, preferably warm or hot and from a hose.	
Spot weld discoloration (formation of this discoloration can be minimized by inserting thin gauge aluminum between welding tip and stainless steel on the side to be kept clean)	1. Mild abrasive cleaner in form of paste with water, or 2. Mild abrasive cleaner in form of paste with phosphoric acid cleaner instead of water, or 3. Stronger abrasive cleaners, or 4. Electrolytic weld cleaning method.	
Stencil markings (some inks used are water soluble and others require organic solvents)	1. Soap or detergent and water, or 2. Detergent and water plus a solvent, or 3. Mild abrasive cleaner, or 4. Phosphoric acid cleaner, but pre-rinse with an ample amount of water.	FOLLOW PRECAUTIONS FOR SOLVENTS. PRECAUTIONS ARE REQUIRED, SEE TOP OF TABLE.
Water scale and stains from water faucets	Phosphoric acid cleaner, but pre-rinse with an ample amount of water. Vinegar may also work.	FOLLOW PRECAUTIONS REGARDING ACID CLEANERS AT TOP OF TABLE.
Water spotting	1. Wipe with damp cloth, or 2. Mild abrasive cleaner.	
Weld discoloration	1. Mild abrasive cleaner in form of paste with water, or 2. Mild abrasive cleaner in form of paste with phosphoric acid cleaner instead of water, or 3. Electrolytic weld cleaning method.	FOLLOW PRECAUTIONS REGARDING ACID CLEANERS AT TOP OF TABLE.

<i>SOILS</i>	<i>CLEANING MEDIA</i>	<i>COMMENT</i>
Weld spatter	Stronger abrasives	

SOURCES OF MATERIALS AND PRODUCTS LISTED

- (1) Nu Steel Company, 1714A S. Ashland Ave., Chicago, IL 60608
- (2) The Simoniz Company, 110 N. Wacker Dr., Chicago, IL 60606
- (3) Johnson Wax, 1525 Howe St., Racine, WI 53403
- (4) Diversey Chemicals, 1855 S. Mt. Prospect Rd., Des Plaines, IL 60018
- (5) Oakite Products, Inc., 50 Valley Rd., Berkeley Heights, NJ 07922
- (6) Texo Corp., 2801 Highland Ave., Cincinnati, OH 45212