Training “Colombo,” Part III—
Soil Removal

In part three of our series of articles on troubleshooting, we will direct our attention to the types of soils present on parts submitted for electroplating/metal finishing. Some of the material in this article has been borrowed from the AESF course on “Precision Cleaning” by Dave Peterson, consultant.

What Is Soil?
The reference to “soil,” in a metal finishing context, is more than just a reference to dirt that may be present on the surface. “Soil” encompasses any material that may be a barrier to the metallurgical bond between the base metal and the coating to be produced on top of that base metal.

A very simple view of the problem can be obtained if one thinks of all the metal atoms below the surface of the part to be processed. Each of these is atomically bonded to a number of other atoms nearby, creating a crystal structure (see Fig 1). Now, picture the very last atom of metal at the surface of the part. The surface atoms do not have other like-atoms to bond to above them. Therefore, these atoms tend to bond with other available ions in an effort at obtaining a stable existence. These other atoms may be oxygen (very popular), sulfur (popular with copper and silver) and numerous other atoms.

On top of these “foreign” atoms bonded to the substrate to be metal-finished, there are manufacturing and storage lubricants sitting on top of the base metal. Some of these are capable of forming chemical bonds with the base metal as well, while others merely reside on top, waiting to be removed. Of course, there are many facilities that disassemble field-used parts (aircraft re-work, for example), in which case the parts may have a complex mix of soils listed, along with metal smears, oxides and corrosion products.

While some soils are relatively easy to remove, others can be downright impossible. Easy-to-clean soils include dust, dirt, light machining oils, animal/vegetable-based lubricants and rust. Difficult soils include synthetic oils (especially oxidized or burned-on synthetics), buffing/polishing compounds, heat-treating scales and any materials containing silicones (not silicates—siliCONES!).

All of this is “soil” to the metal finisher, and the precleaning, cleaning and acid pickling steps used before plating/anodizing are designed to remove it completely—or to the point where it no longer affects bonding of the coating to the base metal.

A metal finisher should be informed as to what operations were performed in the various manufacturing processes used in producing the part, to allow the most economical and effective steps in cleaning. However, along with or in the absence of this information, the finisher can make his own determination of soil conditions using simple tests. Is the soil oily (wet) or dry? How much particulate matter does it contain? These questions can be answered by simple wiping, touching, transferring to fingers and rubbing.

Wet, oily soils may contain fatty acids or esters of animal, vegetable or mineral origin. These may be distinguished by smell (especially those of organic origin) when they have become rancid. Mineral oil soils are more difficult to remove. Greases are heavy-metal soaps (Ca, Zn, Al stearates) and are not saponifiable or possibly not soluble in solvents, requiring other approaches, such as dispersion or emulsification. Dry, oily soils could contain waxes, petrolatum or polymerized oils, which may require high-temperature cleaners to render the soil fluid.

Particulate matter (smut) dispersed in the soil may be an important consideration in the types of cleaning required. Mis-application of the cleaning cycle may make smut removal more difficult. The organic components of the soil are generally easier to remove and may leave smut on the surface. Then electrostatic forces hold the particles more tenaciously to the surface, rendering removal more difficult.

If a soil contains considerable particulate matter, therefore, it may be advisable to resort (initially) to less-efficient cleaners so that particulate matter is removed along with (or in preference to) the other soil components.

Metalworking Lubricants
Parts that have been stamped, drawn or machined will usually be smeared with lubricants. If the lubricants are
known to contain vegetable oils, then agitated soaks followed by spraying might be the answer. Soils containing straight mineral oils, however, present a more difficult problem. Solvent cleaners (with or without emulsifiers), alkaline soaks and alkaline sprays in a proper sequence are frequently used.

Parts that have been polished and buffed are considered to be difficult to clean. Materials contributing to this difficulty are abrasives, waxes, greases, fatty acids, metallic soaps and vegetable fibers. The job of cleaning becomes even more difficult when the soils have aged, because they tend to harden and dry with time. Vapor degreasing with chlorinated solvents and pressure spraying with hot alkaline solutions are frequently used. In a few cases, the parts are not satisfactorily clean until hand-wiped.

There are occasions when castings coated with very thin films of die lubricants are stored for considerable periods prior to plating. In storage, with changes in humidity and temperature, the parts may corrode. Before polishing and buffing such parts, one should remove the oil and any corrosion products in an alkaline soak solution, followed by a dip in an acidic solution. Failure to do this will result in the imbedding of this mix of corrosion product and oxidized lubricant into the surface of the metal, creating a huge cleaning problem.

Sometimes cleaning of parts is required before heat treatment to remove organic substances that tend to form carbonaceous material (a burnt appearance) during heat treating and subsequent quenching. Hot alkaline soak solutions are often used for this purpose. Strong acid dips are used for parts coated with heat scales. Sometimes the steps are repeated to attain the desired results.

Frequently, protective coatings of phosphate are applied on metals to absorb lubricants (such as soaps or oil) to facilitate forming parts by drawing, stamping or other fabricating operations. After the parts are formed, the soils remaining may be removed by a combination of solvents and a strong alkaline soak or chelated alkaline solutions. The latter removes the phosphate coating. Insoluble, impregnated (*i.e.*, absorbed) soaps, however, can build up in the cleaning solution; subsequently, they are also difficult to rinse off. Filtering may satisfactorily remove the soaps and some oils to extend the useful life of the cleaner and help eliminate rejects resulting from inadequate stripping of the phosphate coating and cleaning.

Metalworking lubricants may be combined with other soils, such as dust, fingerprints, dirt and corrosion products. This type of lubricant varies in composition to such a degree that it is critical to know what kind of lubricant is on the part, in order to optimize the cleaning cycle. Metalworking lubricant may contain additives, such as:

- Boundary additives
- Extreme pressure additives
- Corrosion inhibitors
- Foam suppressants
- Emulsifiers
- Dispersants
- Biocides

Boundary additives maintain lubrication when hydrodynamic lubrication breaks down. Extreme pressure additives are either phosphorus, sulfur or chlorine-based. They chemically bond to a metal, minimizing friction at high-pressure loadings, and are very difficult to remove chemically. Foam suppressants may be polyacrylate or silicone-based. Silicone based foam suppressants wreak havoc on any metal finishing line involving electroplating, by contaminating all processes and resulting in blistered deposits.

Each of the above additives may pose a unique cleaning problem. Consultation with lubricant suppliers and cleaning process suppliers is extremely important in making changes to the cleaning cycle. The following are brief descriptions of commonly encountered lubricants:

### Mineral Oils

Mineral oils are used where lubrication is of primary importance and cooling is secondary. They fall into two groups; paraffinic (straight chain), and naphthenic (ring structure). Paraffinics are usually used as engine oils because of their favorable viscosity index, while naphthenic oils usually are used for metalworking because of their higher solubility for additives.

### Emulsions

Emulsions are also referred to as “soluble” oils. They are typically composed of a mineral oil, emulsifying agents, boundary additives and extreme pressure additives. They are usually mixed with water, forming a “milky” white emulsion. These lubricants have good lubricity and cooling properties.

### Semi-synthetic Lubricants

Semi-synthetic lubricants are also referred to as “micro-emulsions.” They may contain small amounts of mineral oil, emulsifying agents, boundary/extreme pressure additives, foam suppressants, corrosion inhibitors and biocides. These lubricants are more effective at cooling than reducing friction because of the high water content.

### Synthetic Lubricants

Synthetic lubricants do not contain oil. They are based on polyglycol, polyisobutylene or poly alpha-olefin compounds. These are transparent liquids containing dispersants, corrosion inhibitors and foam suppressants. Synthetics excel at cooling over lubricating.

### Natural Oils

Natural oils have animal/vegetable origins. Vegetable oils typically consist of C12-C18 saturated and unsaturated carboxylic (fatty) acids. Animal derivative oils consist of triglycerides and fatty acids. As lubricants, fatty oils tend to be inferior to the preceding materials in all respects, except boundary lubrication.

### Waxes & Tallows

Waxes and tallows are common lubricating ingredients in polishing and buffing compounds. They may be of synthetic or natural origin.

### Acid pickling

An acid dip is also commonly called a “pickle,” although this term is most commonly used for the removal of heat treat scales and heavy oxides. The acid dip neutralizes any alkali remaining after the rinse and solubilizes it. Light oxides, including those formed during anodic electrocleaning, are readily removed. The acid chemically attacks the surface, providing a light or micro-etch and activation, which promote better adhesion of subsequent deposits.

Heat treat scales or heavy oxides are removed (pickled) in either more
concentrated heated acids or in alkaline descaling solutions. Scale removal is usually done as a separate operation outside the plating line. Heat treat scales are usually mixtures of the metal oxides and may require several pickling steps for removal.

Commonly encountered acid pickling problems include:

1. **Inappropriate choice of acid**—Numerous cases of poor adhesion have been solved by substitution of the correct acid mix for the job. Lead, for example, does not dissolve well in sulfuric acid. It reacts with the sulfate to form lead sulfate, a solid material. Lead can be present in brass (see Fig. 2) and steel. Acids containing fluorides will readily dissolve the lead, generally improving adhesion. Silica films on the surface of parts can result in poor-quality deposits. Silicon is a commonly encountered alloying element in cast iron and aluminum parts. Silicon compounds are very soluble in hydrofluoric acid and fluoboric acid (HBF₄).

2. **Galvanic displacement**—Metals that are more noble will produce immersion deposits on substrates that are less noble. For example, steel pickled in acid containing copper contamination will obtain an immersion deposit of copper. Nickel-plated parts can obtain an immersion deposit of gold from plating solutions that contain a high concentration of gold. These immersion deposits have a low level of adhesion when over-plated. Knowledge of galvanic series (covered earlier in this series of articles) can be used to troubleshoot suspected cases of immersion deposits.

3. **Inappropriate acid concentration or other operating condition**—Each acid has an optimum concentration and temperature. An acid pickling problem can often be traced to a weak level of concentration or operation at too low a temperature. One frequently encountered operational error is chemical control of an acid by titration with phenolphthalein (ostensibly to determine the residual or “free” acid concentration). Because this indicator changes color at a high pH (about 8.3), a significant amount of caustic is used in the formation of metal hydroxides, which results in artificially high titrations and an artificially high reading of free acidity. In reality, the acid is too weak. Free acidity titrations should be made using methyl orange indicator (pH ~ 4.3), which does not pose this problem.