Surface Preparation of Metals Prior to Plating

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ABSTRACT

Generally accepted as a critical step in most electroplating processes, surface preparation of metals prior to the metal electroplating is presented. Definition of the clean surface influence of basis metal and the choice of cleaning methods are discussed. Soak, spray, electrolytic, acid, solvent and ultrasonic cleaning are elaborated as well as acid dip and pickling steps.

The mechanisms of cleaning action are detailed, starting with the role of inorganic builders, through surfactants and solvent actions. The basic surfactant chemistry will be discussed to provide the understanding of soil removal. The fundamentals of formulating science and know-how are fashioned for different types of industrial formulations using a number of typical formulas as appropriate examples. Because numerous papers and books are published on cleaning, an extensive reference section and glossary is provided

INTRODUCTION

The most important requirement in electroplating technology is cleanliness of the surface to which coatings are applied. In addition to the few insignificant exclusions, parts to be plated cannot be introduced into an electroplating solution without pretreatment of some kind. The chemical and physical nature of a metallic surface has a very marked effect upon the quality of any electroplated metal that may be used to protect it. The presence of grease, oil, corrosion products, dirt, or other extraneous material affects the adherence, continuity, and general durability of plated deposits. In general, it may be said that the character of an electrodeposit is no better than the surface to which it is applied, and consequently it has come to be recognized that the production of protective, decorative or functional metal deposits of high quality is dependent upon the proper and thorough pretreatment of the surface of the basis metal. This in turn requires proper equipment and chemistry[1].

Cleaning operation frequently has been regarded as of minor importance and, as a result, this phase within a plating operational sequence has received scant attention. However, the ever-increasing severity of cleaning specifications, the necessity of programming more closely-scheduled cleaning sequences, high labor costs, and the tendency toward design of more complicated parts, and environmental issues have rapidly advanced metal cleaning from a guesswork procedure to that bordering to a science.

Metal cleaning is usually accomplished by six general methods of handling the work in relation to the cleaning media, namely: (a) soak tank, (b) electrocleaning tank, (c) spray washer, (d) solvent vapor degreaser (e) steam gun, and (f) abrasion with grit, shot blast or tumbling. The two last-mentioned methods may be omitted in present discussion since mechanical or out-of-the plating line methods are not considered. Interested readers can find details on those methods in reference books[2, 3]. Method d) has been discussed to some extent. The other three will be considered in detail here.

I. DEFINITION OF CLEAN SURFACE

In the preparation of almost all metals for decorative plating, one of the most, if not the most important consideration, is the preplating sequence: cleaning process. This is so, because the appearance, adhesion and acceptance of the finished article depend primarily on a sound foundation for the final finish, which is achieved only with an active and clean substrate. Clearly, only a properly designed preplating sequence will result in quality parts. It is not question of whether or not cleaning is required, but what type of cleaning should be used.

Clean can mean many different conditions to many people. Cleaning is loosely defined as the process of removing unwanted contaminants or dirt from a surface. A practical definition[4] of word clean is “ containing no contaminants that would interfere with satisfactory deposition of one adhering finish”. It is differentiated from other finishing processes in that the cleaning process does not alter the surface physically or chemically. A properly cleaned surface is just the same as it was prior to cleaning, except for the missing soil[5]. For example, to the spray painter, "clean" can be simple freedom from oil or grease. A plater will need to go further, in that his work must also be free of rust, scale, oxide and smut. A nickel-chromium decorative plater would be especially more critical, since minor rust and scale would appear on finished parts as white frosty spots, pits, roughness or even black spots. A cyanide zinc plater may not be as critical, since less than thoroughly clean parts would come acceptable, mostly because cyanides, inherently, are good cleaners because of their high alkalinity and ability to complex many metal ions.

Can conditions of clean and active surface be achieved ion a reasonable, uncomplicated and cost effective manner? For the plater, we can contentedly state that such a condition can be attained. Today, platers are taking parts, as they receive them, and are placing these parts through a cleaning process cycles in hand lines, hoist lines, automatic lines and strip lines with even more successful than ever before. If we want to be successful in cleaning today, we must handle cleaning processes with the same care and control as we do with plating processes. The day of the single cleaner tank is gone forever. Contemporary cleaning systems must remove oil, grease, scale, rust and inert particles. In other words, they must degrease, saponify, emulsify, acid dip (pickle), neutralize, activate, etc. in order to obtain a "clean" part for plating. To do all this, several tanks and solutions are required, depending upon the type of soil, available time and temperature, and the basis metal being processed.

To measure the degree of cleaning more sophisticated methods for cleanliness evaluation are now available: Radio Isotopes[6], UV Fluorescence[7], Evaporative Rate Analysis[8-12], Atomizer test[13], X-ray Fluorescence[14], Water Spray[15], Modified Contact Angle Method[15-17], Conductivity Method[18], Solubility Parameter Technology[19], Beta-backscattering[20], Surface Potential Difference[21], Optical Stimulated Electron Emission[22-25] Electrochemical Meassurments[25,26], Kinetic parameters (overpotential)[27] among others. *Kuhn*[28] elaborated in detail a number of methods for measuring surface cleaningless, ranging from simple to more sophisticated instrumental methods. The final test, of course, is the end result: an acceptable finish.

Perhaps the most universal practical measure of the "clean surface" which is usually reliable, but not necessarily foolproof, is the " water break free" surface. This means that the part will be enveloped with a film of water, which does not form droplets or water beads. If a part is processed by alkaline type of cleaning, a quick dip in a mild acid, followed by a clean rinse is usually more indicative. On iron and steel parts, a uniform continuous cooper coating is fair indication of a clean surface[29].

II. THE BASIS METAL

The composition, physical properties and chemistry of the basis metal influence the selection of the cleaning procedure[30]. The condition of the basis metal is equally important. For example, a piece of metal with heat or welding scale requires much more processing than non-oxidized cold rolled steel. High carbon steels require a different cleaning process than low carbon types, etc.

The cleaning medium must be designed to be compatible with the metal being processed. A cleaning process that does an excellent job of soil removal but severely attacks or even slightly etches the metal surface is usually unacceptable. Therefore, it is important to select a medium, which either does not attack the metal, or one, which the attack is controllable to produce a desire effect. This brings up the degree of cleaning. Process cycles should be made as uncomplicated as possible thereby reducing costs. For example, it would be unreasonable to set up a cleaning cycle for phosphatizing, chromating, electropolishing or anodizing as one would for electroplating – the reason being simply that the cleaning prior these processes are not as critical as those prior to electroless plating or electroplating. Then again, it is wise not to cut corners where sound cleaning may be sacrificed. Consequently, it is extremely important to match the cleaning cycles to the particular plating system taking into the consideration the type of soil to be removed, from both the economical and functional viewpoints.

III. CHOICE OF CLEANING METHODS

Durney eloquently describes the definition of soil[3] where he compared the soil with the weed: "A weed is a plant that is out of place. A rose bush in a wheat field is a weed. A wheat stalk in a rose garden is a weed. A rust proofing oil on a part in storage is not a soil. Only when a part moves to the finishing room does it become a soil". Poet *John Milton*[31] observed in a bit more lyrical way: "*… that soil may best/ Deserve the precious bane* ". Obviously the type of soil, as well as both the amount of it present and degree of adhesion to the metal surface are factors that must be considered. Other important factors will include the cleaning cycle and the proper method of soil removal. In addition to the composition of the cleaner, the selection of a proper cleaning cycle will depend on a number of variables. Some of them are the design and fragility of component parts, the contemplated methods of parts handling, and the production requirement. With the ever-increasing government regulations of effluents, it is now universally accepted that surfactants be biodegradable, meaning that they can be destroyed by the bacteria present in sewage and waste treatments plants.

There are many, many different types of soils that can contaminate parts to be plated. The examples of some of the common soils that platers are encountering in their daily practice are :

1. *Mill oil.*

2. *Forming lubricants*: a) Sulfonated or chlorinated types as applied to metals such as brass. b) Lard oil – as used in forming aluminum and as a protective coating.

3. *Drawing Compounds* – lubricants containing molybdenum disulfide or powdered graphite and chlorinated oils.

4. *Rust preventative oils* – high viscosity oils containing sulfonated soaps or organic corrosion inhibitors.

5. *Shop soils* – dirt, dust, metal chips, cutting oils, marking inks, and fingerprints.

6. *Polishing and buffing residues* – can and do contain metallic particles.

7. *Metallic smuts* – powdering of the basis metal mixed with the oils on the surface.

8. *Carbon smuts.*

9. *Oxides and scale, and weld spots.*

It is often assumed that all soils can be easily removed. Often neglected is that soils can change character on standing, unfortunately in the direction of becoming more difficult to remove. Sometimes they can attack the base metal, leading to additional troubles latter. In addition to all other variables, time of standing has to be accounted for. However, the cleaning operations can be much less troublesome, and reject rates lower if the origin and the nature of the individual soils are more widely understood. Clearly, the types of cleaning methods for removing the above soils is closely related and directly dependent on the composition, condition and the amount of the soils present. It can be deliberated as follows:

A. SOAK CLEANING

The workhorse of the industry, soak cleaners are intended to remove the major portion of heavy, oily soils, quickly, effectively, safely and economically. In addition, they should also meet P006 sludge reduction mandate, OSHA regulations, facilitate analytical control and simplify waste management[32]. The parts are submerged in tanks containing hot alkaline cleaning solution. The concentration and temperature should be as high as it is safe for the particular metal. In this way the cycle time is minimized. Agitation is required, although not universally practiced, in order to in addition to chemical and thermal energy, speed up solubilization, wetting, emulsification and saponification of the soils. The soak cleaners are generally classified as light and heavy duty.

i. *Light Duty Soak Cleaners*. Numerous metal finishers use these of type cleaners, especially those who process buffed metals. These cleaners are composed of inorganic builders, wetting agents, buffering salts, sequestering agents, dispersants, inhibitors, and sometimes solvents and coupling agents. Powder blend or liquid concentrates are formulated to accommodate specific applications. They function by wetting, emulsifying, dispersing and solubilizing the soil. They are rarely used at room temperature, but rather at temperatures ranging from 66^0C (150^0F) to boiling, at concentrations from 4 to 10% by volume or 4 to 8 g/l (6 -12 oz/ gl). They are frequently used for light type of soils and non-ferrous metals.

The builders used in light-duty alkaline cleaners are those yielding a lower pH range of 11.2–12.4, for a concentration range of 3 to 4 g/l (4–6 oz/gl). They differ from the heavy-duty alkaline cleaners, in that they contain little or no caustic soda (NaOH) or caustic potash (KOH), thus they are of little value where saponification of soils and oils containing the fatty acids is required. By virtue of having the lower pH, they are also less stable to acidic contamination from acid drag-in than heavy-duty cleaners. The popularity of light-duty alkaline cleaners is due to their effectiveness in removing contamination from aluminum, steel, copper and zinc base die-castings without etching or tarnishing the base metal. This is made possible with silicates, which effectively inhibit or protect zinc and aluminum from etching at the otherwise etching region pH: 11.2–12.4. The light duty alkaline cleaners are preferred for the removal of light petroleum oil residues, buffing compounds, marking inks on aluminum sheet and residual inorganic salts.

A typical cleaning composition for zinc and zinc die-castings is presented in Table **1**. Specific wetting agent mentioned in the text are the ones that author is experienced with. The best combination, usually depends on type of the soil. For the properties of wetting agents reference manual[32a] should be consulted.

Table 1. Alkaline Cleaning Solutions for Zinc & Zinc Die Castings

Chemical composition & operating conditions	Soak Cleaning	Spray Cleaning
NaOH, beads (%).	10.0	10.0
Na_2CO_3 ,dense (%).	34.4	34.4
Na- glucoheptonate (%).	5.0	4.8
Na-metasilicate, pentahydrate (%).	38.8	34.0
Nonionic wetting agent[a] (%).	4.0	2.5[d]
Anionic wetting agent[b] (%).	1.0	0.1[e]
Cerelose Dextrose[c].	1.0	0.1
Borax, decahydrate.	0.8	0.8
Na-tripolyphosphate.	-	5.5
Temperature (^{0}F/^{0}C).	180/82	170/77
Time (minutes).	1 – 2	1 – 2
Concentration (oz/gl)	4-6	2-4

a. Triton CF-54 or equivalent; b. Gafac RA-600 or equivalent; c. For Cr(VI) reduction;
d. Triton DF-12 or equivalent; e. Zonyl A.

***ii**. Heavy-duty Soak Alkaline Cleaners:* The major consumer in the cleaning industry, these enjoy the most widespread use of any type of cleaning. They are composed of balanced blend of highly alkaline builders, such as sodium or potassium hydroxide, carbonates and trisodium phosphate (TSP). In addition they usually contain silicates as dispersants and corrosion inhibitors, along with sequestering agents, like sodium tripolyphosphate (STPP), tetrapotassium pyrophosphate (TKPP), and tetrasodium pyrophosphate (TSPP). Various surface-active agents* are always present, with occasionally coupling agents, like sodium xylene sulfonate (SXS). They are developed to remove a specific type of soil. Cleaning is usually performed under conditions that promote the speed and completion of the cleaning reactions, such as elevated temperatures [60–70^0C (~140- 200^oF)], high concentrations [80–240 g/l (½ - 2 lb/gl)], and high pH (~ 12.4 –13.8). The typical, basic heavy, medium and light duty soak cleaner formulations are given in Table **2**., together with light duty, liquid formulation.

TABLE 2: Basic Starting Formulations for Soak Cleaners for Ferrous Metals

Ingredient, %	Heavy duty	Medium duty	Light duty	Liquid
Na-carbonate, light	22	40	45	
Na-metasilicate, beads	20	14	25	
NaOH, beads	40	22		
Na-tripolyphosphate, STPP			25	
Nonylphenol, 11-13 moles EO[a]	2.9	3.9	4.9	3
Ethylene–oxide ester condensate[b]	0.1	0.1	0.1	0.1
Sodium Xylene Sulfanate (40%)				12
TKPP (60%)				12
TSPP	10	4.0		
Na_3PO_4 , TSP		16		
KOH (45 %)				12
Na-gluconate	5			
Water				48.9

a. Igepol CO 720, Maccon –10, Triton 101 or equivalent; b. Zonyl A; c. Hydrotrope, Triton H-66 or equivalent

Function of individual ingredients is elaborated in chapter VII.

Those formulations are usefully used as general cleaning mediums for the removal of gross contaminants such as animal and vegetable fats and oils, mineral oil, fatty oils, grease, and rust preventatives and drawing compounds. These compounds are chiefly used for cleaning ferrous metals, and alkali-resistant glass; less commonly for copper and copper alloys because of possible “caustic burn” (tarnishing), and least commonly, for zinc and aluminum because of their reactivity in highly alkaline media. Choice of pH for cleaning different metals and soils is given in Table 3.

Table 3: Choice of pH for Cleaning Different Metals and Soils

Substrate and/or soil	**Cleaner pH**
Magnesium	11
Aluminum	9 11
Copper or Brass	7 10
Zinc, Diecasting or Galvanized steel	7 10

Rust preventatives, machine coolants, natural fatty oils, and greases	7
Steel and Stainless steel	Any pH
Synthetic cutting and drawing fluids	Any pH
Plating over Nickel	7
Carbonaceous soil, road and hard water salts	7

The main action as saponification, where NaOH or KOH chemically reacts with these fatty acids to form water-soluble soaps. Unfortunately, sometimes these saponified fats or oils form metallic, sodium or potassium "soaps" that are often much more difficult to remove than the original fats or oils. If there is other dissolved metallic salts in the solution, insoluble metallic salt will be formed, which cannot be rinsed of or dissolved in acid dip solutions. The role of the silicates in heavy-duty silicated cleaners is primarily to emulsify and disperse soil and to act as corrosion inhibitors. Consequently they are used for the removal of petroleum oils and greases. For mixed fatty acid-petroleum oil soils, saponification plus emulsification and dispersion are required that calls for the use of caustic-silicate formulations.

A secondary, but still important use for heavy-duty alkaline cleaners, are the removal of obnoxious, carbonized or partially coked contaminants formed by the breakdown of petroleum, vegetable or animal fats and oils.

Carbon smuts or other lightly adhering particles on the surface of the parts can sometimes be removed by proprietary smut removing compounds. Some specially formulated electro cleaners can be equally effective. Lightly adhering can be defined as being moved light finger pressure across the surface.

Also included in the category of heavy-duty alkaline cleaners are alkaline descaling and rust-removing compounds. These contain caustic soda or potash plus, a chelating or complexing agent, e.g. sodium gluconate capable of removing rust and hard water scale from metal parts by dissolution and undercutting. They are often fortified with surfactants that are stable at high pH. Since only the iron oxides are removed, there is no attack of the base metal and, therefore, no danger of hydrogen embrittlement. Caustic-gluconate compounds are also used for etch-type aluminum cleaners. However, since the reaction of NaOH/KOH with aluminum is rapid and is accomplished by a copious evaluation of hydrogen gas, the time should be carefully controlled. For difficult smuts, periodic-reverse current is used, at 5-15 A/dm^2 (~ 50-150 A/ft^2).

B. ELECTROLYTIC CLEANING

i. *General*. In preparation of metal for plating or finishing, it is seldom that electrocleaning stage is not used. Exceptions are hard chromium plating, electroless plating, plating over aluminum, anodizing phosphatizing and chromating. Electro cleaners are usually considered as final cleaners. They are basically heavy-duty alkaline types, but are always employed with DC current – either cathodic (direct), anodic (reverse) or periodic reverse (alternating anodic and cathodic currents), PRC. Even though they usually follow precleaning step, in some cases final electro cleaning alone will suffice.

The objective of final cleaning is to remove completely all soil and to activate the metal surface. Activation is usually obtained by using reverse current electrocleaning. The gas scrubbing of the generated oxygen assists soil removal, while the reverse current aids in its removal and prevents the deposition of any metallic film or non-adherent-metallic particles. A dilute mineral acid dip almost always follows the final cleaner, to neutralize the alkaline film on the metal surface, and to remove light oxide layer.

Parts containing heat-treat, welding, or other oxides may require a double cleaning cycle, depending on the degree of oxidation. In such cases, the part is usually anodically electro cleaned (after precleaning if necessary to remove the heavy soils), acid dipped to remove the oxide, final electro cleaned, and acid dipped to neutralize the alkaline film. The second electro cleaner (final cleaner) is used to remove any smut developed from the scale removal in the first acid dip. The first cleaner removes any oil or other soil, which would reduce the effectiveness of the scale removal properties of the first acid dip.

ii. *Electrocleaning Formulations*. Alkaline cleaning blends used for electrolytic cleaning, typically contain mixture of alkaline material, to provide high conductivity at established pH and to have enough reserve alkalinity. High alkalinity is needed for steel, lower for zinc, copper and brass. Alkali metal hydroxide, carbonate, silicate and phosphate are used as a principal source of alkalinity. Sequestering organic additives, such as gluconates, EDTA or trisodium nitriloacetate are also commonly present[33]. Formulation of electro cleaners in addition to basic fundamentals, all attention on foam control and optimal current densities. A problem with excessive foam in electrocleaning is that hydrogen and oxygen gas accumulated in the foam can explode at a sparking electrode. While this is more of a nuisance than a menace in most cases, it can make for an annoying situation and is taken to mean as poor plant practice. Another difficulty is that foam dried onto the work may be difficult to remove by rinsing, and shows up as a pattern in the final electroplated product. Water spray with fog nozzles may be necessary to wet down the work to prevent drying. Foam blanket is necessary in order that the spray of entrapped caustic by the gas bubbles, which are released at the working electrode (electrocleaner parts), will be held on the surface of the tank long enough to permit liquid to drain back into the tank[34]. An ideal foam blanket will have 1-3 inches of foam at the surface. Wetting agent that is stable at high pH is employed, in order to supply the proper foam blanket, and to help wetting and emulsification. Due to the lower cost sodium salts are more frequently used, although potassium based electrocleaners have better solubility, lower electrical resistance and better throwing power. Potassium salts are used in special occasions, e.g. when electrocleaning very large parts where otherwise very large voltages will be required, to obtain high current densities required. Electrocleaning durrent densities and operating conditions for different metal and alloys are given in Table 4.

Table 4. Electrocleaning Current Densities & Operating Conditions

Metall	*Current Density*^{a} *(A/dm*^{2}*)*	*Polarity*^{b}	*Alkalinity*^{c}	*Temperature (*^{0}*C)*	*Time (min)*
Steel, Low Carbon	5-10	A,C, PRC	50-100	60-90	1-5
Steel, High Strength	3-5	A	50-100	60-90	1-5
Stainless Steel	5-8	C	50-100	60-90	1-5
Copper	5-8	A,C	50-100	60-90	1-5
Brass	2-4	A,C ,A-inh	15-20	50-70	1-3
Zinc Diecast	2-4	A,C ,A-inh	50-70	50-70	1-3
Nickel and Ni-alloys	2-3	C	30-60	50-80	1-5
Lead and Pb-alloys	5-8	C	---	50-60	1-3
Silver and Ag-alloys	2-3	C	---	50-60	1-3

Note: a. For barrel operations, fraction of Current Density is used; b. *Polarity*: A=anodic current, C=cathodic current, PRC= Periodic Reverse current; A-inh=Anodic current with inhibited electrocleaner; c. *Alkalinity*, as g/l of NaOH.

Silicates are very popular as they rapidly peptize and disperse oils and also have emulsifying[35] and corrosion inhibition properties. A proper ratio of hydroxide to silicate is needed to prevent insoluble silicate films from adhering to the work and affecting plate adhesion. Silicates are often used to prevent burning of steel at high current density. Nonsilicated cleaners, using different types of inhibitors, are also available. Also important is proper ratio of silicate to phosphate[36]. Phosphates, gluconates or other water softeners and conditioners are also added in order to help sequester hard water constituents. Oxidation and reduction effects vary with the metal, and usually determine whether cleaning should be anodic or cathodic. Metals that are passivated upon oxidation, such as nickel, stainless steel, or aluminum, are cleaned cathodically (aluminum is seldom electro cleaned). Brass is cleaned cathodically to avoid solution of the zinc component at the anode.

On the other hand, zinc and zinc die-castings are cleaned anodically for another reason[37]. Because of the sensitivity of the metal to attack by alkaline electro cleaners, it is desirable to use inhibited cleaners. When silicate is used as an inhibitor, an insoluble film seems to develop when cleaning is cathodic. Hence, cleaning is anodic, with specially formulated cleaners, under mild conditions, and for short times. Steel, which is relatively insensitive to oxidation-reduction effects, can be cleaned anodically or cathodically. At high current densities, there is a tendency toward browning of the steel unless an inhibitor, silicate, is present in the cleaner. Stainless steel can also be cleaned either way, although more drastic pickling action is required when anodic cleaning is employed. The trend, in recent years, has been strongly towards anodic cleaning of steel. Basic electrocleaning formulations and operating conditions are presented in Table 5. Suppliers of proprietary electrocleaners usually tailor the parameters to specific applications, which may vary from the amounts presented in this table.

Table 5. Basic Electrocleaning Formulations & Operating Conditions

Ingredient, %	Steel	Copper	Brass	Zinc
NaOH	50	25	10	20
Na_2CO_3	4	23	38	28
Na-tripolyphosphate[a]	5	10	10	10
Na-metasilicate	40	40	40	40
Wetting agent(s)[b]	1	2	2	2
Operating conditions				
Cleaner concentr. (g/l)	60-120	30-60	24-45	30-45
Time, minutes	2-10	0.5	0.5	0.5-1
Current density (A/dm^2)	50-100	20-50	15-50	20-50
Temperature ($^0C/^0F$)	80-95/175-200	70-80/160-165	60-70/140-160	70-80/140-175

a. Some other sequestering agent may be used. b. Usually an alkyl sulfonate or alkyl ether alcohol

***iii**. Anodic, (reverse) electrocleaning*: The work is made anodic (positive) in an alkaline electro cleaner using low voltage (3 to 12 V) DC current. Current densities vary from about 1 to 15 A/dm^2 (~10-150 A/ft^2), depending on the metal being cleaned and the cleaning time. Cleaning times of ½ to 2 minutes generally suffice for most applications. Higher current densities are possible when shorter cleaning times are used.

Anodic electrocleaning is desirable for cleaning whenever possible, because of the fact that the metal is actually being slightly dissolved as well as cleaned. This action removes metallic smuts and oxidation products and prevents the deposition of non-adherent metallic films. Anodic current generates thin, fresh oxides that can oxidize organics, and also be easily removed in subsequent acid dipping step. Without this oxidation, some stubborn organics may remain insoluble. The oxygen generated at the surface creates a scrubbing action that assists soil removal. In addition, hydrogen embrittlement is avoided by using anodic cleaning.

It is important to control the current density, temperature, and concentration, particularly on non-ferrous metals to avoid etching and tarnishing. Prolonged reverse current cleaning, high current densities, high temperature, and low concentrations are to be avoided, particularly on zinc based die castings[37] and brass[38] and, to prevent dezincification and over etching. An authority on electrocleaning[39] observed that little is gained on current densities above 40 A/ft^2, and nothing above 70 A/ft^2. Anodic electrocleaning release half as much gas as cathodic at same current densities.

Reverse current alkaline cleaning is not recommended for aluminum, chromium, tin, lead or other metals that are soluble in alkaline electro cleaners.

***iv**. Cathodic, (direct) electrocleaning*: The parts are made cathodic (negative) and the same equipment, voltage, and current densities are generally used, as described under anodic leaning. Hydrogen is liberated at the surface of the work. The volume of hydrogen liberated at the cathode is twice that of oxygen liberated at the anode for a given current density. Therefore, more gas scrubbing is achieved at the cathode than at the anode. For this reason cathodic cleaning is sometimes employed as a precleaner followed by anodic cleaning. Soil removal is accomplished by the mechanism described under alkaline precleaning and assisted by gas scrubbing.

The work is actually being “plated” in a direct current cleaner. Any positive charged material is attracted to, and may be reduced and deposited on the surface. Any film (metallic) deposited is usually non-adherent, but difficult to detect and remove. Such films can cause poor adhesion roughness and/or staining of electroplated metal. Exact effect of this is still open for conjecture. Author of this paper had long successful with cathodic electrocleaning of steel.

Parts critical to hydrogen embrittlement (e.g. spring steel) should not be cleaned cathodically unless adequate steps are taken after processing to remove the hydrogen. Generally, heat treatment for 1 hour a 200°C (~400°F), immediately after processing will remove the embrittling effect of hydrogen. Parts with hardness exceeding 40 Rockwell C can be embritlled and should be baked after plating.

Chromium contamination of cleaners is sometimes unavoidable, due to the use of the same rack for chromium as well as other plating. Direct current cleaning is more susceptible to staining from chromium-contaminated cleaners than reverse current cleaning.

Direct current cleaning is used for the following applications:

- To clean metals such as chromium, tin, lead, brass, magnesium, and aluminum, which are dissolved or etched by anodic cleaning.
- To clean and activate high nickel steels, buffed nickel or high nickel alloys, and when plating nickel over nickel or prior to chromium plate[40,41]. Anodic cleaning would produce a passive film on the nickel, due to oxidation, which would prevent the deposition of bright chromium.

***v**. Periodic reverse electrocleaning (PRC)*: Since direct and reverse electrocleaning have individual advantages and disadvantages, the best answer is to use both, either in separate tanks, or in one tank, by periodically reversing the current. PRC electrolytic cleaning is used generally to remove smut, oxide and scale from ferrous metals. It is by far the most effective way of electrocleaning. Alkaline compounded materials containing sequestering or chelating agents are usually used. The work is made alternately cathodic and anodic, using DC current at 6 to 12 V. Work may be cleaned on racks, in a barrel or as continuous metal strip. Cleaning and scale removal are accomplished by incorporating the mechanism of alkaline cleaning and the use of reducing and oxidizing conditions, coupled with strong metal chelating.

One of the advantages of PRC cleaning is to eliminate the acid treatments on certain types of parts where entrapment of acid aggravates bleed-out after alkaline plating (brass, copper, zinc, cadmium, tin). Oxides and light rust may also be removed without the danger of etching or the development of smut usually encountered from acid pickling. When PRC electrocleaning, sometimes the charge on the parts as they are exiting can be critical. In other words the parts leaving should be all cathodic or anodic polarity. The most effective, correct polarity will be the one that shows no discoloration on the metal, may enhance the luster, or gives the most rapid flash gassing in the acid dip. If no acid is used, excellent adhesion and no skip plating evidence the correct polarity.

***vi.** Bipolar electrocleaning*: This particular kind of electrocleaning is used mainly in continuous strip lines where high amperages and/or voltages are required. In order to prevent excessive currents and potentials being applied on contact rolls and metal strips as well to minimize detrimental stray currents[42] and electrochemical corrosion of equipment, bi-polarity is utilized as means of electrocleaning. Anodes and cathodes are separated and by such arrangement opposite polarity are induced on the strip. It is important that strip finish anodic at the end of the cycle to prevent any possible, unwanted cathodic deposition. High current density design cells are utilizing any means of enhancing cleaning via close spacing forced flow, grid arrangements and similar.

***vii.** Physico-chemical aspects of electrocleaning.* Electrocleaning action is, in part provided by scrubbing action of hydrogen and oxygen gases that are generated on the parts or counter anodes, according to simple reactions: $4\ OH^- - 4e \Rightarrow 2H_2O + O_2\uparrow$ and, $4H_2O + 4e \Rightarrow 2H_2\uparrow + 4\ OH^-$. Cathodic and anodic processes, in electroplating as well in electrocleaning steps are directly dependent on the applied current density (CD). By convention, this is taken as amperes per of surface area, (A/dm^2 or A/ft^2), of both sides of the electro cleaned part. However, the primary current distribution, which is dependent on geometry of the parts, and, consequently working CD is not uniform, tending to be higher at edges and lower in recesses. In accordance with Faradays Law, at given time, the higher the CD, the greater is the evolution of gaseous hydrogen or oxygen, metal dissolution, and cleaning.

There is a point diminishing returns, as at very high current densities, damaging dissolution (etching) and oxidation (tarnishing) effects become more prominent.

Often treated as empirical and non-scientific art, in many plating plants, effort is not made to calculate the actual electro cleaning current density. These instances are especially true where parts are of irregular shape or vary from batch to batch. Still, practitioners are more content to control the voltage and ignore the amperage, considering that, with a constant resistance, one is proportional to the other, according to Ohm's Law : $E=I \times R$. This is acceptable, as long as the resistance is kept constant. It should be, however kept in mind that resistance depends on anode/cathode distance, type of the electrocleaner, its concentration, temperature and the type and the condition (e.g., passivity) of counter electrode. Electrocleaning is usually carried out at four to nine volts. If only low voltages are available, resistance of the electrocleaner can be too great for the DC power supply output to provide adequate CD, and electrocleaning can be marginal. A cleaner of higher conductivity should be used (e.g. potassium based) and the electrocleaning system examined for poor contacts or other electrical problems.

Monovalent ions such as potassium (K^{1+}), sodium (Na^{1+}), chloride, (Cl^{1-}), or hydroxyl (OH^{1-}), are more mobile than polyvalent ions, such as orthophosphate (PO_4^{3-}). The hydroxyl ion is especially mobile, so that the strong alkalis, e.g., potassium hydroxide or sodium hydroxide are efficient current carriers and are present in high proportions in "high conductivity" electro cleaners. These ions are also more mobile at higher temperatures, which is for this reason favored in electrocleaning as well as for enhanced detergency of the surfactant system that is incorporated in the electrocleaner formulation.

The relative effects of conductivity of the electro cleaner on cleaning have been assessed only qualitatively. The difference between a "high conductivity" and "low conductivity" electrocleaner might be 10 to 25% of the total resistance. Other factors such as condition of the contacts on the rack or on the bus bars, variations in total surface area, shape of the parts as they influence current distribution, or surface film on the opposing electrode may be equally significant. Resistivities of an basic alkaline electrocleaner and some common plating baths are given in Table 6.

Table 6. Resistivity of Alkaline Electrocleaner vs. Common Plating Baths

Bath composition	*Concentration*[a]	*Resistivity*[b]
Alkaline Electrocleaner:		
-Sodium carbonate	30	19.0
-Trisodium phosphate	15	
-Sodium hydroxide	8	
Watts Nickel Bath:	240	19.5

-nickel sulfate	45	
-nickel chloride	30	
-boric acid	0.23	
-sulfuric acid		
Chromium Bath:	250	2.0
-chromium oxide	2.5	
-sulfuric acid		
Na-Cyanide Copper Bath[c]:	120	6.8
-copper cyanide	135	
-sodium cyanide	30	
-sodium carbonate		
Acid Copper Bath:	200	5.6
-copper sulfate	75	
-sulfuric acid		
a. In g/l; b. In Ω-cm @ 25°C ; c. High efficiency bath.		

viii. *Chromium Contaminations*

After chromium plating, the chromium metal deposited on the racks is normally stripped, in the separate tank, before the same racks are loaded with the parts and send again through the line. If this is not done, or if done incompletely, the chromium is dissolved in the cleaner, in the hexavalent state (Cr^{6+}). Moreover, the anodic cleaner is often used as a mean of stripping chromium from the racks, and loading the electrocleaner with unwanted Cr^{6+}. Another source of chromium contamination of the electrocleaner is the chromic acid, from the chromium plating tank that is trapped in cracks or holes of improperly maintained plating racks.

The effects of "chromium contamination" are often argued. It is quite likely that effects are minimal in the anodic cleaning of steel, but quite significant in cathodic cleaning of steel, where surface films may form which prevents good adhesion of electroplate. It is considered that the greatest effect of Cr^{6+} contamination is the possibility of drag-over to the copper or nickel plating bath, where chromium is very detrimental. Obviously, this is dependent on effective rinsing and can be avoided.

Hexavalent chromium can be reduced to the trivalent state, in which form it appears to be less harmful. This is done by the addition of small amounts of reducing agents e.g., 0.2 to 0.4 % (~ 0.5-1 oz/gal), of sodium bisulfite ($NaHSO_3$), hydrosulfite ($Na_2S_2O_4$), or metabisulfite ($Na_2S_2O_5$). For emergencies, sugar can be used, just like in old times. This effect is a transient one, as the reducing power of the sulfites is eventually lost and the chromium reoxidizes at the anode. Eventually, excessive quantities of reducing agent are required and it is cheaper to replace the bath.

It is not good practice to depend upon the electrocleaner to provide all the required cleaning. Rather, it is to be considered as a safety factor, and certainly, less trouble is experienced when an electrocleaning stage is present. If it becomes contaminated, on the other hand, it can become dangerous because it is too close to the electroplating bath and particularly if there is no sufficient rinsing between the electrocleaning and plating stages.

ix. *Maintenance and Operation of Electrocleaning Equipment*[43]. Electrocleaner tank configuration is probably least considered when designing of any plating line, because of the large operating window. Corrugated or mesh steel can be used as anodes or cathodes to provide optimum surface area and solution circulation. They should be positioned in such way as to be easily accessed for periodic inspection and cleaning. Periodic cleaning of the anode/cathode is necessary to remove plated-on smut, oxides, and other charged particles. Using the tank as the anode or cathode is not recommended, because the current distribution is fixed and little control is obtained. This leads to uneven current distribution and a source for stray currents[40]. Many electrocleaning problems, such as under- and over-cleaning, have been traced to such a practice.

Polypropylene or lined tanks are recommended for alkaline electrocleaners fitted with steel, stainless steel, or Teflon heaters. Recirculating pumps are recommended to prevent stratification and ensure overall homogeneity. It should be noted that the solution inlet and outlet must be located at two opposite diagonal top and bottom corners of the tank for efficient solution movement. Various methods of solution filtration can also be incorporated into the electro cleaning system.

D. SPRAY CLEANING

Spray cleaning is a powerful, simple and effective cleaning method and it should be used whenever it is possible[44-45]. Pressure from spray nozzles is adding mechanical energy to thermal energy given by heated spray chemicals and together with chemical energy supplied by chemical action of spray cleaner ingredients makes one effective combination. In general, it is highly effective on any surface that it can be “seen” directly by spray[46]. Different effects can be achieved by changing the pressure of the spray, spray pattern and the volume of the sprayed cleaner. The physical effect as provided by spray cleaning can enable one cleaner to perform many jobs under a wide variety of circumstances. An efficient spray washer makes possible the use of cleaners which have desirable features of good rinsing and scale prevention characteristics, even though their soil removal ability might be less if used in soak cleaning. In fact, it is sometimes possible to gain all the advantages inherent in nonsilicated sequestering type cleaners in spite of poor oil removal properties.

The spray washer is usually located after the soak cleaning operation and before the electro cleaner. In addition to the influence of cleaner formulation (light duty, mildly alkaline with low foam wetting agents) the following design details should be considered:

a. Duration of time and the length of spraying washer. This is dictated by production requirements, optimum cleaning time and line speed.

b. Spray-jet angles, spacing and patterns for uniform coverage of work.

c. Size (caliber) of nozzle selected according to distance from nozzle to work surface and pump specification, selected on delivering the required volume of sprayed solution.

d. Temperature and concentration of the cleaner.

e. Filtration for preventing clogging of the nozzles.

f. Solution reservoir of sufficient volume to fill the supply lines to the jets, without starving the pump.

g. Control of overspray from the ricochet from the walls and from the parts.

On the down side, spraying liquid is relatively inefficient way to deliver mechanical energy to the cleaning object, since only a portion of energy is directly impinging the parts that needs cleaning. In addition, atomized liquid evaporates rapidly, requiring the frequent water additions as well the considerable amount of heat is needed to maintain the required cleaning temperature. Spray cleaners are used at about 4-16 gr/l at 68-74 ^{0}C with spray pressure from 0.7-3.5 kg/cm^2. Formulations are similar to soak cleaners, except that wetting agents are of a low foaming type.

E. ULTRASONIC CLEANING

Sound to nearly all of us, is anything we hear, while to the physicist is a form of vibrational energy. Most of us also can remember the fascinating phenomenon of the great singer Caruso shattering the wine glass with his voice. The range of sounds audible to the human ear is from 20 to about 20000 vibrations /sec. This is sonic sound. Around and above these frequencies, it is called ultrasound. Ultrasonic is a branch of acoustics that deals with mechanical sound waves at all frequencies above the audible range.

Ultrasonic cleaning functions because of changes in pressure and temperature that occur within vapor bubbles that implode[47]. There are constantly changing negative and positive pressures, which cause the simultaneous formation and implosion of thousands of minute vapor bubbles. This is termed *cavitation*. It is the formation and bursting of these vapor pockets with their fantastic pressures and temperatures (approximately 10,000 PSI and 20,000^{o}F) that does the cleaning. The sound waves are simply the mechanical means to achieve cavitation. It is important to have sufficient power to generate cavitation. Transducers must be located properly and close enough to the parts to be cleaned which minimize energy loss through the solution.

Ultrasonic cleaning generates a number of specific advantages for the electroplater. Since it is based on sound, it is omni directional.

Ultrasonic cleaning can be of alkaline, solvent, acidic or detergent base (neutral) nature. Effective cleaning action occurs anywhere that cleaning chemistry and ultrasound penetrates e.g., crack, pores, blind holes, etc. Maximizing the ultrasonic cleaning process was expertly treated by *Fuchs*[48-49].

The basic components of an ultrasonic cleaning system consists of a tank for the cleaner, a transducer which converts electrical energy into mechanical (sound) energy, and a source of high frequency alternating current (a generator that changes 60 cycles/second AC into high frequency, A-C) [44,48-53]. Maximum cleaning efficiency is obtainable for the different temperatures for different cleaning media. Another interesting fact is that dilute detergent based solutions are more effective than concentrated ones under identical conditions when sonic energy is utilized. The cavitations produced by ultrasound are well documented in the practice by their ability to drive the packed dirt from deep or blind holes. This sound approach attracted a number of progressive finishers. The cost of the necessary equipment will limit adoption of this method in many cases, especially when large parts are being processed. Nevertheless, to our knowledge, it is the best approach so far suggested.

F. SOLVENT CLEANING & VAPOR DEGREASING

The organic solvents used for cleaning applications are the non-flammable chlorinated hydrocarbons: trichloroethylene, (Trichlor), perchloroethylene, (Perchlor) and 1,1,1 trichloroethane (Ethyl chloroform)[54-56]. Most organic solvents are considered unacceptable for reasons of toxicity, flammability, effectiveness as ultrasonic mediums, or ease of recovery. In Table 7 are listed required solvent properties.

Table 7. Required Solvent Properties

1. Effective cleaner for variety of organic soils.
2. Noncorrosive.
3. Nonflammable.
4. Low toxicity.
5. Mild or moderate odor.
6. Dries on ambient temperature.
7. Leaves no bondable surface.
8. Leaves no compounds with ODP, halogenated compounds, water, ketones, aromatics or any of the 189 compounds listed by the US Clean Air Act as Hazardous Air Pollutant.

Unlike aqueous cleaners, the solvent cleaners function by dissolving soil: oil, grease, wax, asphaltic materials, resins and gums. They are used for hard surface cleaning of all metals, glass and certain plastics. Since these solvents are also relatively toxic and possess rapid evaporation rates (Table 8) when they are used in vapor degreasing equipment, the inhibited or stabilized forms are used. This is because these may be recovered by distillation and automatic control of these factors must be exercised.

Table 8. Physical Properties of Vapor Decreasing Solvents

Solvent	Boiling Range (^{0}F)	Surface Tension (dynes/cm)	Evaporation Rate[a] (CCl_4=100)	Solvency[b] (cc)	Toxicity[c] TLV, (ppm)	Flash Point[d]
Perchloroethylene $Cl_2C= CCl_2$	250-254	32.3	39	90	100	None
Trichloroethylene $HClC= CCl_2$	188-190	28	84	130	100	None
1,1,1Trichloroethane $H_3C- CCl_3$	161-165	33.6	100	124	350	None
Trifluoro trichloroethane CCl_2FCClF_2	118	19.6	170	31	1000	none

Note: a. Evaporation Rate is relative value. A low rate, e.g., perchlor (=39) indicates that it will evaporate 39/1000=0.39 times as fast as CCl_4.

b. Kauri- Butanol Value; it is a measure of the solvent power (ASTM D1133).

c. TLV= Threshold Limit Value. This is maximum allowable concentration of solvent vapor, at work place per million parts of air; the higher the number, the less toxic the material. d. Tag Closed Cup

These solvents may be used however, in properly designed degreasing tanks, as a last resort either for temperature sensitive applications or for those applications where particulate matter is the major contaminant. In the event that removal of solvent soluble residue is also involved, the contaminated solvent may be reclaimed by distillation in an auxiliary still. Because of its low toxicity in comparison to Trichlor or Perchlor, ethyl chloroform ($H_3C- CCl_3$) is commonly selected for solvent cleaning in non-vapor degreasing applications.

Although one must recognize the chemical activity of a metal in the selection of a cleaning procedure, this factor is virtually non-existent in solvent vapor degreasing, since neither etching nor staining of the part will be experienced. Thus, when other factors are compatible to this method of cleaning, solvent vapor degreasing is a natural choice in cleaning a variety of materials. Neither the shape nor the fragility of a part is considering to be a governing factor in vapor degreasing since the parts may be cleaned thoroughly without being subjected to a mechanical action. This method will realize good penetration even in the deepest recess. Where the soil is heavy or the part is so light as to limit the amount of flushing by vapors, immersion and/or spraying with liquid solvent can be performed within a degreasing unit prior to the vapor rinse. Since vapor degreasing may be performed on an automated basis, it is frequently preferred when high productivity is involved.

The operation that is to follow the cleaning step is also a selection factor. Thus, vapor degreasing is ideally suited to the cleaning of work prior to inspection or subsequent processing where the work is best handled dry. Where the work is to be wetted in the next operation, i.e., part will be plated, vapor degreasing is frequently used to remove soil economically and to minimize contamination of subsequent treating solutions.

The normal cleaning sequence used in vapor degreasing consists of vapor clean, plus vapor rinse and dry. The initial vapor cleaning treatment is conducted in the vapor zone over the boiling sump. It offers the advantage of elevated temperature melting and dissolving actions plus the beneficial concentration of gross contaminants in one section of the degreaser.

Cleaning is next conducted in continuously distilled solvent for the final removal of greases, oils and particulate matter. Removal of particulate matter from the solvent is effected by either intermittent or continuous filtration. The temperature in the sump is maintained thermally well below the boiling temperature of the solvent to effect a second condensation of pure solvent on the work piece upon its withdrawal from the degreaser. For this treatment, the part is suspended in the hot vapor until it attains the vapor temperature, thus emerging from the degreaser as a clean dry part. Very slow exit speed, 3 ft/min, must be used to prevent vapor from escaping into air, and to ensure that no liquid solvent remains on the part.

The selection of a vapor degreasing solvent is made based on the physical properties of the soil, the solvent (Table 6) and the substrates involved. For example, Perchlor is specifically used where high temperature solvency is required as in the removal of high melting point waxes. Trichlor on the other hand is the more popular of the two solvents because it offers greater solvency at a lower operating temperature; hence, a lower operating cost. For certain temperature sensitive operations, the use of ethyl chloroform may be justified because of its lower boiling temperature (74^0C/165^{o}F).

Where selective solvency is a requirement, as in the cleaning of assembled devices containing plastic or painted components, the use of trichloro-trifluoroethane is recommended. Its low boiling point (48^0C/118^{o}F), low Kauri Butanol value (31) low surface tension (19.6 dynes/cm) and low toxicity (1000 ppm) combine to fulfill a need not met by the chlorinated solvents. Regardless of the solvent selected, none will remove water-soluble contaminants. These must be removed in a solvent emulsion or in an aqueous cleaning treatment before or after vapor degreasing.

The popularity of vapor degreasing originates from the rapid solvent cleaning action achieved and the fact that subsequent drying operations are eliminated. The latter is particularly important for intricately shaped parts where the presence of residual water cannot be tolerated. Vapor degreasing by itself does not usually insure that the part is sufficiently clean for the final electroplating step.

G. EMULSIFIABLE SOLVENTS & EMULSION CLEANERS[57, 58]

There appears to be some reluctance toward the use of emulsion-type cleaners, as compared to the more widely accepted methods of solvent cleaning, vapor degreasing, and alkaline cleaning procedures. This may be due to a lack of knowledge of the characteristics displayed by this class of cleaning materials and the advantages gained, particularly when it is used as a pre-cleaner in the removal of stubborn contaminants.

There are two distinct types of emulsion cleaners. One is the stable emulsion that is a single-phase solution type, whereas, the other is termed a diphase emulsion cleaner. The latter type, as its name implies, is a two phase solution type in which neither phase is completely or permanently emulsified in the other. Within the class of stable emulsion cleaners, if we are to be technically correct, a further division may be made in that both, emulsifiable solvent and emulsion cleaners are available. Both of these stable emulsion types are frequently considered synonymous; however, there is a difference, even though it is very slight. Basically, both are of the same formulation, but an emulsion cleaner is one that is diluted with water, whereas, the emulsifiable solvent cleaner is used without the addition of water. In general, the emulsifiable solvent and the emulsion cleaner will perform in a similar manner. However, the effectiveness of the cleaner is reduced in proportion to the water content of the mixture.

i. Emulsion cleaners contain water, an emulsifier and a petroleum hydrocarbon, typically kerosene. The commercial products contain the solvent and emulsifier who is added to water in varying proportions prior to use. Emulsifier is usually a higher alcohol or wetting agent. Additional effectiveness may be obtained by addition of surface active agent. The normal dilution is one part concentrate to ten parts water. When used as an ultrasonic medium, the tap water makeup is first thoroughly degassed. The concentrate is then added to effect the desired dilution. The emulsion cleaners are used at an elevated temperature of 50-70°C (~120-160°F) and are preferably followed by a hot water rinse. These cleaners function well as ultrasonic mediums yielding bath uniformity difficult to achieve in either aqueous or solvent media alone.

Emulsion cleaners are formulated to combine the functions of both aqueous cleaners and solvent cleaners to yield a cleaner that possesses both detergency and solvency powers. For this reason, they are very well suited for the removal of gross contaminants that are otherwise difficult to remove in a single cleaning treatment. The cleaner residue from an emulsion cleaner is a thin oily residue that offers temporary rust protection to the parts after this cleaning operation. The presence of this oily residue is a distinct advantage for in-progress (intermediate) cleaning, but its presence serves to prohibit the use of emulsion cleaners for final cleaning operations.

ii. In the emulsifiable solvent cleaning, unlike with the emulsion cleaners, no water is involved. Water does enter into the cleaning operation. However, it is used in the subsequent pressure rinsing operation, which serves to emulsify and remove both the loosened soil and the emulsifiable solvent. These effects are made possible by virtue of the emulsifiable solvent formulation.

The commercial emulsifiable solvents may be used in the undiluted condition or diluted with the appropriate type of hydrocarbon solvent prior to use. Since the resultant solvent assumes the characteristics of the solvent base, both flammability and/or toxicity must be considered. Those based on petroleum hydrocarbons must be treated with caution when used as ultrasonic cleaners, as the flash points of the emulsifiable solvent is being the limiting factor.

The use of emulsifiable solvents based on the non-flammable chlorinated solvents is more acceptable for ultrasonic applications, since these may be thermally degassed prior to use as an ultrasonic medium without the danger of fire. The same considerations in respect to toxicity apply to the emulsifiable solvents as for the chlorinated hydrocarbon solvents.

When cleaning prior to plating, alkaline cleaning should always be used after emulsion cleaning to remove thin oil film left by the emulsion.

H. ACID CLEANING[59]

Certain soils, especially those that are inorganic, either are removed in acid cleaners or are dissolved in the acids, or both. As distinct from pickling and derusting, the main emphasis is on cleaning effect, and solutions are therefore more mildly acidic. It is not the object of acid cleaners to remove heavy grease or oil deposits, such as removed by alkaline solutions or solvents, but rather to remove light grease, oxide films and similar inorganic films. They are generally used in final or near final preparation of metals prior to plating. A large number of compositions are available and can be classified in general terms as:

γ Mineral (inorganic) acids based, e.g. hydrochloric, sulphuric, phosphoric.

γ Solid acids, related to the sulfuric acid, e.g., Na- bisulfate, sulfamic acid; Ferric sulfate or chloride, monosodium phosphate, ammonium persulfate, and bifluoride salts.

γ Organic acids, e.g., gluconic, citric, tartaric, lactic, EDTA, acetic, oxalic, hydroxiacetic among others.

The acid cleaners will have one or more of the above acids or their salts, appropriate low molecular weight acid-stable anionic surfactant, e.g., ethoxylated nonyl phenol, water soluble organic solvent, e.g., butyl cellosolve, ethylene glycol monobutyl ether (EGBE), defoaming agents and in some applications a corrosion inhibitor. In some cases, chromic acid based solutions are used to clean iron and stainless steel (SS). For SS, a solution containing 60 gr/l of CrO_3 +60 gr/l of H_2SO_4 +60 gr/l of HCl is used at room temperature. Another solution for SS is HNO_3 (10-50 vol. %) + HF (1-3 vol. %).

The advantages of using organic acids vs. mineral acids are numerous. Most of these acids are non-volatile, have low corrosivity, safer to handle and can sequester dissolved metal.

Typical operating conditions in Table 9 and composition of acid cleaners for cleaning of ferrous metals is presented in Table 10.

Table 9. Typical Operating Conditions for Acid Cleaners for Ferrous Metals

Type of acid cleaner	Concentration		Temperature		Current density
	g/l	oz/gl	^{0}C	^{0}F	A/dm^2 / A/ft^2
Soak	60-120	8-16	70	160	--
Spray	15-30	2-4	60	140	--
Barrel	60-120	8-16	Room	Room	--
Electrolytic	60-120	8-16	21	70	10/100

Table 10. Basic Composition of Acid Cleaners for Cleaning of Ferrous Metals

Constituent [%]	Soak		Spray		Barrel	Electro
Phosphoric acid, H_3PO_3	70.0	--	70.0	--	--	--
Na-acid pyrophosphate, $Na_2H_2PO_7$	--	16.9		15.4	16.9	--
Na-bisulphate, $NaHSO_4$	--	80.0	--	80.0	79.0	--
Sulfuric Acid, H_2SO_4	--	--	--	--	--	55-70
Nonionic wetting agent^{a,b}	5.0	3.0	2.4	2.5	1.0	--
Anionic wetting agent^c	0.1^c	0.1^c	0.1^c	0.1^c	0.1^c	0.1^c
Low foaming wetting agent^d	--	--	2.5	2.5	3.0	1-2
Corrosion inhibitor	a/n^e	a/n^e	a/n^e	a/n^e	a/n^e	a/n^e
Water	24.9^f	--	25^f	--	--	balance

a. Triton X-100 or equivalent. b. EGBE (ethylene glycol monobutyl ether) is sometimes used;
c. Zonyl-A; d. Triton DF-12 or equivalent; e. as needed; f. Before dilution

Acid cleaners often suffer from rapid soil loading, particularly metal loading, that often requires decanting and dumping of the cleaner solution. This in turn leads to relatively high cost as compared to alkaline cleaning.

I. ACID DIPPING, ACTIVATION AND PICKLING

i. General. Acid treatments, prior to the plating step may be classified into three categories mostly used: acid dipping, activation and pickling. Acid descaling and bright dipping are out of the scope of this paper. Diluted mineral acid is usually used , complemented with additives. However, mixtures of acids or acid salts are utilized to improve their reactions with metal. Their actions are increased by using higher acid concentration, temperature and agitation. They decrease in rate as solution becomes more concentrated in dissolved metal.

Surfactants and wetting agents are added to: a) reduce surface tension and emulsify residual oils, b) and provide a thin foam blanket to prevent the corrosive effects of mists, c) provide more uniform acid action, d) reduce dragout losses, and e) as dispersants they can be added to prevent redeposition of removed soils.

All acid solutions should be selected to meet the following qualifications:

γ The metal surface should not be disturbed any more than desired.

γ The metal salt formed from the reaction between the metal and the acid must be water-soluble.

To illustrate the later point, sulfuric acid would not be suitable for preparing lead or leaded brass for electroplating. This is due to the formation of insoluble lead sulfate, which would form a non-adherent film between the basis metal and the electrodeposited metal. Sulfamic acid, citric acid or fluoroboric acid can be used.

When parts are acid treated, in order to minimize or prevent attack on the basis metal, acid inhibitors should be added to the acid bath. They function by suppressing the dissolution action of acid on basis metal. They also reduce hydrogen evolution and the likelihood of hydrogen embrittlement. They should be stable and not prone or susceptible to forming difficult to remove films. They reduce the roughening and pitting due to the excessive metal dissolution. This is extremely important to the parts that must maintain close tolerances on dimensions. This usually applies to the machined parts or on the parts that must retain a smooth, low micro-inch (RMS) finish. Inhibitors, consisting of various chemical compounds, can be quite specific to individual mineral acids. They also prevent the immersion deposits in aged and contaminated baths.

ii. Acid Dips. This is the last step prior to the plating sequence. This simple step has three purposes: a) to remove any residual alkalinity left on the cleaned and rinsed metal surface, b) to remove any oxide or superficial tarnish films formed due to the exposure to the cleaners or to the air during previous rinsing or during the transfer time, and c) provide active and preferably micro etched surface for assuring good adherent electrodeposits.

iii. Activation. Activation acid dipping is used to not only to neutralize the alkaline film and to dissolve any light oxide, scale and other acid soluble soils developed in the final cleaning, but also to activate the metal surface prone to form tenacious oxides, e.g., nickel or stainless steel. In immersion treatments, more concentrated acids, acid mixtures or acid salts are usually used with wetting agent. For difficult metals, activators are used, e.g., fluorides, persulfates, or proprietaries. For electro activation, the work is made cathodic. The evolution of hydrogen at the surface of the metal provides gas scrubbing, which increases the rate of oxide removal. The reducing action of hydrogen, decrease or eliminates passivity, e.g., on stainless steel or buffed nickel, which is to be electroplated.

iv. Pickling. Pickling is used to remove scale and oxides, usually resulting from heat-treatment, forging or casting operations. It can be performed as immersion dipping or cathodically. Steel sheets from which rolling scale is to be removed are normally immersed in warm sulfuric acid (H_2SO_4). Brass articles are generally treated in a mixture of nitric (HNO_3) and H_2SO_4 acids (except leaded brass), while a number of special solutions are used for various alloys [2,59,60]. When a metal that possess an oxide layer on the surface is dipped into an acid, the acid will first attack the oxide, initially producing metal salt and water. Next, however, the acid may attack the base metal, producing a metal salt and liberating hydrogen, which will come to the surface as bubbles. Since the goal of pickling is simply to remove the oxide scale, inhibitors are added. With them present, the pickling time is usually increased, since dissolution rate of oxide as well of metal is decreased (albeit at slower rate). Their principal purpose is: a) to slow down attack on the metal by making it difficult for the hydrogen to be evolved from the surface, b) to reduce roughening and pitting due to excessive metal dissolution.

For pickling steel, cold hydrochloric acid (HCl) or warm sulfuric acid is typically used Phosphoric is outstanding, albeit more expensive, pickling acid as the resulting iron phosphate produced has rust preventative qualities. For pickling (etching) aluminum an alkali solution may be used. Tribasic sodium phosphate, Na_3PO_4, is suitable for light pickling and caustic soda with gluconate is added to prevent early precipitation, for deep etching (roughening). The parts may then be dipped in diluted HNO_3, (1:3) to remove any smut. Cast aluminum is generally acid dipped in a hydrofluoric (HF) acid, mixture of nitric and HF acids, or in solution of fluorides salts such as ammonium bifluoride, in order to remove silicon. Copper and brass are treated with by H_2SO_4/sodium dichromate or H_2SO_4/HNO_3 acid mixtures. Stainless steel is treated with an acid dip containing HCl or HF acid and/or ferric sulfate.

Electrolytic acid pickling is similar to electrocleaning. However the effect of the current is much more aggressive and should be checked in the laboratory before it is used on the production line. This method is most frequently beneficial if used for activation of nickel after stripping chromium for chromium replating.

Ether cathodic, anodic or periodic reverse DC current may be used to aid activation, increase scale removal, remove protruding metal slivers, or smoothen ("level") rough surfaces. Anodic (reverse) current is used to remove protruding metal slivers and to smoothen rough surfaces by electropolishing action. Highly concentrated acids are generally used for this application.

J. WATER RINSING

i. Introduction. Rinsing is often the most overlooked aspect of surface preparation of metals. Long ago, in 1928 *C.F. Nixon*[61], presented a paper on drag-out showing that the substantial amount of valuable plating salts can be lost through this method, if rinsing is inadequate. Dragout losses and rinsing methods were advanced due to the studies by pioneer in this field, Dr. Joseph B. Kushner, starting in 1935[62] and lasting through the next few decades[63,64]. Other practicing scientist, *J. B. Mohler*, contributed numerous papers on this sbject[65,66]. *Mooney*[67] defined rinsing as removal of a harmful clinging films of process solution from a work piece by substituting an innocuous film of water in its place.

ii. Principles. This vital step is necessary to: a. stop actions of chemicals from the cleaning solution, b. prevent contamination of the subsequent process, and c. prevent staining of the parts. Clearly, avoidance of excessive drag-in of alkalis from cleaning tanks into the rinse system, prior to plating must be implemented. Adequate part drainage above the cleaner tank prior to transfer to the rinsing operation is thus the first requisite for successful rinsing, and it was early recognized by *Gustaf Soderberg*[68]. He provided some experimental data and calculations on the amount of alkaline cleaner solution dragged into a rinse tank (Table 11).

Table 11. Dragout Volumes From Alkaline Cleaner

Type of Parts	gal/1000 ft^2
Vertical Parts-well drained	0.4
Vertical Parts-poorly drained	2.0
Vertical Parts-very poorly drained	4.0
Horizontal Parts-well drained	0.8
Horizontal Parts- very poorly drained	10.0
Cup shaped parts, very poorly drained	8-24+

Obviously, cup shaped parts and other intricately shaped parts with blind holes and cavities can drag out significant volumes of solution. The time of drainage is important, and Soderberg recommended slow withdrawal and rapid transfer rates.

The basic rinsing variables**[64]**, which influence the amount of cleaner residue remaining on the cleaned part, are: the number of rinses, agitation, and type of rinse system and rinse temperature. These factors, in turn, determine the overflow rate required for an immersion rinsing operation and total fresh water consumption. Multiple rinses are more efficient than single rinses, with the optimum, pragmatic balance being three rinses. Where practical, as a bare minimum, at least two running rinses arranged in a counter-current or cascade fashion are recommended, particularly for the difficult-to rinse caustic-containing heavy-duty alkaline cleaners**[69]**. Self evident, but not universally followed fact is that water consumption will be drastically reduced by cascading the final rinse into the previous rinse and that rinse to the previous one. Maximum efficiency of rinsing tanks design and accompanying controls is not difficult to achieve, as the principles involved are well understood.

For thorough rinsing of silicated cleaner residues and initial warm water rinse (50-66^{0}C/120 – 150^{o}F) offers the advantage of higher solubility of the cleaner residue in that way minimizing possible "silicate bake on" in a subsequent drying operation. In those cases where silicate bake on may occur between cleaning and rinsing due to long transfer intervals, a fogging type spray during transfer is definitely needed**.**

Rinsing can be effective only if it reaches a part. Part orientation, loading, and rinse flow dynamics are important but often-overlooked considerations. For efficient rinsing, agitation is essential. Air agitation, sparging, ultrasonic, forced pumping, cathode rod movements are commonly used. In those cases where part geometry permits, an alternate hot-cold spray rinse is an efficient method of rinsing. For highly configured parts that have small crevices or blind holes, ultrasonic agitation is recommended to expedite the exchange of water for alkali in remote recesses.

iii. Spray rinsing. Spray rinsing is what the name imply, i.e. rinsing with spray or fog of water with sufficient force to remove all or most of the carry-overs from preceding tanks. This is a valuable addition to overall rinsing operation, since, in effect, it is increasing the number or counter flowing rinsing stations. Sprays may be positioned to rinse racked parts as they leave any rinse station or as they emerge from the plating or processing tank. Each set of sprays should be supplied with water pumped from the following rinse tank. There are two advantages of spraying over the final rinse tank: city water line pressure eliminates the need for a pump, and any over spray beyond the rinse tank is free of dragout. Pumps or city water pressure should be activated only when processed parts are actually in the spray zone. This will conserve water and allow the use of higher flow rate nozzles[70]. Spray rinses are most efficient when they are turned of or on automatically when entering into and leaving the rinsing station.

iv. *Rinse aids*. Obviously, good rinsing involves intimate contact between the work surface and the rinse water. The use of a designated, surface tension reducing wetting agent in the rinse water which promotes intimate contact with and displacement of the concentrated solution film, will greatly improve the rinsing qualities of ordinary water. In addition, if air is being used for rinse tank agitation, the wetting agent will increase the number of air bubbles formed to further aid the process. Since only about 0.02% (or less) of the appropriate wetting agents are needed to do such a job, a simple automatic liquid feeder can be used to meter the wetting agent into the rinse tank. It is quite economical to use such a scheme, particularly if three or more rinse tanks in series are used. For example, if with a three rinse system uses 0.2 gpm of water, it means that the amount of wetting agent used = 0.2 gl/min X 60 min/hr X 8.3 gl/lb X 16 oz/ lb x 0.02 lb/100 lb = 0.32 oz/hr, of wetting agent or about 2.56 oz (~ 72 ml) per eight hour day, a negligible investment.

K. FILTRATION

Filtration, as practiced in the plating industry is a chemical engineering operation, which has been simplified to the point where it is considered to be a maintenance function. However, modern quality control of plating systems calls for engineered use of filtration as a control factor. Although not outstandingly effective in dealing with high levels of oil, filtration will remove fine suspended particulates that tend to buildup in cleaning baths and can ultimately redeposit on the parts being cleaned. Filtration of the cleaners is gaining in popularity with the aim of prolonging the bath life between dumps. Several filtration techniques have been proposed, ranging from simple bag filtration to complete systems of oil skimmers, coalescers, microfiltration[71,72] and ultra filtration[73-74]. Since the cost of such systems varies appreciably, a feasibility study must be undertaken before adopting a particular system. In general, however, it has been reported that any type of filtration does increase the bath life at least by 20% and up to 50% or more[75]. Factors to be considered in selecting a filter system are dirt load, flow rate, filter surface area, micron retention and frequency of filtration.

The dirt load should be the heaviest that will occur and filter media selected for particular loads and particle size. The coarsest possible cartridge should be used since it has, largest holding capacity, longer life, increased flow rate and is less expensive. In addition, with use, openings become smaller as large particles load the filter pores and pores become smaller, resulting in that smaller particles will be removed.

Flow rates refers to tank capacity. For example, 1000 GPH into a 500-gallon tank is two turnovers per hour. The flow carries solids to the filter and brings solutions in contact with cartridge. It is necessary and critical that filters have capacity corresponding with flow rate.

The frequency of filtration and purification for the average plating solution is once per hour. For the cleaning solutions, *Berg*[76-77] recommended at least twice per hour and up to 10 turnovers per hour. He emphasized that this turnover rate is to be the average, not the actual. For instance starting at 1000 GPH and reducing to 200 GPH would make the average about 600 GPH or only about one turnover per hour for a 500-gallon tank.

Depth type cartridges are frequently used, obtainable for removing particles from 100 to 1/2 micron size and of the materials comparable with the chemicals from cleaning solutions.

The selection of the proper filtration system, coupled with an effective method of oil removal, will prolong optimum life, and more uniform action of the cleaning bath.

L. LIQUID FORMULATIONS.

Liquid cleaners for both spray and soak applications have been around for many years. The use of liquid cleaners to replace powders has been gaining wider acceptance in the industry. They are formulated to economically provide all the performance criteria of the powders[43]. The advantages of liquid cleaners include the capability of automatic feeding tied to conductivity controllers. The automated system continually monitors the solution strength and makes additions on demand. Consequently, better bath control is achieved, eliminating wide swings in concentrations. As a consequence, liquid systems have substantially increased bath life in many installations.

Automatic recording capabilities of concentration and temperature can be achieved for statistical process control.

Tank additions of liquid concentrate eliminate the hazards associated with additions of alkaline powders to hot cleaner solutions.

M. BIOLOGICALLY ACTIVE CLEANERS.

Unique bacterias and enzimes[78-80] can help traditional surfactants to clean the parts. The baths with oil and greases is good habitat for oil-loving bacteria, as they appreciate organic soils as their meal. They can extend the bath life and significantly reduce the sludging of the bath.

N. LOW TEMPERATURE CLEANING.

The reduction in energy consumption achievable by low-temperature cleaning (LTC) is very attractive from the standpoints of reduced energy costs[81] and increased flexibility during an energy crisis.

While maintaining the temperature of a bath requires less energy than bringing a solution to its operating temperature, the energy reduction is very substantial at lower temperatures. On the other hand, LTC has limitations. The cleaner is more expensive and difficult to select for the following reasons:

1. A high concentration of surfactant is required, compared with conventional cleaners. Cleaning is improved rapidly as the concentration is increased—but only up to a point, after which the improvement in cleaning per unit of increase in concentration drops markedly. However, if LTC is adopted, we still may need to pay additional money for surfactant to achieve the desired degree of cleanliness, even at a lesser improvement per unit increase in surfactant.
2. More expensive surfactants may be needed, and a combinations of surfactants are required to obtain satisfactory cleaning and to overcome the loss of a "safety factor" available with high-temperature cleaning; greater attention must be devoted to maintaining the proper conditions (e.g., solution concentration and level of agitation) to compensate for the normally better cleaning achievable at higher temperatures.
3. Solvents may be required to reduce the viscosity of the soil so that detergency is improved. The amount of solvent that can be justified in a commercial bath is too limited to dissolve soil but can be very significant in modifying the properties of the soil so that it can be removed by action of the builders and wetting agents.

IV. TESTS & CONTROL METHODS FOR CLEANLINESS

The degree of cleaning required for the surface of a part is a function of, and dictated by, operations to follow cleaning[82].Test methods used to determine the cleanliness of a surface range from crude to highly sophisticated. Unfortunately, with few exceptions, these remain a research tool, rather than production tool. In actual practice, the cleaning process is in most cases, actually controlled by combination of visual water break and white glove tests plus solution analysis.

i. The Eye as Analytical Instrument

The easiest, quickest and most straightforward method for recognizing that something is incorrect with the cleaning process is by looking intently at the parts themselves. If cleaning is marginal or insufficient, it will be more often than not indicated by a change in the appearance of the surface of the part or worse, in the plated deposit. The human eye is a critical instrument. It can detect minute changes in color and appearance better perhaps than some very elaborate and expensive instruments. Unfortunately, however, in most cases Kushner's Third Law holds: *When you can see it, it's too late!* The secret is to be able to see it before it makes trouble and this is no mean secret. In addition, there are certain changes in the deposit that are not visible to the human eye. An example of this is an improper cleaning that acts to decrease adhesion of the deposit. The deposit will look just about the same as it did before when it is removed from the plating bath. However, it can be that found, later in the field that the parts are peeling as a result of this visually indiscernible change in the deposit. Nevertheless, the eye is the first line of defense, so the eye should be trained to note even the slightest changes in color or appearance.

ii. Water Break test

The water break test involves examination of a surface for the presence of a continuous water film that has “no water breaks.” The part will exhibit a surface that resembles the freshly waxed car after the rain. It is an indication that all organic soils are removed. The test is subject to possible misinterpretation due to the retained surface film from inadequate rinsing or presence of hydrophilic smuts with possible oil trapped under the smut. If a water-break-free film of water is present, it is indicative of the absence of hydrophobic surface contaminants. Oils, greases, and water-insoluble organic compounds would be examples of hydrophobic contaminants. The water break test does not confirm the presence or absence of hydrophilic particulate contaminants or oxides. The key for the test is to use fresh uncontaminated water. Wetting agents or rinse aids, used in final rinse may hide poor cleaning.

iii. White Glove test

The quick and simple, time honored white glove test is used to show the presence of inorganic soil removal and, to a certain extent, organic contaminants on a surface after cleaning. The part may be tested while still wet from rinsing or after drying. The surface of the part to be tested is wiped with a white glove, cotton swab, or towel tissue. The material used to wipe the surface is then examined for the presence of black, gray, or off-white residue or oil staining. If contaminants are found to be present, microscopic examination or advanced chemical or surface analysis can be performed on the part surface or the item used to wipe the surface to more precisely determine the origin and the nature of the contaminants.

iv. Pumice Scrub test

This is popular and useful test to determine and differentiate problems associated with cleaning or plating sequence. The part is removed from the after cleaning and scrubbed with a soft, wet bristle dipped in pumice. After thorough water rinsing cleaned part is returned on the rack and plated. If the part is brighter than others after plating is indication of insufficient cleaning. If there is no improvement after plating the problem is in all probability related to the plating sequence.

v. Other test methods

Sophisticated physical and chemical analytical methods can be applied to test for residual contaminants on surfaces that have been cleaned[6-28]. Samples of parts that have been cleaned and dried can be immersed in a turbulent solution of a solvent. The solvent can then be analyzed for organic contaminants and insoluble particulate matter.

vi. Control methods.

There is still not readily available, especially for the small and medium size plating facilities, a quick, simple and reliable method for the determination of when the useful "life" of the cleaner is approaching its end. In many plants, the "death" of the cleaner is first appreciated by a batch of rejects due to the insufficient cleaning. The procedures regarding the maintenance of the cleaners are still haphazard in many plants. The trouble is mainly to the difficulty in difficulty in analyzing proprietary compounded cleaners, especially as they age, and become loaded with carbonates, products of hydrolysis of complex phosphates, saponified oils, dissolved metal ions, etc. Methods for the routine quantitative control of cleaners are mostly semi-empirical, and analyses are often in terms of gram/liter or ounce/ gallon of the compounded cleaner rather than as the component chemicals. Some procedures are available from the vendors or in the open literature[83-88]. A single endpoint or a double end-point titration is usually made to estimate the effective alkalinity. The cleaner is titrated with a standard, usually 1 N acid. " Free" alkalinity is titrated with an appropriate indicator, e.g. Methyl Orange or Sulfoorange to about pH 10.5-11 for orange to yellow color change. "Total" alkalinity, which includes alkalinity contributed by all the alkaline chemical constituents of the cleaner, is titrated to a ph of 8.6 - 9.0 with phenolphthalein end point (pink to colorless). Table 12 gives the pH and alkalinities for all common, commercial grade alkaline components[88].

Table 12. pH and Alkalinity of Alkaline Builders

Chemicals (Commercial Grade)	*pH* 0.1 %	0.5 %	1.0 %	*Alkalinity*[a] PO[b]	MO[c]
Sodium hydroxide,	12.0	12.7	13.3	122	122
Sodium orthosilicate	11.8	12.6	13.0	100	100
Sodium sesquisilicate	11.6	12.3	12.6	58	60
Sodium metasilicate	11.3	12.0	12.5	45	48
Trisodium orthophosphate.	11.5	11.8	11.8	18	35
Sodium carbonate	10.7	11.3	11.3	56	95
Tetrasodium pyrophosphate	10.0	10.1	10.4	12	38
Sodium sequicarbonate	9.6	9.7	10.0	28	68
Sodium tripolyphosphate	9.1	9.0	9.5	----	----
Sodium tetraphosphate	8.5	8.4	8.5	----	----
Borax	8.5	8.7	9.2	20	28
Sodium bicarbonate	8.0	8.2	8.4	3	61
Sodium metaphosphate	6.5	6.2	6.9	----	----

a. As number of millieqivalents of acid required to bring 1L of 0.5 % solution to PO and MO end points; b. PO=phenolphthalein; c. MO= Methyl Orange

If sodium hydroxide, phosphates, and carbonates are present, these can be estimated with reasonable accuracy by titration to pH's 10.5, 8.5 and 4.2. If silicates or borates are present, then titration for available alkalinity may be practical, but are only approximate. As the effective concentration of wetting agent(s) is reduced since the oil is accumulated in the cleaning bath, it may be advisable to control this critical ingredient, even with an indirect, approximate method. A simple method with affordable equipment is to check the surface tension with stalagmometer. The number or drops or time needed to empty the instrument can be compared with the fresh cleaner and utilized as simple guide for the state of surfactant used. In any event, the chemicals that are present must be known or determined in order to make a complete analysis. For many cleaners it is necessary to resort to gravimetric analyses for P_2O_5, Na_2O, CO_2, and SiO_2. In addition, it may be necessary to analyze for borates and wetting agents, so that a complete chemical analysis becomes impractical for routine purposes.

An alternative for complete analytical control is to maintain the bath by a recommended method for technical control and to make occasional cleaner tests. This consists of a standard procedure for measuring the cleaning time for a panel reproducibly contaminated with a standard soil. Many methods of this type have been used to evaluate cleaners, but they have not been applied for control, since it is difficult to produce a standard soil that will represent the production cleaning problem.

A commercial cleaner is accepted by application to a particular production need. Thus, the real trial is in the processing line or, at least, on a pilot plant basis. Thus, the obvious answer given to our question becomes the practical answer. Technical analyses are still used rather than complete chemical analyses, in a majority of the plants.

V. THE FACTORS LIMITING THE USEFUL LIFE OF AQUEOUS CLEANERS

Among others, one of the puzzling intangibles of metal cleaning art is the subject of useful "life". Certainly, the first requirement of any metal cleaner is that it renders the surface both chemically and physically clean. The next requirement is longevity of acceptable performance before it must be replaced, and the final, obvious requirement is the total operating cost of the cleaner, including energy, reprocessing, maintenance, and waste disposal costs. The six main aspects responsible for changes occurring in cleaning solution, that will be further discussed, fall into two main categories: chemical changes and physical changes. The first two, saponification and carbonation, would be categorized as chemical effects, while the last four are physical effects. The seventh, indirect aspect is a proper maintenance.

1. Saponification. 2. Loss of free alkalinity- carbonation. 3. Soil load. 4. Drag-out. 5. Volume of solution. 6. Depletion of wetting agents. 7. Maintenance.

All plating practitioners are, or should be familiar with those seven fundamentals, wherever they are processing the metal surface for subsequent plating, anodizing, galvanizing, chromating, electropolishing, metal coloring or other finishing treatments.

1. Saponification. The saponification reaction is the basic mechanism of primary cleaning reaction. Any saponifiable or soap forming oils present on the work will chemically combine (react) with alkalis in the bath, usually the caustic soda, (NaOH) or caustic potash, (KOH), to form soaps (R-ONa) and glycerol ($C_3H_5(OH)_3$), according to the reaction:

$$(RO)_3C_3H_5 + 3\,NaOH \rightarrow 3\,R\text{-}ONa + C_3H_5(OH)_3$$

The saponification reaction is actually a neutralization of an organic acid with a base with the formation of a salt, which, in this case, is the soap. The result is partial loss of free alkali and a gain in the solution of the crude surface active agent, such as, e.g., Na-stearate, Na-oleate, Na-rosinate, or some other metallic soap depending on the saponifying material.

There is a profit and loss balance resulting from these chemical reactions. The loss in free caustic reduces the electrical conductivity, an important parameter in electrocleaning, which in turn reduces the gas evolution at any given voltage. A full effect of the reduction in free caustic, which particularly applies to anodic cleaning at high current densities, is the danger of anodic polarization. This is caused by insufficient sodium or potassium ions present to neutralize the acid radicals, such as silicates, phosphates, rosinates, etc. formed at the surface of the processed parts. The gain in soap formation, will promote cleaning to some extent except, obviously, if the soap content builds up too high, introducing gelatinous solutions and excessive foaming in electrocleaning baths. Saponification can cause a further problem in regions where hard water is used. This is due to the formation of insoluble calcium and magnesium soaps which deposit on the parts as a curd and which are extremely difficult to rinse off.

2. Carbonation. This second chemical change is also a simple acid-base neutralization. In this case, the weak acid is carbonic acid gas (carbon dioxide, CO_2), present in the air, which combines with the stronger alkalis, such as NaOH, KOH, silicates, and phosphates to form sodium carbonate (soda ash), or potassium carbonate. Even, though it makes only 0.035 % of the atmosphere[89], the large amount of air can be passed through the cleaner with, e.g., air agitation and neutralize the alkaline builders. Here again, the free caustic is the preferential victim of the reaction process, although other important ingredients, silicates and phosphates are also subject to conversion to carbonates. If an alkaline cleaner is allowed to stand for a prolonged period of time it will slowly absorb CO_2 and will eventually become excessively high in carbonate content. This is true even though the solution is not used to clean dirty work. It is seen then that, after long periods of shutdown, one cannot expect the solution to be in the same condition as it was prior to the shutdown.

Treating this as a profit and loss balance situation follows that there is no profit but all loss. While it is true that formed sodium or potassium carbonate in itself will exert some cleaning action, it is relatively inefficient. The electrical resistivity of e.g., sodium carbonate solution is four times that of caustic soda and here again there is a loss of current carrying capacity at a given voltage. Furthermore, sodium or potassium carbonates are a relatively poor emulsifiers and dispersing agents. Consequently, this property will suffer proportionally to the carbonation occurring in the solution. As a consequence of carbonation, there is a loss in electrical conductivity, emulsifiability and dispersability.

3. Soil Load. This important and often neglected aspect is a physical build-up of unsaponifiable oils and greases and a wide variety of solid soils incidental to buffing, handling and storage operations prior to the cleaning. As work is put through the cleaner solution, oils and greases are emulsified and distributed throughout the bath. Solid particles, such as abrasive grains, dust, dirt, metal chips, etc., either fall to the bottom if they are comparatively coarse particles or are suspended throughout the bath in a disperse condition.

The soil load probably limits the useful cleaner life before any of the other components reach their permissible limits. It is strictly a function of the amount and condition of the work put through the solution. It is almost impossible to correctly foresee how long the bath may be operational prior to replacing it.

In the case of the emulsified oils and greases, the older reasoning was that a cleaner of higher emulsifying power could disperse more of them, which would be an advantage. The newer opinion[57] is that a cleaner, which will separate the oils and greases but not emulsify them, gives better results. By skimming the accumulated oils from the surface of the solution with an overflow skimmer, the oil load in the solution is kept at a minimum and there is less danger of oil drag-out into the subsequent acid dips, activators, or plating solutions. The same reasoning does not apply to the solid soil, since it cannot be skimmed-off from the surface. Some is removed by settling, but in general, these solids should be dispersed so that the metal surface rinses free of all foreign matter.

4. Drag-Out. This aspect has less to do with limiting the cleaner life than to wasteful extravagance. Of course, some work is of such nature that recesses and pockets carry out a large volume of cleaning solution, as it also does all along the plating line in the acid dips, rinses, plating solutions, etc. Racking the work to the best advantage to give maximum drainage is the only practical means available to keep this loss at the lowest possible amount. Periodic titration checks should be made on the solution so that revitalizing additions can be made to overcome this waste. Heavy drag-out removes dirty cleaner solution and if compensated by regular additions, tends to oppose the deterioration resulting from soap, carbonate and soil build-up. However, this compensation is obtained at the expense of increased cleaner consumption, in addition to waste treatment cost. The conscientious operator comparing the increased cleaner life against the amount of additions required must determine a cost balance.

5. Solution Volume. This aspect pertains to the arithmetic relationship between area of work cleaned and volume of cleaner solution. Clearly, the larger the volume of solution for any given work loads, the longer it will require overloading with soil or grease. Conversely, a tank that is too small will very quickly reach its limit in soil tolerance, resulting in too frequent dumping of the solution. There is no fixed numerical value for this relationship. It might be argued that the volume of the cleaner solution cannot be too large, but in the interests of dimensional economy, it would not be good engineering to have the cleaner tank too cumbersome in size. It also might be possible to have a volume so large in relation to the amount of work that change of the active ingredients from evaporation, thermal degradation, dragout, carbonation, etc would reduce the cleaning efficiency before it had a chance to give maximum returns on the investment. Generally, the cleaner tank is designed as is the plating tank, i.e., to accommodate the largest piece to be treated.

6. Depletion. By definition, the wetting agents used in cleaners are surface active materials. As such they distribute themselves at the surfaces of solid particles or at the interfacial surfaces of oils and greases in the processes of emulsification, dispersion and surface tension reduction. Eventually that they become depleted in the solution to the extent that the detergent and emulsification action is compromised. All proper cleaners also incorporate the sequestering agent(s) whose function is to keep soluble metallic anions in the solution. However, the situation can arise, where metal accumulation can overpower the sequestrant's capacity. The metal ions (that are cations), can in turn react with anionic surfactant, resulting in the loss of wetting abilities. These actions are inherent in all cleaners and are compensated for by the additions of fresh cleaner, as a whole or as a separate surfactant package. Cleaner vendors should provide sufficient surface active materials in their formulated products to have a reserve with the intention that the wetting action will be effective throughout the life of the cleaning solution.

7. Maintenance. Proper maintenance of the optimum cleaning action is necessary and almost mandatory in order to balance the six previous aspects, resulting in maximum results from the alkaline cleaning bath. The cleaner must be kept within allowable limits as regards the soil load in order to function properly. When this aspect becomes so high that the dragout contaminates subsequent solutions or the work cannot be rinsed soil-free, no amount of additions to the cleaner bath will restore its working efficiency. Once more, the limit is set by a slow build-up in the bath and not by any "break-down" of the cleaner. There is no simple way to determine this end-point in any particular application except by educated experience. It is often justifiable to make up a new cleaner more regularly, according to the dictates of past experience, given that they are far cheaper than the labor lost due to rejects.

The volume should be sufficiently large to tolerate the soil load from one to four weeks. Longer periods may cause excessive carbonization and in some cases, excessive soap build-up. During these one to four week time periods, there must be sufficient active alkalinity maintained by regular additions of new material to support electrical conductivity and rapid emulsification, saponification and dispersion of the oils and greases. Shorter periods of operation before replacing the solution may lead to higher cleaner consumption. However, this item is much cheaper than the labor cost invested in rejects or lost time due to shutdowns in the midst of a day's production run.

The life of a cleaner is best determined by observation of results in an actual application. A log of analysis and performance of the cleaner is most helpful to anticipate and determine the cleaner's productive life. Effort should be made for a scheduled, intermittent complete chemical analysis to determine the changes in composition with time. In addition, the measurements of specific gravity and conductivity have been found useful in some cases, since these are simple and rapid methods. A good log coordinated with observation of the effectiveness of the cleaner will help to establish the productive, usable life.

If wetting agent is essential for good cleaning, then the wetting agent should be maintained by laboratory foam test, or observation of the foam blanket on the cleaner.

The cleaner will not suddenly lose cleaning power due to changes in the major chemical present. Since the cleaning power changes gradually, the loss of cleaning power can be observed over a longer periods by watchfully observing the elapsed cleaning time. If the normal cleaning time is one minute, the work should clean in half this time to maintain a margin for safe cleaning. A fresh cleaner may clean in ¼ minute. Empirically, the minimum cleaning time for a fresh cleaner can be estimated by hand dipping of production parts for various times. This test can be repeated at varying intervals as the cleaner is used. An increase in cleaning time will indicate unfavorable changes. The log may reveal changes in analysis, practices, or the work that account for this. If the cleaning time gradually increases, then the life of the cleaner will be anticipated by extrapolation to a cleaning time equal to the processing time.

The seven aspects presented above, indicate that the life limits of modern cleaner formulations are normally caused by deterioration ascribed to various chemical and physical changes and are not normally due to any sudden breakdown of the chemistry of the cleaner.

VI. INTRODUCTION TO THE CLEANING ACTION

In addition to previously discussed soils, in order to obtain a clean, active metal surface, other important aspects must be encountered and considered. These include final surface finish requirements and type and the composition of the base metal. The solvent is usually water, and one effective cleaner through the synergetic action of its main ingredients (surfactants, builders and sequestrants), aided by heat and agitation, and applied in properly designed equipment will perform the expected tasks. Those aspects will be briefly presented next.

1. *Builders*: Colloquially called "cleaning boosters", they are the principal bulk component of the alkaline cleaners. Several builders are usually used in a given cleaner, in varying proportions,

depending on, the metal being cleaned, cleaning method and application. They contain non-surfactant materials that are selected from the following two types: inorganic and organic. Inorganic types are: a. Hydroxides, b. Silicates c. Carbonates, d. Phosphates and (occasionally), e. Borates, and f. Sulfates. They build up (boost) the action of the surfactant and may actually react with some oils to form soaps. Their function will be elaborated in more detail in Chapter VII.1

2. *Surfactants*: Their widely accepted usage of for cleaning applications duly demonstrates their importance as a key ingredient of cleaning baths. The surfactants (surface active agents) needed and used are available in a great number and variety.

At this point they will not be specifically discussed in detail, but rather in general form, since further details will be presented in Chapter VII.3

The surfactants are classified in to four groups according to how the surfactant molecule ionizes in water: anionic, nonionic, cationic and amphoteric. Soap is an example of an anionic surfactant derived from a multitude of natural or synthetic raw materials.

The surfactants used for cleaning purposes must perform a multitude of actions: provide wetting action by lowering surface tension as a first requirement. It also has to emulsify oily matter, solubilize the water-insoluble soils (oils) and disperse aggregates (deflocculating). For these reason, they are frequently used as a combo of at least two. A properly chosen surfactant will lower the surface tension of water in concentrations as low as a fraction of one percent. Although this low concentration of surfactant will promote wetting of the part to be cleaned as well as the soil to be removed, it should not be interpreted as a necessarily adequate concentration if emulsification and dispersion must also be achieved. In practice, the surfactant concentration is usually empirically determined by the quantity of oily matter that must be emulsified and from the desired life of the cleaning bath before replacement. For this reason, the surfactant concentration may vary from a low of 0.25% to a high of 10% in specific cases. Since all of the synthetic surfactants are essentially neutral compounds (pH 6-8), their use poses little, if any, hazard to the operators.

3. *Chelation / Sequestration*: This is the ability of the cleaner to remove or inactivate undesirable metal ions from the solution by forming stable, soluble complexes with metallic impurities. They are widely used, chiefly to alleviate undesirable properties of some metal ions, without necessity of precipitation or removing them from the solution. Chelation and sequestration, are the interchangeable terms used in the formulating jargon. The parent world “chelate” is derived from the Greek word meaning “crab’s claw”,

which refers to the tenacity of chelators to holds the metal ion. The chemistry of chelating agents in metal cleaners will be further elaborated in chapter VII.2

4. *Heat*: Heat increases cleaning efficiency by increasing the speed of wetting, emulsification and saponification reactions. Every 10^0 rise in temperature above 100^oF can double cleaning efficiency. However, because of the nature of some base metals and the make-up of soil, surfactant, and solvents, upper limits must be established. The excessive temperature can "set" some soils and also cause detrimental reaction between the substrate metal and the soil, which in turn will make it more difficult to clean. The optimum temperature is the one that will keep the part wet upon entering the next processing tank. The parts should not be too hot to allow the dragout solution to evaporate to dryness by the heat retained by the parts.

5. *Agitation:* Agitation is important, since the cleaning mechanism is diffusion controlled. It speeds up the cleaning reaction by bringing fresh cleaner to the soil and also by mechanical dislodging the reactant materials. Mechanical agitation is preferred over air agitation. As the air is leaving the surface of the bath, it is saturated with water vapor. Water, which has a large heat carrying capacity, due to the large heat of evaporation value ($\Delta_{evap}H$=40.6 kJ/mol @ 100^0C)[90], will remove large amounts of heat. Now, the energy must be consumed, to offset the heat loss, and to heat additional make-up water. In turn, as more make-up water is added, the mineral impurities will be increased and with the time concentrated, as a consequence more of the cleaner is consumed. Proper agitation will assist the cleaning process by mechanically dislodging soils as well the solids from the parts. The best system to use for agitation is the submerged, strategically positioned nozzles that vigorously circulate, preferably filtered, cleaning solution, using sparger piping and dedicated pumps.

6. *Cleaning equipment*: Equipment is basically a mechanism, whether manual or automatic, for conveying work from one point to another, performing it successfully through each step in a process cycle. This equipment can be in the form of a cleaning tank(s), that are operated manually, hoist line, automated hoist line, or a sophisticated full automatic machine. It must be properly designed and engineered for good metal finishing or metal cleaning. This can include, however, a multitude of factors. It starts with the proper tank design, that needs adequate volume, proper tank linings and tank coils for heating and cooling plus temperature regulation. Next items to consider are sufficient rinse flow, rinse turnover, number of rinses, electrical bus work, DC power, electrical contact, rack spacing, electrode spacing, anode to cathode spacing, transfer times, skip mechanisms, delayed set downs,

agitation, filtration, accessibility to tanks for chemical additions, solution proximities, dwell times, type and size of spray nozzles, pumps, dragout, etc.

7. *Cost of the cleaners* : This must be considered carefully for successfully obtaining good cleaning at a reasonable cost. Some plants can run their cleaner solutions for longer periods before dumping and making up a new cleaner than other. This is as a result of employing specific conditions in their overall operation. Unfortunately, the industry has no hard and fast rule or calculation by which a dumping point can be determined. Some guidelines are given by *Durney*[91]. Nevertheless, one cleaner can provide a longer life of good cleaning than another by the very nature of its chemistry.

When the end product of the cleaning reactions, a “clean” surface, is obtained, the metal finisher can now successfully electroplate, phosphate, bright dip, anodize, strip, electro polish, chromate, or etch, etc. If his final processing solutions are all in good operating condition, if his handling equipment is correct and in good condition, and if the parts are properly racked for processing, it makes for a good system.

VII. THE ELEMENTS OF CLEANING FORMULATIONS FUDAMENTALS

In order to understand the action of a cleaner, or to formulate a cleaner for a particular metal cleaning operation one has to be familiar with the action performed and properties of commonly used cleaning ingredients. In the following elementary study of fundamentals, it is obviously necessary to discuss the actions of individual chemical ingredients, rather than proprietary formulated products. The proprietary products are formulated on the same principles that are presented next. The only difference is that their exact nature is understandably maintained as a trade secret. The interested plater practitioners, plating chemists and plating engineers will hopefully gain some insight into the workings of the component chemicals and their mixtures, which are discussed below.

VII.1. INORGANIC BUILDERS

a. Inorganic Phosphates: They have some buffering capacity, antiredeposition properties, and some act as sequestrant and surfactants boosters. Their properties are listed in Addendum, Table **18**.

- Ortho phosphates, are not used to any great extent in heavy-duty alkaline metal cleaners other to provide alkalinity range. In general, phosphates exhibit "detergent" properties similar to those of silicates, though to a lesser degree. They also have a considerable peptization capacity for causing larger particles to be dispersed into much smaller. The complex (condensed) phosphates, which are well known for their sequestering properties and which are employed to a greater extent, will be further discussed.

•Sodium tripoly-phosphate (STPP), $Na_3P_3O_{10}$, is the most commonly used condensed phosphate. It has good soil suspending properties and high sequestering abilities for most multivalent cations. With time and high temperature, it will react with water to form less condensed phosphates and eventually orthophosphate[92-94] (Table **13**). In aqueous solutions, it provides a mildly alkaline medium (pH 9.8). It has buffering capacity, although not as good as ortho or pyrophosphates. In hexahydrate form it not prone to moisture pick-up.

•Tetra sodium pyrophosphates (TSPP), $Na_4P_2O_7$, and more soluble and more expensive potassium salt, (TKPP) are powerful detergent booster ingredients exceeding the properties of STPP, but they are less stable.

• Sodium (SAPP) $Na_2H_2P_2O_7$, or potassium (KAPP), acid pyrophosphates, having a low pH (4.3), are invaluable when the formulation needs lower pH (e.g., aluminum cleaners).

• Mono sodium phosphate (MSP), NaH_2PO_4, has a low alkalinity (pH = 4.8), which is suitable for acid cleaners and boiler compounds, etc.

• Di sodium phosphate (DSP), Na_2HPO_4, has higher alkalinity (pH = 9.0) which makes it suitable for buffered cleaner with low NaOH contents.

•Tri sodium phosphate (TSP), Na_3PO_4, because of its high alkalinity (pH = 12.0), is used when alkalinity and conductivity is needed, e.g. heavy duty soak cleaners and electro cleaners.

Table 13. Possible Modes of Hydrolysis of $Na_3P_3O_{10}$ & $Na_4P_2O_7$

1) $Na_5P_3O_{10} + H_2O$ ® $Na_3\,HP_2O_7 + Na_2\,HPO_4$
2) $2Na_5P_3O_{10} + H_2O$ ® $Na_4\,HP_2O_7 + 2Na_3\,HP_2\,O_7$
3) $Na_3HP_2O_7 + H_2O$ ® $Na_2\,HPO_4 + Na\,H_2\,PO_4$
4) $Na_3HP_2O_7 + Na\,H_2\,PO_4$ ® $Na_4\,P_2O_7 + Na\,H_2\,P_2\,O_4$
5) $Na_4P_2O_7 + H_2O$ ® $2Na_2\,HP\,O_4$

b. *Hydroxides*: Sodium hydroxide (Caustic Soda), NaOH and potassium hydroxide (Caustic Potash), KOH are the principal ingredients in most heavy-duty soaks and electrocleaners. Their function is to breakup by saponification and to emulsify heavy soils, and to provide high conductivity. Caustics have the highest degree of alkalinity to neutralize acidic soils. However their emulsifying ability is very poor for the non-saponifiable soils. The term saponification in this context stands for the reaction of any free alkali with animal or vegetable fats or with the fatty acids, which can be obtained by hydrolysis of fats. The resulting product is more or less water soluble, has some surface active properties, and is known to all of us as soap, and can assist in the soil removal. The higher the pH of a cleaning solution, the more free alkali is available, and the faster is the rate of the saponification. They have poor rinsability, that has to be compensated with appropriate wetting agent.

c. *Silicates*: They function as detergent builders and for saponification of fatty acids that are common in greases and lubricants. They have soil suspending qualities plus some corrosion protection abilities[95], and high conductivity suitable for electro cleaners. However, they should be used in conjunction with NaOH and/or ortho phosphates to prevent the silicate anion from being attracted to the anode. A combination of silicates and complex phosphates offers a synergistic effect that results in more effective detergency than corresponding amounts of either component used alone. Rinsing and acid dipping should be adequate and sufficient after electrocleaning with silicated electro cleaners[86]. Frequently used silicates are hydrous or anhydrous metasilicates of sodium (SiO_2: $1Na_2O$). Sometimes, typically in liquid formulations, liquid or powder polysilicates are used as partial or incomplete replacement for the phosphates[97], e.g. Na orthosilicate (SiO_2: $2Na_2O$). Orthosilicate and metasilicates, are highly alkaline salts. They develop their alkalinity by hydrolysis. This is a process of "decomposition" in which the products react with water yielding a less soluble compound, in this case, silisic acid and free alkali. The silisic acid in a colloidal state has excellent solid soil dispersing properties. Further, sodium silicate has a high alkaline reserve. The hydrolysis proceeds only to a given point, unique for each substance, until a given alkalinity level is obtained. Further hydrolysis, yielding free alkali, takes place only when an acidic substance is introduced into the solution, thus using up alkalinity, or in chemical terms, using hydroxyl ions. Consequently, the silicates, because of their unique alkaline reserve, are known to be, next to NaOH/KOH, excellent buffers for cleaning processes, which involve acidic soil or need for alkaline hydrolysis including saponification. They maintain nearly their original pH upon introduction of acidic soils and contaminants. Buffering action of the formulated cleaner is desirable property, so that optimum pH for cleaning can be maintained in spite of contaminations. While alkalinity has been demonstrated to be an important contributor to deflocculation, the polyelectrolyte nature of the soluble silicate anion itself is favorable for maximum dispersion. This is readily seen by comparing the superior suspension characteristics of sodium silicate, contrasted to that of NaOH or Na_2CO_3. The dispersing power of sodium silicate is effective over a wider range of alkali concentration than other salts.

The ratio of silica to alkali may have some effect on dispersion efficiency. Generally, for clay or siliceous soil, the higher ratio silicates exhibit greater suspending power than sodium metasilicate. Soluble silicates are complex mixtures of silicate anions. The larger the anions are 2 or 3- dimensional products of silicate monomer, $[SiO_4]^{4-}$. In some more siliceous silicate solutions, i.e., SiO_2; Na_2O ratios > 2, some of the silicate condenses to polymeric (colloidal) silica. Negative charges on the anions are balanced by protons or by cations, typically alkali metals[98]. Negatively charged colloidal anions are often spoken as micelles. While exact constitution of alkali silicates are not clearly established, it has been convenient to speak of "crystalloidal " and "colloidal" silica. Crystalloidal silicate is considered monomeric, and colloidal silicate as polymeric or aggregated. Polymerization or aggregation increases with increasing ratio, as shown by the weight-averaged molecular weights of Na and K silicates[97] (Table 14).

Table 14. Molecular Weight of Alkali Silicates Solutions at Varying Mole Ratios

Alkali Metal Silicates	*Mole Ratios*	*Aver. Mol. Wt. in Solution*
Sodium silicates, SiO_2/Na_2O	0.41	60
	1.01	90
	1.69	120
	2.09	160
	2.62	265
	3.30	320
Potassium silicates, SiO_2/K_2O	1.00	56
	1.75	115
	2.50	295
	2.80	304
	3.31	495
	3.62	628
	3.97	848

They are environmentally acceptable. They are derived from, and ultimately return to nature, as SO_2 and soluble K or Na compounds. Since they are among earth's most common chemical components, they offer minimum potential for harmful environmental effects.

d. *Carbonates*: They are typically used as sodium carbonate, (Soda Ash), Na_2CO_3, and can act as a water softener. Although not an outstanding softener, its popularity stems from its modest price. It has a dual functionality: in addition to raising the pH it also increases the adsorption of the liquid surfactants and solvents. This is an important role as in anhydrous form (Light Soda Ash) it can absorb significant amounts of liquid ingredients of powder cleaning formulation (e.g. surfactants, solvents, etc.) and prevent caking of the blend. Sodium carbonates also serve as buffers, but they do not have the other important 'detergent' qualities of the silicates, such as dispersion and retention of soil redeposition. Bicarbonates are used when lower pH is necessary, like in a cleaners for aluminum.

VII.2 SEQUESTERING AND CHELATING AGENTS

Chelating agents have become important in compounding of cleaners, especially with the demand for formulations containing little or no phosphate. Phosphates are suspected of causing eutrophication of lakes and streams and are banned in some jurisdictions. To compensate cleaning action of the phosphates, chelating agents replaced them for many purposes, although at higher cost.

The effect of chelating of metal ions on detergency can be described in such simple terms as tying-up metal ions resulting in effective water softening. Chelating also prevents deposition of metal soils or ions which will discolor the surface or impair adhesion, or which may interfere with subsequent treatment of the metal surface. Soils complexed to the soiled surface by metal ions are liberated when chelating (complexing) agents can sequester the stabilizing metal ion.

Sequestering can be accomplished with a group of organic chelating agents, such as sodium gluconate, sodium citrate, trisodium nitrilotriacetate (NTA), tetrasodium ethylenediamine tetra acetate (EDTA), and triethanolamine.

The most commonly used is ethylenediaminetetraacetic acid (EDTA), and its derivatives. These products are very effective at all pH’s and are not subject to reversion by hydrolysis. Effective for controlling iron only bellow pH 9. Also used are Citric and Tartaric acids (good for low or medium pH) as well gluconates and their derivatives (for high pH).

Sequestering and chelating can inactivate or tie up undesirable impurities in the cleaning bath. For instance, (Ca^{+2}) is chelated by common industrial chelating agent ethylenediamine tetra acetate, to form new compaund $CaEDTA^{-2,}$ which is highly soluble and will not react with common precipitants for calcium such as carbonates and sulfates: $Ca^{+2} + EDTA^{-4} \cap CaEDTA^{-2}$. This reaction shows equilibrium; the reaction goes in both directions. The extent of magnitude of these competing reactions is primarily dependent on the strength or metal-binding power of the chelating agents and on the pH and on the presence of the competing anions, especially on those, which tend to precipitate the metal anion. Generally the chelating reaction is in order of millions or billions of times stronger than that the opposite reaction toward the left.

Complex phosphates, such as sodium tripolyphosphate, tetra sodium pyrophosphate, and sodium hexametaphosphate, combine (sequester) with calcium and magnesium ions and therefore preventing them from entering many unwanted reactions, e.g., precipitation. A negative feature of the complex phosphate is that they hydrolyze or 'decompose' to simple phosphates and therefore lose their sequestering properties (fff **11**). This is a slow process, which depends on many factors, including temperature and alkalinity.

Knowledge of and experience with the functions of sequestrants is of premium importance. The basic metal, dependence on pH, synergism with other builders, their stability, relation to surfactant systems involved, stability at high temperatures and cost effectiveness are among factors that makes the life of a formulator interesting. The synergetic effect is most pronounced in practically all cleaning compounds, either alkaline, neutral or acid formulations. This effect means that in combination with others ingredients, the net result is much greater than if each component is acting alone. Every ingredient can influence or "catalyze" the other to achieve the optimum performance.

VII.3 DETERGENCY AND SURFACTANTS

1. *Introduction*. Practical detergency is a particularly difficult subject, encompassing complex mixtures of soils bonded to a variety of the substrates. This makes efficiency of the of different cleaning formulations dependent both on soils and the substrate. Detergency may be defined as a theory and practice of the removal of foreign material from solid surfaces by chemical means. This definition covers the extensive and important subject of soil removal from metal surface, plastics and so on. It excludes, however, purely mechanical cleaning (e.g., abrading down the surface) or purely chemical processes (e.g., by chemical dissolving of impurities)[**99**]. This definition requires the formulator to consider the following: the nature of the soil to be removed, the substrate or surface to which it clings, the process by which the soil is to be removed, the type of water to be used, and its temperature. The substrate or surface may be metal, metal-alloy, ceramic, glass or plastic. The type of soil can be insoluble particulate, carbonaceous, or oily. An effective cleaning compound must perform certain basic functions during the process of soil removal. These basic functions include: neutralizing acidic soil components, emulsification of oils and greases, deflocculating particulate soil, suspending soil and preventing redeposition. Surface active agents (surfactants), a.k.a wetting agents are the broad classification of a series organic compounds that by nature can be anionic, cationic, nonionic or amphoteric in aqueous solutions. They are used for surface tension alternation, solvency and co-solvency, emulsification and foam control. Some surfactant are used to make a stable mixture or solution of materials that are otherwise incomparable i.e. oil and water, oil and inorganic salts (hydrothropes).

In order to formulate the particular product each surfactant should be evaluated for its specific activity or function, individually or in combination with others. These materials are quite specific and selective in their functions. Therefore a "al purpose" combination or formulation is probably non-existent.

2. *Mechanism of Detergency*. The first step in cleaning mechanism is to replace air and the thorough wetting of soiled substrate by the cleaning solution. The subsequent removal of soil can occur via number of processes. The soil can be rolled-up and displaced from the substrate by the cleaning solution. It can be removed in layers by emulsification. Alternatively, the surfactant can penetrate the soil to make inverse micelle, followed by solubilization or emulsification. The final step is to maintain the soil in suspension, to prevent redeposition.

We should recall that primary function of surfactants in alkaline cleaner compositions is to improve detergency and wettability. The surface-active agents can do or aid in doing a magnitude of functions:

1. Acting at a liquid-solid interface, they can wet an otherwise difficult wettable surface prior to cleaning.

2. They can cause water to penetrate and spread underneath an oily film, for example, to lift the oil from a piece of oily steel and allow it to float off or be removed in other ways. In such an instance, they are acting, at two interfaces: water-steel and water-oil.

3. They can do just the reverse, causing oil to penetrate and spread. This phenomenon is used to assist in emulsion-cleaning operations.

4. Acting at a water-oil interface, they can assist the formation of an emulsion, which may be one of two kinds. Water containing a very large number of tiny oil droplets (the so-called oil in water or O/W emulsion) or oil containing minute water droplets (the water in oil or W/O emulsion). The O/W type of emulsion is used in emulsion cleaning operations.

5. They can penetrate through the under solid deposits ranging from scale on forgings to hard-dirt deposits, wetting both the soil and the surface to be cleaned thus permitting easier separation by mechanical or chemical means.

6. Acting at a water-soil interface, they can serve to keep removed soil particles from redepositing on the cleaned surface.

7. Acting at a water-soil interface, they can keep soil particles in a state of maximum subdivision; that is, in a condition where they have maximum surface area so that the soil stays suspended and dispersed instead of clumping and settling.

8. They can produce a foam and cause soil particles to be entrapped by that foam, so that the soil is removable by skimming or similar mean.

The important function of surfactants in cleaning compounds is to lower surface and interfacial tensions. The surface tension is the attraction between molecules within the body of a liquid. Any attempt to increase the surface area of such a liquid, as by the formation of films, is opposed by this force. It tends to pull surface molecules into the body and to adjust the surface to a minimum area. Water has the highest surface tension of most liquids. This results in relatively poor wetting ability when compared with many organic liquids.

While it is difficult to explain in simple terms how surface-active agents can lower the surface tension of water, it is probably of interest to know that the majority of common surface-active agents lower the surface tension of water from approximately 72 dynes/cm to a range of 28-40 dynes/cm. Interfacial tension is the force of repellency at the interface of two liquids, which are only slightly miscible. The degree of miscibility of each liquid in the other determines whether the interfacial tension will be high or low. Water, with a surface tension of 72 dynes/cm, for example, and a paraffin oil with a surface tension in the range of 30 dynes/cm, would show a relatively high interfacial tension of 40-45 dynes/cm. If, however, the surface tension of the water is reduced by the addition of a surface-active agent to approximately the same value as that of the oil, then the interfacial tension of the three-component system will approach zero. The more the interfacial tension between oil and an aqueous solution approaches zero, the easier is for the detergent to bond the water to the oil. To summarize, the interfacial tension values between mineral oils and water for the majority of surface-active agents are between 1 and 8 dynes/cm. Initial values, without surface-active agents, are around 45-55 dynes/cm.

Liquid-solid interfacial tensions, which follow the pattern of liquid-liquid interfacial tensions, are not easy to measure. Contact angle measurements are used. Arbitrarily, it may be said that if the angle is greater than 90^0, the liquid does not wet the solid. If the angle is less than 90^0 but greater than 0^0, the liquid partially wets the solid. If there is no contact angle, the liquid completely wets the solid[100].

- *Redeposition*. In addition to solubilization and emulsification of certain soils, solid dirt particles are physically removed and must be held in suspension until rinsed away, rather than allowed to redeposit (reabsorb) on the cleaned surfaces. Because the cleaning processes are somewhat closed processes, there will always be possibility that the soils removed from the substrate will redeposit onto the surfaces a result of the lack of colloidal stability of the dispersed soils. For oily soils removed by solubilization, the process is thermodynamically driven so that is essentially one-way street and redeposition is minimal. Solid soils on the other hand can not be solubilized and redeposition must be retarded by other kinetically controlled means[101]. Suspension of the soil depends on particle size, solution density, interfacial forces and surface charges. In the past, soap or detergent foam was utilized to entrain soil particles. With the advent of modern low-foam surfactants, the inorganic detergent builders supply most of soil suspension and dispersion action. Surfactants also help accomplish this by adsorbing onto (surrounding) the oil droplets in a such a way that the hydrophilic groups are in a aqueous phase and that hydrophilic groups are in the oil phase. This adsorption stabilizes the droplet and helps prevent it from coalescing with other droplets[102].

1. *ANIONIC SURFACTANTS*. They are preferred for most metal cleaning applications. They are very soluble in water and may be added as either a liquid or solid to the bath. The first surface-active agent, common soap, was used for centuries. Chemically, it consists of a long chain of carbon atoms, which is oil soluble, and a terminal group, which is water-soluble. Detergency results from these properties which cause alignment of the molecules at oil-water, oil-air, oil-metal, or solid-water interfaces. Unfortunately, soaps have shortcomings that are well known. They react with hard water metal ions, such as calcium and magnesium. These alkaline earth (calcium, magnesium) soaps are not only water insoluble, but they are water repellents. Soaps are also not the best substances to rinse off a metal surface because of their limited solubility in water. For these reasons, they are almost completely replaced with synthetic surfactants.

The insolubility of alkaline earth soaps provided the stimulus for the development of synthetic detergents. Great varieties of synthetic detergents have been made with varying and controlled characteristics. They provide good detergency for most soils and greatly improve rinsing properties of the cleaning solutions. The synthetic detergents are closely related to soaps in their surface-active behavior. In order to possess surface-active properties, their molecules-as with soap-consist of two parts that exert opposing effects when in contact with water, one part being oil- friendly, the other part being water-friendly.

2. *NONIONIC SURFACTANTS*. This class is rapidly gaining favor as addition agents but must be used with greater care than the anionic. They are sparingly soluble in water and are typically heavy pastes or viscous liquids. The solubility range is so wide that some resemble oils so closely that they are scarcely dispersible in water, although maintaining the ability to lower surface tensions. Others may give clear solutions in water and be insoluble in most organic solvents and oils, but the majority of commercial significance possesses a fair degree of organic solubility coupled with water solubility. A careless addition may result in incomplete dissolution of the nonionic detergent, and, in turn, ineffective cleaning results. Properly used however, the nonionics offer distinct advantages: they do not form calcium or magnesium salts in hard water, nor do they react with acids. Moreover, they are

compatible with both anionic and cationic detergents and thus, they may be used in surfactant blends. From a process standpoint, the nonionics are popular because their residues are nonconductive. For this reason, they are usually specified for use in cleaning electrical or electronic equipment.

The nonionics are primarily regarded as emulsifiers. They are, therefore, good oil-dispersing agents, excellent solubilizers, and good detergents.

3. *COUPLING AGENTS (HYDROTROPES).* They are needed to increase solubility of slightly soluble ingredients in concentrated liquid cleaning formulations. Examples are odium xylene, toluene or cumene sulfonate or organic phosphate esters. They are all anionic surfactants that will solubilize not only other surfactants but slightly water- soluble solvents as well.

B*iodegradability.* Because of the increasing importance of water pollution control and abatement, the concept of biodegradability was added as a new requirement for surface active agents during the decade or so ending in 1965. Biodegradable surfactants are those that are decomposed easily or readily by the biochemical processes typical of sewage treatment and surface streams. Microorganisms can destroy most, if not all, organic compounds, utilizing them as food to provide energy and growth requirements. However, the rate and completeness of destruction will vary. A yardstick considered reasonable by sanitary engineers is that surfactants are "biodegradable" if they are as readily decomposable as the soluble organic matter of sewage.

VII.4 OTHER INGREDIENTS

- Solvents are sometimes added to solubilize greases and oils that do not become saponified or emulsified. Butyl Cellosolve, M-pyrol, Ethylene Glycol, Dimethyl formamide are among examples of them used among others.
- Sodium Sulfate is sometimes added as" filler" for cost reduction or as a conducting salt for electrocleaning formulas.
- Corrosion inhibitors are used when transfer time is long between cleaning and acid dip stations.
- Borates have some sequestering ability and are used in some systems.

VIII. TROUBLESHOOTING CLEANING OPERATIONS

VIII.1 GENERAL[103]

Trouble in cleaning may be quite obvious or may be very obscure. Plating operations generally are complex and consist of many steps, so that very often it is not obvious whether trouble is due to cleaning or some other phase of the plating operation. Systematic approach is a must[104]. It can be accurately stated, however, that the majority of plating troubles can be traced to flawed or substandard cleaning.

When trouble occurs and faulty cleaning is suspected, an initial close observation of the work should be made after each cleaning and rinsing step. Things to look for are water breaks (especially after acid dips), excessive darkening or etching, smuts, irregularity in appearance, and stains. Good lighting is required for accurate observation, and the troubleshooter should be one who knows from experience how correctly cleaned parts should look after each cleaning step. Parts emerging from rinses and acid dips should also be examined for evidence of visible oil films either being picked-up or not being removed. Using the White Glove Test, described in chapter IV, invisible films should be checked. Cleaner concentrations, temperatures, current density and any special standards recommended by the supplier such as pH, conductivity, spray pressure, etc. also should be determined. In addition, the wrong polarity in electrocleaners, time in tanks, transfer times, and the possibility of tanks being skipped if it is a hand line, should be validated. All these factors have a influence on the proper functioning of cleaners. If any of these have suddenly become out of commended limits or purposely changed, they should be considered a possible source of the trouble.

The type and nature of the soils being removed must also be taken into account. If buffing or drawing compounds or oils and lubricants have changed, the new soils may be more difficult to clean Buffing compounds are notoriously difficult to clean due to their composition (Table 20-addendum). This in turn, may require a change in the composition of the cleaners or a change in the cleaning method. Likewise, a substantial increase in the quantity of soil, particularly buffing compounds on the work could cause trouble.

Time honored ways to establish whether cleaning is the cause of the trouble is to separately hand clean a few parts with a soft brush and mild scouring cleaner, e.g. pumice. After rinsing, and skipping regular cleaning or acid dipping sequences, those positively clean parts are introduced directly into the plating solution. If the same trouble is manifested on these parts, it can usually be concluded that the trouble is in the plating baths or elsewhere and not in the preplating part of the cycle.

VIII.2. SOAK CLEANING

a. *Heating*: Soak tank needs sufficient heating capacity to keep the solution at the proper temperature during peak production runs. If steam coils are used, check for leaks diluting the solution. Check that submerged heating coils, electric heaters, and heat exchangers, are not insulated from the solution by scale or sludge build-up. Check the operation of the thermostat, temperature sensors and recirculating pumps.

b. *Agitation Shield and Overflow Dam*: Properly agitated solution should continuously bring fresh cleaner solution to the work. The soils should be skimmed from the solution surface over the dam.

c. *Contamination:* Heavier than normal production runs can cause excessive soil loading of the cleaner. Check the concentration and age of the cleaner. Scrutinize introduction of any new soils that might cause the cleaner to become prematurely depleted. Troubleshooting chart for soak cleaners is given in Table 15.

Table 15. Troubleshooting of Alkaline Soak Cleaners

Trouble	***Probable Cause***	***Remedy***
Excessive etching in cleaner.	pH tool high or loss of inhibitor.	Adjust pH; Ad inhibitor.
Corrosion spots.	Alkalinity left on surface.	Predip in $NaHSO_4$ or HCl and rinse.
Insufficient cleaning.	1. Weak or worn-out cleaner. 2. Excess foreign matter on work.	1. Make up or renew, adjust pH and wetting agent. 2. Degrease in vapor degreaser or solvent emulsion cleaner.
Smut formation on work in cleaner.	On copper-containing alloys if pH is too high.	Reduce pH, avoid free caustic in cleaners, and use sufficient inhibitor.
Excessive scum formation.	Breakdown of Cu, Mg & Ca sequestering agents, absorption of CO_2 by cleaner to form excess carbonates. Excess carbonates used in original cleaner formula.	Select cleaner with ample reserve of sequestering agents, e.g., polyphosphates. Avoid CO_2 from gas burners, etc., by proper vents around tank area. Use carbonate-free cleaner.
Insoluble film formation that interferes with plating step.	1.Too highly inhibited. 2. Excessive transfer time between cleaner & rinse.	Select proper amount of soluble inhibitor. Reduce transfer time & select cleaner with wetting agent that promotes good rinsing.

VIII.3. TROUBLESHOOTING SPRAY CLEANING

a. *Heating*: Check thermostats, scale on heating coils or heat exchanger tubes, and solution temperature. Descale the power washer if necessary with inhibited hydrochloric acid or a proprietary descaling product to improve heating efficiency.

b. *Spray Risers*: There should be enough spray risers, properly positioned and directed to contact all surfaces. The nozzles should be periodically inspected and cleaned. The nozzle patterns , distribution of the solution within spray patterns and total volume of sprayed solution will significantly change as nozzles wear down with use.

c. *Spray nozzles.* Check the spray patterns. As the nozzles wear with time and age, solution distribution, and volume can significantly change. As the V-jet-type nozzles wear, the spray pattern becomes uneven, the flow rate increases and solution is delivered more in the center of pattern.

d. *Pumps and Lines* : Check on the return side to be sure that no air is being draw in the system causing excessive foaming.

e. *Baffles:* The cleaning and rinsing stages must be properly baffled to prevent one from contaminating or diluting the other.

f. *Contamination*: Excessively dirty cleaning solutions cannot be expected to function properly. Grease overflow dams must function properly. Production must not be excessive before a new cleaner is made up.

Table 16. Troubleshooting Spray Cleaning Operation

Trouble	*Probable Cause*	*Corrective Action*
1. Parts dirty	a. Underconcentrated spray cleaner.	a. Analyze and adjust as required.
	b. Solution temperature out of range.	b. Check thermostat and adjust accordingly; clean coils and heat exchanger.
	c. Insufficient residence time for spray cleaner contact.	c. Adjust accordingly.
	d. Chemistry not sufficient for the specific cleaning requirement.	d. Conduct appropriate evaluation to determine if surfactants or alkalinity should be changed; consider separate precleaning of troublesome parts.
	e. Insufficient pressure or spray nozzle plugged.	e. Adjust pressure, replace or clean plugged nozzles; confirm water conditioner blended into spray cleaner; install spray head delivering desired pattern on parts; check for damaged pump impeller.
	f. Wrong spray pattern.	f. Align positioning and size of the nozzles.
2.Parts falling of the racks.	a. Pressure too high; risers too close to parts.	a. Adjust the spray pressure and/or positioning of the nozzles.
3. Mottled appearance on the surface of the parts.	a. Redepositing previously removed soils.	a. Service mechanical oil removal devices; determine if cleaner service life has been exceeded and replace with fresh make up.
	b. Interstage drying.	b. Clean blocked nozzles.
4. Excessive foaming.	a. Pressure too high.	a. Adjust pressure; replace/clean plugged nozzles
	b. High concentration of cleaner; cleaner too highly wetted; saponification of fatty acid oils.	b. Analyze and adjust as required.

VIII.4. ELECTROCLEANING

a. *Current Density*: When cleaning anodically, excessive current density may etch a buffed surface or cause excessive darkening. When cleaning cathodically, excessive current density will in rare instances possibly cause plating-out of dissolved metals, and some electrically charged colloids as a non-adherent smut. Too low a current density (cathodic or anodic) can be the cause of poor cleaning. Confirm the current with tong ammeters (if available) and calculate appropriate current density. Good electrocleaning of steel requires a minimum of 5 A/dm^2 and 8 to 10 is better. Brass and zinc die-casting and nickel plate normally are cleaned at 2 - 4 A/dm^2.

b. *Bus Bars*: The bus bars have to be of sufficient size to carry the current required for a workload. Typically 158 A/ cm^2 (1000 A/in^2) cross section of copper bar is required. The bus bars have to smooth and clean to insure good contact. Electrical resistivities of metals and alloy used in electroplating is presented in Table 21 (Addendum).

Table 17. Troubleshooting Electrocleaning Problems

Problems	***Probable Causes***	***Remedy***
Etching; Tarnishing	1.Too high a current density. 2. Cleaner non-inhibited for nonferrous metals. 3. Wrong polarity. 4. Temperature too high for nonferrous metals. 5. Excessive oil in solution.	1. Adjust current density. 2. Use correct electrocleaner. 3. Check polarity. 4. Reduce temperature. 5. Increase conc. or replace cleaner
Roughness	1. Cleaner too weak causing "burns" on steel. 2. Excessive current density in anodic cleaning, pulling alloying elements to the surface. 3. In cathodic cleaning, depositing charged particles & smut on surface. 4. Incomplete rinsing of electrocleaner.	1. Increase conc. or replace cleaner 2. Calculate & adjust proper CD. 3. Reduce CD. 4. Improve rinsing/agitate rinses.
Haze under plate	1. Temperature too high causing dry-on film. 2. Cleaner too weak. 3. Incomplete rinsing after cleaner. 4. Inefficient precleaning or soak steps.	1. Reduce temperature. 2. Adjust conc. or replace. 3. Improve rinsing/agitate rinses. 4. Check & adjust.
Poor adhesion; Blisters; Pitting in deposit	1. Cleaner too weak. 2. Current density too low or too high. 3. Cleaning time too low or too high. 4. Reverse of intended polarity. 5. Hexavalent chromium contamination. 6. Excessive oil/grease in cleaner. 7. Insufficient rinsing after cleaning.	1. Adjust concentration or replace. 2. Calculate & adjust proper CD. 3. Use correct time. 4. Check& correct polarity. 5. Use Cr reducer; Replace bath. 6. Increase conc. or replace cleaner 7. Improve rinsing; agitate rinses; use warm rinses.

c. *Polarity*: Be sure that the polarity is proper for the job. Cathodic cleaning should seldom be used as a final electrocleaning step due to the danger of plating-out dissolved metals and possible hydrogen embrittlement. There are exceptions to this rule, as in electrocleaning lead, magnesium, nickel, silver, and some stainless steels. If doubt exists as to polarity, check with a voltmeter or trace back the conductors to the DC source.

d. *Insulation:* To prevent, ubiquitous stray currents and bipolar effects[42], the tank has to be insulated from the floor. The work, electrode rods and electrodes have to insulated from the tank. Insulated joints on steam, drain and water lines should be provided. Troubleshooting chart is given in Table 17.

VIII.5. RINSING

Rinses should be kept clean and overflowing. Some cleaners require warm rinses for maximum efficiency. The cleaner supplier's instructions should be followed. It is poor shop practice to use a common rinse tank for several purposes. Air agitation in rinses is definitely beneficial.

VIII.6. COMMON PLATING FAILURES ASSOCIATED WITH CLEANING

Some of the typical failures attributable to cleaning and their possible causes are noted below. It should be realized, that there are a number of other reasons for these failures, not necessarily associated with cleaning.

a. *Blisters, Peeling or Poor Adhesion*: Improper polarity in electrocleaner; over-cleaning (current density too high or cleaning time too long); no current in the electrocleaner; oil and grease not completely removed.

b. *Pitting*: Oil and grease not completely removed. If pitting is widespread and on all parts, the trouble is probably in the plating tanks.

c. *Stains:* A problem often associated with bright-plated work. The most common cause is cleaner drying on the work during transfer. It can be eliminated by lowering the cleaner temperature, decreasing transfer time, installing fog nozzles to keep parts wet until they reach the rinse tanks, or by using cleaners designed to prevent staining of sensitive nonferrous metals. It also can be caused by incomplete soil removal, particularly tightly adherent oils of a polar type are almost impossible to remove in alkaline cleaners. Solvent degreasing or emulsifiable solvent pre-dips may be required.

d. *Roughness*: It is caused by failure to remove smut or other solid particles. Sometimes this can be traced back to improper use of vapor degreasing, which removes the oil but not the solid particles. If this is a cause, a high-pressure solvent spray will often help. Incomplete rinsing of alkaline soak or electrocleaners due to excessive water hardness or an exhausted cleaner bath may also cause roughness. Magnetically charged particles can also cause roughness on plated steel parts[106,107].

CONCLUSION

With the objective of the cleaning operation clearly defined, one should be able to choose the system or variation thereof that best suits the line size and production rate requirements. Although the details of reaction mechanisms are not completely understood nor are they readily accessible, enough fundamental chemistry is available to permit efficient process control and modification of cleaning requirements, if needed. Based on the brief introduction to inorganic builders and surfactants and their role in the cleaning mechanism, presented were general discussions of various aspects of their properties, uses and limitations. Anyone browsing related literature would soon realize, that here exists a wide range of works on the subject, organized in a variety of ways, and providing various amounts of specific details. The more inquisitive reader is provided with a quick access to some of the useful concepts related to uses and actions of the components of the industrial cleaners. With some data compilations included, the discussion provided should help point the way to possible solutions of cleaning problems and an understanding of many difficult situations. Where more in depth treatment is required, appropriate references are provided.

The world of surface chemistry, surfactants and their applications, has become one in which the exact meaning of words and phrases are sometimes jumbled by the growth of two basic schools of investigators-the industrial scientist and the academician. To relieve some of the confusion that may arise on the part of the non-specialist, provided is a glossary of some of the most common terms encountered in the practice of the art. Although the definitions given may differ slightly from those found in other references, they are, hopefully practical and meaningful for the understanding of the concepts and phenomena under discussion.

It is customary to discuss and confer the cleaning cycles in considerable detail. This means describing the ideal, or near ideal cleaning cycle, which if followed studiously, will result in the production of excellent plated products, providing that the preplating (cleaning) and plating baths are also in ideal conditions. The reader can work out the extent to which the system can deviate from ideality without running to the difficulties. The most practical cleaning cycles deviate from ideal leaving very little comfort since cleanliness requirements can not be significantly reduced, if all. Quality plating is still required, regardless whether or not the cleaning cycle is ideal.

A successfully operated cleaning process requires careful audit and selection of proper chemistry as well the proper equipment that facilitates and augment the effects of the chemistry.

Because of potential personnel hazards from the use of strong, concentrated and hot cleaning compounds involved, and the potential environmental impact of a large-scale operation, careful planning and equipment design must accompany the choice of a chemical system.

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Table 19. Phosphates as Components of Cleaners Formulations

Product	Formula	M.W.	P_2O_5 [b]	pH[a]	Remarks
-Monosodium phosphate, anhydrous, MSP	NaH_2PO_4	119.98	59.15	4.8	MSP's are available as anh. & as a monohydrate as powder& granules. Used in acid cleaners, boiler compounds, etc.
-Monosodium phosphate, monohydrate MSP	$NaH_2PO_4.H_2O$	7.998	51.43	4.8	
-Monopotassium phosphate, anhydrous MKP	KH_2PO_4	136.09	52.15	4.5	
-Disodium phosphate, anhydrous, DSP-A	Na_2HPO_4	141.96	49.99	9.0	DSP's anhyd. & crystal. More alkaline than MSP. Used in cleaners, water softeners & boiler treatments; as buffers in specialty formulations. Hygroscopic & v. soluble.
-Disodium phosphate, Crystalline. DSP-C	$Na_2HPO_4.12H_2O$	358.15	19.81	8.9	
-Dipotassium phosphate, anhydrous DPP-A	K_2HPO_4	174.18	40.75	9.1	
-Trisodium phosphate, anhydrous, TSP-A.	Na_3PO_4	163.94	43.29	11.8	High alkalinity makes it a good builder for soaps, detergent & specialty products. The hygroscopic TSP has a very much higher water solubility, which is almost constant @ 25 -75°C.
-Trisodium phosphate, hemi hydrate.	$Na_3PO_4.1/2H_2O$	172.95	41.03	?	
Trisodium phosphate, monohydrate TSP-MH.	$Na_3PO_4.12H_2O$	18196	39.00	12.0	
-Trisodium phosphate, crystalline. TSP-C.	$Na_3PO_4.12H_2O$	380.14	18.67	12.0	
-Tripotassium phosphate, anhydrous. TKP-A,	K_3PO_4	212.27	33.43		Available only anhydrous. Bulk density ranges from 67-45 lb/ft^3.
-Sodium tripolyphosphate, anhydrous, STPP.	$Na_5P_3O_{10}$	367.88	57.87	9.6	Largest single phosphate used in the detergent field. It is used as a builder in many metal cleaning products.
-Sodium tripolyphosphate, hydrated	$Na_5P_3O_{10}.6H_2O$	475.97	44.73	9.7	
-Potassium tripolyphosphate	$K_5P_3O_{10}$	448.42	47.48	9.7	
-Sodium acid pyrophosphate, SAPP. $2(NaH_2PO_4) \rightarrow Na_2H_2P_2O_7-H_2O$	$Na_2H_2P_2O_7$	221.95	63.96	4.2	pH =4.3, in the MSP range. Not nearly soluble as its parent components. Valuable in acid cleaning formulations.
-Sodium hexametaphosphate, Polyphos	$(NaPO_3)_6$	-------	65.5-68.7	6.1-7.7; 6.8-6.9	Sequestrants, used in water softening. Rapid reversion to TSP under mild alkaline conditions.

-Tetrasodium pyrophosphate, anhydrous, TSPP.	$Na_4P_2O_7$	265.91	53.38	10.1	TSPP's were used extensively, but replaced by the more stable STP. In heavy-duty liquids & need for a more soluble sequestrants, TSPP & TKPP regained importance. Organic substitutes for both products are being used now more, e.g. EDTA, NTA etc.
-Tetrasodium pyrophosphate, crystalline. TSPP-C.	$Na_4P_2O_7 . 10H_2O$	446.07	31.82	??	
-Tetrapotassium pyrophosphate, anhydrous, TKPP. (Also available in 60% soln.)	$K_4P_2O_7$	330.35	42.97	10.3	

a. 1% solution; b. as % ; c. M.W.= Mol. Weight

Table 20. Buffing Compound- Typical, Basic Composition for Solid Blocks

Copper & Soft metals	Steel
1.Pitch	1. Green chromium oxide
2.Carbon (lamp) black	2. Octadodecanoic acid
3. Octadodecanoic acid	3. Tallow
4.Tallow	4. Petrolatum
4.Petrolatum	5. Alumina white powder
5.Hydrogenated tallow fatty acid	6. Brown aluminum oxide; white for stainless steel.
6.Monocrystaline silica, Tripoly or potassium aluminum silicate (higher PEL number)	
7.Triethanol amine (for liquid compounds)	

Notes. Ratio: powder 70-80 %, binder 20-30 %; Melting point: 50^0C /123^0F;
Acid No:90 ; Saponification No:190.

TABLE 21. Electrical Resistivity of Metals & Alloys Used in Electroplating

Material	Temp °C.	Resistivity Ω-cmγ10^{-6}	Vol. Con.	Material	Temp. °C.	Resistivity Ω-cmγ10^{-6}	Vol. Con.
Aluminum				*Lead*	20	22.	7.8
Pure	20	2.66	65	*Lead*	100	27.8	6.2
Pure	100	3.86	45	*Nickel*	20	6.84	25.2
2S	20	2.92	59				
3S	20	3.45	50				
Beryllium Copper				*Palladium*			
	20	10.0	17		20	5.8	16.
				Platinum	20	98.5	16.3
Bronze							
Phosphor (5% tin)	20				20	4.5	
Phosphor (8% tin)	20	9.6	1813	*Rhodium*	100	6.6	38.
Silicon (3%)	20	13.0	7	*Rhodium*	100	2.115	26.
Aluminum (10%)	20	25.0	12.6	*Silver*	18	1.63	80
	20	13.7		Silver			106.
					20		
Cadmium							
	18		23	*Steel*	100	14.2	
Cadmium	100	7.54	17.5	Mild (SAE-1010)	20	19.0	12.2
Carbon	0	9.82	0.05	Mild (SAE-1010)	100	71	9.1
Chromium	28	3500	13.3	Stainless (18-8)	20	77.6	2.4
Cobalt	20	13.3	27.6	Stainless (18-8)	100	50.6	2.2
Copper-anneal	20	6.24	100.	Stainless (13% Cr)		58.4	3.4
Copper-anneal	100	1.7241	76.	Stainless (13% Cr)	20		3.0
Gold	20	2.28				11.5	
Pure	100		73.4				15.
				Tin			
Pure	0	2.35	58		20		
14 Karat	0	2.97	13		20	48.6	
				Titanium			
Graphite		13.2	0.22				3.55
		800					
				Zinc (pure)		5.9	
							28.3

Note: Vol. Con.= Volume Conductivity (Copper=100)

TABLE 22 . GLOSSARY OF SURFACTANTS & SURFACE CHEMISTRY

Adsorption: The adhesion of a thin film of molecules to a solid or liquid surface.

Amphoteric Surfactant: A surface-active material that ionizes in aqueous solution. The surface-active ion may bear a negative or a positive charge, depending upon the pH of the solution, including also those that are zwitterionic (possessing permanent charges of each type).

Amphipathic Compound: A substance containing one or more polar groups segregated from a relatively large no polar group.

Anionic Surfactant: A surface-active material that ionizes in aqueous solution. The ion that bears a negative charge on the active portion of the molecule and has a pronounced tendency to concentrate at the interface between two phases.

Anisotropic: The condition of having different properties in different directions, invariably due to an orientation of the elements making up the structure.

Autophobic Liquid: One that is unable to spread on its own adsorbed film.

Biodegradability. A measure of the ability of a surfactant to be degraded to simpler molecular fragments by the action of biological processes. especially by the bacterial processes present in wastewater treatment plants, the soil. and general surface water systems.

Cationic Surfactant: A surface-active agent that ionizes in aqueous solution, with the surface-active ion bearing a positive charge.

Cation Exchange Capacity: The capability of a solid to exchange cations initially present on the surface for those in the contacting solution.

Chemisorption: An adsorption process in which the forces involved are of the same magnitude as in chemical reactions.

“C" Point (Cloud point): For nonionic surfactants - the temperature (or temperature range) at which the turbidity appears and surfactant begins to lose sufficient water solubility to perform some or all of its normal functions as a surfactant.

Coalesce: The act of combining to form a single body, as in the case of two oil droplets in an emulsion coalescing to form a larger droplet; the irreversible union of two or more drops (emulsion) or particles (dispersions) to produce a larger unit of lower interfacial area.

Collector: An agent used in ore flotation to promote attachment of solid particles to air bubbles.

Contact Angle: The angle formed by a droplet in contact with a solid surface, measured from within the droplet. An *advancing contact angle* is formed when the droplet advances onto a fresh surface. A *receding contact angle* is formed when the droplet is withdrawn from a portion of the surface on which it has been in contact; the angle formed between a solid surface and the tangent to a liquid drop on that surface at the line of contact between the liquid, the solid, and the surrounding phase (usually vapor or air), measured through the liquid.

Coupling Agent: A material that increases, the miscibility of two liquids or a liquid and a solid.

Counter-ion: The (generally) non-surface active portion of an ionic surfactant species necessary for maintaining electrical neutrality; an ion with electrical charge opposite to the charge on the surface of an aggregate.

Critical Micelle Concentration (cmc): A narrow concentration range, in which surfactant ions or molecules begin to aggregate and form micelle.

Cryoscopic Forces: Forces associated with the freezing of liquids and the crystallization of solids.

Detergency: The process of removing unwanted material from the surface of a solid by various physicochemical and mechanical means.

Dispersion: The breaking up of solid aggregates, and maintaining the individual particles in suspension; the distribution of finely divided solid particles in a liquid phase to produce a system of very high solid/liquid interfacial area.

Electric Double Layer: The excess of ions of one charge type present at an interface and the equivalent amount of ions of opposite charge present in one liquid phase, generally water. In the *diffuse double layer*, it is assumed that the charges in the liquid phase are distributed in accordance with a Boltzmann relation.

Electrocapillarity Effect: The change in interfacial tension that occurs with the charging of an interface.

Electrokinetic Phenomena: The relative motion of a charged surface with reference to the bulk solution.

Electrochemical Potential: The sum of the chemical potential and a term whose magnitude depends upon the internal potential of the phase.

Electro-osmosis*:* The movement of a liquid with respect to a solid wall as the result of an applied potential gradient.

Electrophoretic: The movement of colloidal particles in an electric field.

Emulsifying Agents. Surfactants or other materials added in small quantities to a mixture of two immiscible liquids for the purpose of aiding in the formation and stabilization of an emulsion.

Emulsion: A colloidal suspension of one liquid in another; a system consisting of two immiscible liquids, with one dispersed as small droplets in the other. In certain complex emulsions, a portion of the liquid constituting the external phase may also be found dispersed within droplets of the second liquid.

Fatty Acids: A general term for the group of saturated and unsaturated monobasic aliphatic carboxylic acids with hydrocarbon chains of from 6 to 20 carbons, the name deriving from the original source of such materials, namely animal and vegetable fats and oils.

Fatty Alcohols: Primary alcohols with carbon numbers in the range of C6-C20 historically derived from natural fats and oils, but more recently obtainable from petroleum sources.

Film Balance: An instrument for measuring the difference in surface tension between a pure liquid and one covered with a surface film.

Film Elasticity: The tendency of a foam film to resist distortion by changing its surface tension to oppose expansion or compression.

Flocculation: The agglomeration or sticking together of solid particles or liquid droplets; The (often) reversible aggregation of drops or particles in which interfacial forces allow the close approach or touching of individual units, but in which the separate identity of each unit is maintained.

Foam: Bubbles of gas whose walls are thin liquid films.

Foam Booster: An additive that increases the amount or persistence of foam produced by a surfactant system.

Foam Fractionation: The separation of solutes by frothing.

Foam Inhibitor: An additive designed to retard or prevent the formation of foam in a surfactant solution, usually employed at low concentrations.

Foam Transition Temperature: The temperature below, which the foam is slow draining, and above which it is fast draining.

Free Surface Energy: A two-dimensional free energy term applied to a hypothetical surface phase. Used interchangeably with surface free energy.

Frothing Agent: In ore flotation, an agent used to create a froth, which entraps particles, brought to the surface after bubble attachment.

Head Group (surfactant): A term referring to the portion of a surfactant molecule that imparts solubility to the molecule. Generally used in the context of water solubility.

Hofmeister Series: A tabulation of ions of a given charge and valence according to the hydrated radius of the ions.

Hydrogen Bonding: Electrostatic interactions between molecules or portions of a molecule resulting from the Lewis acid or base properties of the molecular units. Most commonly applied to water or hydroxyl containing systems (e.g., alcohols) in the sense of Bronsted-Lowry acid-base theory.

Hydrophilic: Having an affinity for water. A *hydrophilic surface* is one that is wet by water. A *hydrophilic emulsifier* is soluble in water and promotes the formation of an oil-in-water emulsion; a descriptive term indicating a tendency on the part of a species to interact strongly with water, sometimes equated (incorrectly) to "lipophobic," defined below.

Hydrophobic: The opposite of hydrophilic, having little energetically favorable interaction with water - generally indicating the same characteristics as lipophilic, with the exception that some hydrophobic materials (e.g., perfluoro organics) can also be lipophobic.

Hydrophile- lipophile Balance (HLB): The number and type of hydrophilic and lipophilic groups present in an emulsifier or in a combination of emulsifiers. It is an essentially empirical method for quantifying the surface activity of a species based on it molecular constitution - used primarily in emulsion technology.

Hydrotropic Agent (Hydrotrope): Same as coupling agent.

Interface: The region between two contacting phases, generally two condensed phases.

Interfacial Tension: A force with the dimensions of dynes/cm. A measure of the work required to enlarge the interface by one cm^2. The property of a liquid/liquid interface exhibiting the characteristics of a thin elastic membrane acting along the interface in such a way as to reduce the total interfacial area by an apparent contraction process. Thermodynamically, the interfacial excess free energy resulting from an imbalance of forces acting upon molecules of each phase at or near the interface. (See Surface tension).

Interface. The boundary between two immiscible phases. The phases may be solids, liquids, or vapors, although there cannot be an interface between two vapor phases. Mathematically, the interface may be described as an infinitely thin line or plane separating the bulk phases at which there will be a sharp transition in properties from those of one phase to those of the other, although in fact it will consist of a region of at least one molecular thickness, but often extending over longer distances.

Kraft Temperature: A temperature above which there is a rapid increase in the solubility of an ionic surfactant. Also, the temperature at which the solubility of a surfactant coincides with its critical micelle concentration.

Lipophilic ("fat loving"): Having an affinity for oil. A general term used to describe materials that have a high affinity for fatty or organic solvents, essentially the opposite of hydrophilic. A *lipophilic emulsifier* promotes the formation of a water-in-oil emulsion. Oils wet a lipophilic surface.

Lipophobic ("fat hating"): The opposite of lipophilic, that is, materials preferring to be in a more polar or aqueous media, the major exception being the fluorocarbon materials, which may be both lipophobic and hydrophobic.

Liquid-crystalline Phase: A viscous liquid exhibiting optical anisotropy.

London Forces: Forces arising from the mutual perturbation of the electron clouds of neighboring atoms or molecules; generally weak(~ 8 kJ/mol), decreasing as the inverse sixth power of the distance between the interacting units.

Lyophilic ("solvent loving"): A general term applied to a specific solute and solvent system, indicating the solubility relationship between the two. A highly water-soluble material such as acetone would be termed lyophilic in an aqueous context.

Lyophobic ("solvent hating"): The opposite of lyophilic. A hydrocarbon, for example, would be lyophobic in relation to water. If the solvent in question were changed to octane, the hydrocarbon would then become lyophilic.

Lyotropic Series: Same as Hofmeister series.

Micelle: An oriented aggregation of surfactant ions or molecules. It is composed of a number of molecules of a surface-active material, formed as a result of the thermodynamics of the interactions between the solvent (usually water) and lyophobic (or hydrophobic) portions of the molecule.

Migration Potential: The development of an electrical potential as the result of the movement of small particles suspended in a liquid.

Monomolecular Layer (Monolayer): A film one molecule thick on the surface of a solid or liquid.

Multimolecular Layer (Multilayer): A film two or more molecules thick on the surface of a solid or liquid.

Nonionic Surfactant: A surface-active agent that does not ionize in water and carry no electrical charge. Their water solubility being derived from the presence of polar functionalities capable of significant hydrogen bonding interaction with water, e.g., polyoxyethylenes and polyglycidols.

Nonpolar Molecule: One containing an equal number of positive and negative charges with coinciding centers of gravity. The term nonpolar group is applied to a portion of a large molecule with nonpolar characteristics.

Oil-in-Water Emulsion (OIW): An emulsion in which oil droplets are dispersed in a continuous water phase.

Oleophilic: Same as lipophilic.

Oleophobic: Same as lipophobic.

Polar Molecule: An uncharged molecule in which the centers of gravity of positive and negative charges do not coincide. The term polar group is applied to a portion of a molecule with polar characteristics.

? **Minimum:** A shallow minimum observed in a plot of interaction versus distance between particles. At this minimum, forces of attraction are only slightly greater than those of repulsion, and flocculated particles are readily redispersed.

Sedimentation: The settling of particles due to gravity.

Selective Adsorption: The tendency for one adsorbable species to concentrate at a surface or interface in preference to another.

Soap: The name applied to the alkali salts of natural fatty acids, historically the product of the saponification of natural fats and oils.

Solubilization: The increased solubility of a substance in a surfactant solution relative to its solubility in the pure solvent; the act of making a normally insoluble material soluble in a given medium. The term is applied in two ways: the *solubilization of a hydrocarbon chain* in water by chemical modification - the addition of a head group - and the *micellar solubilization* of a separate oil phase in water or vice versa .

Spreading Coefficient: The change in surface and interfacial tensions caused by the spreading of one liquid on another.

Spreading Pressure: The decrease in surface tension caused by the spreading of an insoluble substance as a monolayer.

Streaming Potential: The potential difference that arises from forcing a liquid through a porous plug or capillary.

Substrate: A substance acted upon, as by adsorption.

Surface: The region between two contacting phases, generally a condensed and a gaseous phase.

Surface-active Agent: The descriptive generic term for materials that preferentially adsorb at interfaces as a result of the presence of both lyophilic and lyophobic structural units, the adsorption generally resulting in the alteration of the surface or interfacial properties of the system

Surface Charge Density: The excess of ions of one charge type per unit area of surface.

Surface Chemistry: A study of phenomena, arising primarily from surface forces.

Surface Excess: The difference between the concentration of solute in the surface region and in the interior of the solution.

Surface Phases: The physical states of monolayers, analogous to bulk phases.

Surface Potential: The change in the potential difference between a liquid and air arising from the presence of a surface film.

Surface Pressure: The decrease in the surface tension of a liquid due to the presence of a surface film.

Surface Tension: The property of a liquid evidenced by the apparent presence of a thin elastic membrane along the interface between the liquid and a vapor phase, resulting in a contraction of the interface and reduction of the total interfacial area. Thermodynamically, the surface excess free energy per unit area of interface resulting from an imbalance in the cohesive forces acting on liquid molecules at the surface; a force with the dimensions of dynes/cm that is a measure of the work required to increase the area of a surface by 1 cm^2.

Surfactant: The widely employed contraction for "surface active agents," used most widely in North America.

Surfactant Tail: In surfactant science, usually used in reference to the hydrophobic portion of the surfactant molecule.

Syndet: A synthetic detergent. European term for surface-active agents.

Tenside: A term for surface-active agents widely employed in Europe.

Water-in-Oil Emulsion (WIO): An emulsion consisting of water droplets dispersed in a continuous oil phase.

Work Function: A measure of the heat of evaporation of electrons.

Work of Adhesion: The work per unit area required to separate two liquids, equal to the sum of the surface tensions of the two liquids less the interfacial tension of the liquid-liquid interface.

Work of Cohesion: The work required to form two sq cm of liquid surface, equal to twice the surface tension of the liquid.