

Is It Clean? Testing for Cleanliness of Metal Surfaces^{P 04937}

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CLEANLINESS: UNGLAMOROUS BUT VITAL!

Regular readers of *Metal Finishing* would probably find it impossible to locate a single issue of the journal in which, one way or another, the cleaning of metals prior to their subsequent surface treatment is not mentioned somewhere. Expert after expert delivers the same simple message—poor cleaning is the most common single cause of defect incidence or coating failures. Among the most common failures from poor cleaning, we can mention poor adhesion of coatings, poor corrosion resistance, blistering and pitting, failure to pass specification/standards tests and stained and/or irregular coatings.

To make matters worse, very few metal-finishing processes today are based on a single coating. Duplex metal coatings, metal plus conversion coatings or metal plus organic coatings are commonly found combinations. When these fail, it is mostly the outer layer that manifests the failure—but what is the real cause? All too often, it goes right back to the lowest of the coatings—and the cause is incorrect cleaning. Troubleshooting such situations is an exercise most finishers (except those who fancy themselves as “private eyes”) can do without.

All of the foregoing is as true today as it has been since finishing began; but thanks to new environmental legislation, nearly all metal finishers in the United States and Europe have changed (or are about to change) their cleaning technologies. This might mean new equipment using traditional organic chlorinated solvents, such that their escape into the atmosphere is controlled. It might mean new organic solvents, such as terpenes, or aqueous or semiaqueous cleaning systems. Metal finishing has been getting mixed messages on this front. Some finishers who have converted to aqueous or semiaqueous systems have expressed

themselves as totally satisfied. Others grudgingly accept that the new methods will do the job but still consider that solvent cleaning gave a cleaner surface or was more “forgiving” to operate as a process. We have even heard of a handful of plants that, having made the switch, reverted to solvent cleaning after what they saw as a disastrous experiment. Whichever the case, now more than ever, metal finishers should be on their toes and asking themselves, “Is it clean?”

What Do We Mean by “Clean”?

The answer to this question depends on the metal-finishing process sequence being used. The most common form of surface contamination is oils or greases that originate from mechanical processing, such as rolling, or are deliberately applied as a temporary protective coating for storage or shipping. Mold-release agents are another source of such films and, if based on silicones, are arguably the most difficult to remove of all such films encountered by the finisher. Films of organic coatings such as these are bad news for nearly all metal-finishing processes. The only exception that comes to mind involves solutions containing strong oxidizing agents such as chromic acid, so chromium plating (but not the nickel deposition that usually precedes it) and chromic acid anodizing are two treatment processes that can probably tolerate the presence of organic film contaminants, although, even here, no one is suggesting that this should be put to the test.

Other forms of surface contamination can broadly be classified as “chemical” (e.g. oxides) or “particulate” (dust). Of these, one can make the following comments. Oxides and hydroxides will be removed by cathodic cleaning, by pickling or indeed by the cathodic nature of electrodeposition processes themselves. Particulates can give rise to plating

problems, causing rough deposits and sometimes pits; however, unlike organic films, they can readily be seen either with the naked eye or with a low-power magnifying glass. Ascertaining their presence on the surface therefore presents no great challenge. In short, in mainstream metal finishing, the presence of organic films is both inimical to successful finishing and difficult to detect.

In the printed circuit board (PCB) and related industries, organic contamination as described above is equally undesirable, insofar as electroplating and electroless deposition are key operations; however, a totally different form of surface contamination is no less critical, namely that due to inorganic salts, usually as a result of incomplete rinsing from preceding plating operations. Such residues, on the surface of a PCB, permit the passage of stray (“parasitic”) currents that can cause premature failure as a result of corrosion (these salts are frequently hygroscopic). This process is sometimes known as “tracking.”

To detect such contaminants, the PCB industry has evolved standard test patterns for measurement of surface insulation resistance. In addition, conductivity measurements of rinse water provide a means by which the danger of low surface insulation resistance values can be signaled. The Institute for Interconnecting and Packaging Electronic Circuits coordinates such standards for the industry. Mainstream finishers in the United States, the United Kingdom and most other countries have no American Society for Testing and Materials specification or similar standard to guide them.

How Clean Should a Surface Be?

There have been various attempts to provide a quantitative basis for measuring surface cleanliness; however, any such units must to some extent depend on the nature of the soil and the

method used for its measurement (e.g., chemical or physical). There is thus no simple answer to the question of how clean a surface should be, beyond suggesting that if a suitable test has been found, the results of that test can be matched to the performance of whatever surface treatment is subsequently applied. Without doubt, some processes are far more sensitive to the presence of soiled surfaces than others. In some cases, the actual surface treatment process incorporates its own cleaning action.

Vacuum-based methods are also a possibility for cleaning surfaces. Even in a moderate vacuum, lowering total pressure will increase the rate of evaporation of an organic from the surface, although this may still take many hours to volatilize completely. In electron or ion beam or plasma methods, the surface can be bombarded with ions such as argon that are highly effective in providing a new and therefore clean surface.

As a generalization, it is probably true that water-based coating processes are more sensitive to even monolayers of organic surface contamination than solvent-based paint processes. In the latter case, because there will almost certainly be some mutual solubility between the organic contaminant and the solvent in the paint, the "barrier" effect that operates in the case of aqueous processes will largely disappear.

METHODS FOR MEASURING SURFACE CLEANLINESS

The importance of being able to assess surface cleanliness was recognized early in the 19th century. In surveying the literature on the subject, there is no doubt that a high point was the American Electroplaters and Surface Finishers Society (AESF)-sponsored research project in the early 1950s, headed by H. B. Linford. This project, a model of its kind, started with an exhaustive review of the literature, went on to make a quantitative comparison of the various tests and concluded by suggesting modifications to some of the older methods. The results were published in successive issues of *Plating*¹⁻¹³ and were also issued by the AESF in booklet form.

The first industrially significant test for surface cleanliness goes back to the

American Civil War, when photographers recognized the importance of having clean glass plates before application of the photographic emulsion to the plate surface.¹² Since then, a number of methods have been developed for measuring surface cleanliness.

- Visual (optical, microscopic)
- Water break
- Spray/atomizer
- Fluorescence
- Contact angle
- Radiotracer
- Stimulated electron emission
- Attenuated total reflection spectroscopy
- Combustion and carbon dioxide analysis
- Surface conductivity
- Scanning electron microscopy
- Auger spectroscopy, ESCA
- Ellipsometry
- Analysis of washings
- Copper displacement
- Dye methods
- Other

These methods can be characterized in two different ways. First, there are complex methods that can only be carried out in well-equipped laboratories. These contrast with the simpler methods that were devised to be used either on the production line or in a very modestly equipped production laboratory. Second, there are methods that indicate only the degree of cleanliness, without offering any insight into the nature of the contaminant, in contrast with other techniques that actually provide a degree of "chemical" information. Examples are (in the first category) techniques that measure wetting or contact angle and (in the second category) attenuated total reflection spectroscopy.

Although the purpose of this report is to provide the most extensive overview possible of such methods, the simpler methods are emphasized. For those with the means and resources to pursue the more complex techniques, the relevant literature is cited.

OVERVIEW OF SIMPLE METHODS

The following methods can usually be implemented without any specialized equipment. They are at best semiquantitative, at worst subjective.

Visual and Optical Inspection

Visual inspection of a bright metal surface by eye reveals only the grossest soils. Neither passive oxide films nor thin layers of grease are thus to be seen. Ellis¹⁴ mentions such inspection as well as that enhanced by the use of a hand-held magnifier. Although the latter enables finer particulate soils to be seen, the invisibility of oxide or grease layers remains. Even if an optical microscope is used, this is still true, and although the latter allows particles down to the limit of optical resolution (governed by the wavelength of light) to be seen, care must be taken that airborne dust particles do not falsify the results by settling on the test surface during the examination or while the sample is in transit to the microscope.

Another visual method is to wipe the surface with a paper tissue or a piece of white cloth, such as cheesecloth, which can then be inspected by eye or with a magnifying glass. A white cotton glove can also be used. This approach has been described by Linford and Saubestre.⁷ In cases where the sample is not bright and smooth, visual examination is of little use, whereas the wiping method may provide some insights.

Even the simple approach based on wiping can be made quantitative, as suggested by Brandon.¹⁵ A pressure-sensitive tape is used to pick up particulate soil and this is then viewed in a densitometer, which records the change in optical density resulting from pickup of the soil.

Wetting Behavior

A clean metal surface is "hydrophilic" and will thus be fully "wetted" by water. The presence of grease will prevent this, and, rather than spreading as a uniform thin film, the water or moisture will break up into discrete droplets. Passive oxide layers behave no differently from pure metal in this respect, and water wetting is thus not a test for the presence of such layers. From this principle, a number of tests have been devised.

Breath Test

Simply by breathing onto a surface and observing the result, a judgment on cleanliness can be formed. A clean surface produces a uniform clouding. A greasy one will show droplets.

Water-Break Test

Water is applied to the metal surface, usually inclined at approximately 45° to the vertical. The formation of discrete droplets suggests the presence of hydrophobic impurities on the surface, usually of long-chain hydrocarbons. Lutter¹⁶ points out that another cause may be the use of hard water. Calcium ions can react with long-chain fatty acids to form hydrophobic metal soaps. If this is suspected, the test should be repeated with deionized water. Lutter makes the further point that, in plants fitted with recycled water from an ion-exchange unit, there is the danger that although calcium ions are removed, the concentrations of nonionic surfactants will build up, and these can interfere with the test.

Cohen and Hook¹⁷ make the point that this test will not detect contamination by soaps or surfactants, nor will it detect water-wettable particles, such as rust, oxides or other finely divided metals. In the same way, the presence of surfactants in the water used for this test will interfere with the results. In some cases, the use of water is undesirable because it can cause rapid rusting. Cohen and Hook also mention that the thinner the water film used in this test, the more sensitive it is. Still other weaknesses in this test are due to "bridging" of a small contaminated area by a film of water.

In another version, described by Linford and Saubestre, panels are rapidly removed from the test bath, and the number of seconds for water break to occur are noted. Panels are withdrawn vertically and should be so held above the solution. Alternatively, after withdrawal, they can be inclined at 45°, with water from a wash bottle being applied, thus flooding the surface for approximately 20 sec. Linford and Saubestre⁷ suggest that the latter method has a slight drawback because it allows oil to migrate downward during the test procedure.

Spray Pattern or Mist Test

This test, although similar to the water-break test, is less sensitive to the presence of soaps or surfactants and thus forms a better basis for a simple, routine works test. The wetted metal surface is sprayed from a distance of 60 cm with distilled water from a spray gun operated at 0.6–1.0-kg/cm² air pressure for 30–50 sec. The resulting

patterns are observed. Two variations are described by Lutter.¹⁶ In the first, which increases the sensitivity of this test, the metal is previously etched in 1% hydrochloric acid. In the second, the spray water is dyed with approximately 0.1% of a blue dyestuff.¹⁸ Cohen and Hook¹⁷ describe how the method can be made quantitative by placing a sprayed panel inside a viewing box with a grid of 100 squares and tracing the pattern with a pencil. The number of squares appearing clean are counted, and this procedure is averaged over five panels. The result, expressed as a number (out of 100), was named the "cleanliness index" by Linford and Saubestre.⁵ An alternative procedure, described by Linford and Saubestre, is to spray the panel after carrying out a water-break test for approximately 15 sec. Because the panels hang vertically, evaporation to dryness begins at the top of the panel and works its way downward until only drops at the bottom remain. The thickness of the resident water film is thus related to its position on the panel, and the spray pattern test is more sensitive near the top of the panel (where the film is thin). Even the slightest trace of oil droplets near the top of the panel can cause quite widespread areas being formed in the spray pattern, whereas near the bottom, the water droplets only form directly above the oil droplet. This makes the time factor critical. In laboratory conditions, clean areas will typically remain wetted for up to a minute, after which dry patches will appear, initially at the top edge of the panel; however, if spraying is commenced too soon (less than 45 sec after drainage), some areas of potential water break may still be wetted because there is still a fairly thick water film on the surface.

Atomizer Test

This variant of the spray pattern test was devised by Linford and Saubestre.⁵ The test is applied to a dry, not a wetted, surface. The resulting wetting action requires a higher surface energy than for the already wetted surface of the spray test. In consequence, this test is more sensitive to the presence of small amounts of grease, etc. Cleanliness can be assessed in terms of the area of wetted surface and also by estimation of the contact angle of residual nonwetted water droplets.⁶

Mercury Droplet Wetting Test

If a droplet of mercury is placed on a truly clean metal surface, it will spread. The presence of grease will cause it to retain a roughly spherical shape. The same is true (and here the mercury behaves unlike water) if oxide films are present at the surface.

Talc Test

The smooth surface to be tested (metallic or nonmetallic) is lowered vertically into a container of water, the surface of which has been dusted lightly with talc. The interaction of the talc particles with the smooth surface is observed. This method has been described by Donelson and Neish.¹⁹

Another use of talc or lycopodium powder is described by Lutter.¹⁶ This is not used directly as a cleanliness test but to detect the presence of oily layers on the surface of a cleaning bath. It will be evident that where such layers are present, however much a metal is cleaned by immersion in solution, on being raised from the cleaning solution, it will pass through such oily films and be contaminated by them. According to Lutter, when paraffins or other nonpolar hydrocarbons are present on the surface, they form spherical or lens-shaped globules. In the presence of polar substances, such as drawing lubricants, the hydrophobic dust particles are displaced.

Copper Displacement Test

If a metal such as steel is immersed in an aqueous solution of copper sulfate, a so-called "displacement reaction" will take place—a pair of coupled electrochemical reactions in which the less noble metal (the steel) is anodically dissolved, to be replaced by the more noble metal (copper) depositing from solution. The old school trick of immersing a copper coin in a solution of silver nitrate to produce a silver coating is another example. If, however, the metal surface is obscured by a layer of grease, this exchange reaction will be impeded or may not take place at all. Linford and Saubestre recommend the following solution composition: 63 g/L copper sulfate (pentahydrate) and 17 g/L sulfuric acid.

The panels are dipped rapidly into solution, held motionless for 10 sec and then removed rapidly and trans-

ferred to a beaker of distilled water in which they are agitated for 15 sec. They are then hung vertically, washed for 20 sec with water from a wash bottle and allowed to dry, preferably using radiant heat from a bright light source, for example. Ether extraction is used to remove any remaining oil patches, and the panels are then examined.

Potassium Ferricyanide Test (Ferrous Surfaces Only)

Rag-bond paper is cut into strips approximately 6 × 12 cm. It is coated on one side with a solution of 50 g/L crystalline white gelatin and 50 g/L sodium chloride (chemically pure grade will do). The strips are laid flat on a sheet of glass, and a glass rod, dipped in solution, is rolled from one side to the other. This process is repeated four times. The paper is then allowed to dry and can be stored ready for use. Before testing, the paper is soaked for up to half an hour in the following solution: 50 g/L sodium chloride, 10 g/L potassium ferricyanide and 1 g/L hydrochloric acid. Linford and Saubestre⁷ make the point that it is wise to include acid in the above formulation because, should it be omitted, the blue color formed tends to be streaky and light, making the identification of oily patches difficult.

The test piece (a metal panel) is laid flat on a piece of glass, and the impregnated paper is applied to its surface, with the gelatin-coated side in contact with the metal. A glass rod covered with an 8-cm length of rubber tubing is rubbed briskly over the metal surface for approximately 15 sec. Additional test solution is poured over the paper until it is completely remoistened. After 3 min of contact, the paper is removed and allowed to dry. Clean areas will be relatively dark blue on the test paper, whereas oil-contaminated regions will appear as colorless or yellowish zones. No notice should be taken of the odd streakiness in blue zones, which may be due to poor surface contact, bad drying or oxidation. This is especially true with respect to the areas close to the edges. If the time of contact is too long, the blue color will partly disappear.

Linford and Saubestre suggest an alternative procedure (generally less satisfactory), and this is to dip the

panel, after testing, into 1 vol % hydrochloric acid and study the blue pattern. Pollack and Westphal²⁰ quote, as a source of information, an article by Macnaughton.²¹

Fluorescence Test

Some mineral oils and greases will fluoresce in UV light, and this has been used as a quantitative means of estimating the amounts present.²² For those greases (mainly animal or vegetable) that do not themselves fluoresce, use of a hydrocarbon-soluble indicator dyestuff may be made. Typically, UV radiation of approximately 365 nm is used. In its crudest form, a subjective assessment can be made using commercially available UV light sources. To place the test on a quantitative basis, the results are photographically recorded, using a UV filter. The sensitivity of the method is linked to the length of the photographic exposure, which can range from 1 min to 1 hr. Such time extension increases the sensitivity by approximately 15 times and allows residues of some 0.12 g/m² to be measured.²³ Since the time that this sensitivity was quoted, there have been advances in both film sensitivity and fluorescence activity of dyes. One would therefore expect even lower amounts of soil to be detected.

Linford and Saubestre⁷⁻⁹ used both mineral and lard oils to test degreasing procedures, and both of these are only faintly fluorescent in UV. They therefore used the dye fluorescent green HW. Although this is described as being "oil soluble," they found it impossible to dissolve sufficiently high concentrations and therefore resorted to an indirect technique. Approximately 1.7 g of dye was dissolved in 50 ml of solvent (Linford and Saubestre used benzene, which would almost certainly be prohibited today). This solution was then heated over a water bath until its volume was reduced to approximately 8 ml. A refluxing action down the container walls prevented crystallization of the dye. This concentrated solution was clear, dark red and free-flowing. While it was still hot, some 400 ml of oil was added to the beaker, and this solution was used for testing. In the case of mineral oil, some precipitation was occasionally seen after a few days, and this was removed by decantation or similar methods.

Animal fats did not produce similar solids.

Lutter¹⁶ makes the point that because such a wide range of organic compounds fluoresce, the presence of dust particles can interfere. Likewise, many surfactants will fluoresce, and these will give false indications even where they are present as fully water-soluble species. A further criticism of the test is that hydrocarbon-soluble dyestuffs can be water solubilized by synergistic effects (i.e., made hydrophilic). In consequence, the degreasing solution and, equally, the adherent water layer on the test sample being withdrawn from it, may contain such water-solubilized dyestuffs, which, because they fluoresce, will again interfere with the test.²⁴

Dye Test

This test, again described by Lutter,¹⁶ seems little known outside Germany. A sample of the cleaning solution is placed in a beaker and raised to its prescribed operating temperature. A sample of metal for degreasing is then introduced. As a result, the heavy soil components (some inorganic, some organic) settle at the bottom of the beaker, whereas lighter oily components float on the surface. An oil-soluble, water-insoluble dye is then added, such as Sudan blue. This colors the hydrophobic phase as well as surface films of metal soaps or monomolecular layers, rendering them visible. The bath is then stirred, using a magnetic stirrer. To facilitate comparison, a constant stirring speed should be set. By study of the system, especially from the size of the droplets of the blue-dyed oily phase, the surface energy and thus the cleaning efficacy of the solution can be judged. The smaller the droplet size, the better it is. After stirring is switched off, the time for the emulsion to re-form is noted. Baths with strong cleaning effect can maintain the oil droplets in suspension for longer or even maintain the emulsified state, as shown by cloudiness of the solution. Depending on the type of cleaning solution used, emulsions can be stable for hours, even days, before breaking up to give a discrete oily phase.

High-capacity cleaning baths are characterized by a transparent and stable blue-colored colloidal solution,

the presence of which can be verified by a Tyndall effect. A further refinement of this test is as follows. A sample of the work being cleaned is withdrawn from the solution. The dyed liquid droplets should all roll off the surface; residual oil droplets can be easily detected thanks to their color. The volume of cleaning solution dragged out in this way can be easily determined by colorimetry.

Yet another variant of this dye test can be carried out by dyeing the cleaning solution yellow, using a color that is totally insoluble in the oily phase. Magnetic stirring is applied, and, in the presence of the finely divided blue-colored droplets, a complementary green color is seen in solution, at times only transiently. As soon as the stirring is stopped, this vanishes. Cleaning baths not suitable for practical use are those in which the blue oily phase rapidly separates from the yellow aqueous phase, rising to the surface.

Emulsion-type baths tested in this way give a milky cloudiness with a green-colored emulsion; high-capacity baths, in contrast, give a totally transparent green solution that is stable for extended periods of time. Only when such baths have reached maximum oil uptake capacity does a discrete blue-tinted upper layer form on the surface!

High-capacity cleaning baths that contain emulsifying agents, solution promoters and hydrotropic substances must first be tested to determine whether they are capable of solubilizing dyestuffs that are normally insoluble in water.

Lutter¹⁶ suggests that the dyestuff tests described above are close to actual conditions, and in addition require little time or materials to carry out. They provide insights into the behavior of cleaning baths and also of specific lubricants or pastes used in processing.

Clock Reaction for Copper and Its Alloys

Granata et al.²⁵ described a simple method, albeit one that is only useful for copper and its alloys. This is based on the so-called "clock reaction." Such reactions, well known to chemists, are homogeneous solution reactions exhibiting a measurable induction period. Strictly speaking, such

reactions might better be described as "alarm clock" reactions because, to the outside observer, nothing appears to happen until the "alarm goes off," when there is, for example, a color change. In this case, a solution is made up with 0.025M sodium polysulfide. This is formed by dilution of a 2.66M stock solution. The copper sample is placed in a Petri dish, and the cleanliness is related to the time taken for the sample to turn black; the cleaner the sample, the shorter the time. Granata et al.²⁵ quote times of 16 sec for freshly abraded copper, increasing to 40 sec after such samples have been exposed to the atmosphere for four days. Formation of oxides on the surface (e.g. by heating in air at 100° C for 6 hr or immersion for a day in sodium hydroxide) increases the times to blackening to 75 and 585 sec, respectively. As an alternative to color change, Granata et al. describe how a potentiometric measurement may be carried out using a saturated calomel reference electrode.

Spreading Wetting Test

Jones²⁶ rightly describes the water-break test as a "go, no-go" procedure and offers an alternative suggestion. A series of solutions are made up, ranging from 80% ethanol and 20% deionized water to one with 1% ethanol and 99% water. These solutions exhibit a range of surface tension from 24.5 (corrected for variations in specific gravity) to 66 dyne/cm. Above this, solutions of potassium carbonate are used to produce (800 g/L) a solution with 101 dyne/cm. By application of a drop of each solution and examination to see whether it forms a bead or a wetting film, surfaces can be "calibrated" with regard to their surface energies.

Another description of the same approach is that by Renaud²⁷ who uses a range of six liquids of varying surface tension. A known, small volume of each liquid is dispensed (5 µl) from a microsyringe, and the degree of spread is observed. Renaud rightly makes the point that the results of this type of test will depend on whether there is any physical or chemical reaction between the test liquid and the film (if any) on the surface. A further exposition of the method has been given by Cohen and Hook,¹⁷ and Bystry and Penn²⁸ have

also described the use of the method.

Other Simple Methods

Pollack and Westphal²⁰ list most of the above methods and others as well. These include the following:

1. *Gravimetric test*—one of the least sensitive.
2. *Mears test (Elms modification)*. Single drops of an aqueous solution containing 32 ml/L of 30% hydrogen peroxide are applied to a surface, and the time taken for corrosion to appear is measured. The test is described as "not very satisfactory."
3. *Simple contact angle test*.
4. *Oil spot test*. A droplet of degreasing solvent is applied to the so-called clean surface and then evaporated. Formation of a ring suggests the presence of oil.
5. *Rock Island drop test*. Distilled water droplets are allowed to fall from a specified height onto the test surface. The method is said to distinguish between a clean surface and one soiled with a 0.01% oil solution.
6. *Ring test*. A drop of water is formed on the ring of a surface tension tester, and this ring is then lowered to contact the test surface. The process is repeated, and the number of such contacts required to transfer all of the water is noted.
7. *Kerosene viewing of water break*. A wetted panel is dipped into a beaker of kerosene lit from below. Near water breaks are displaced by kerosene, giving a sensitivity better than the usual water break. The sensitivity is said to be equal to or better than the atomizer test.

Of the simple methods that Linford and Saubestre tested and compared, they concluded that the ranking of sensitivity was atomizer > fluorescent dye > spray pattern (water break) > potassium ferricyanide dip > copper sulfate dip. Linford and Saubestre's work, which is too extensive to reproduce or even summarize here, provided comparative data not only for the various methods cited above but, in a second classification, in terms of the type of grease used to contaminate the surface of the metal (e.g., animal or mineral in origin).

Table I. Sensitivity of Test Methods

Method	Minimum Detectable Residue (g/m ²)	Relative Sensitivity
Fluorescence	0.225	1
Water break	0.022	10
Radiotracer	0.002	110

MORE COMPLEX METHODS

Included here are techniques that do call for some instrumentation, although they require no very expensive equipment.

Radiotracer Method

Radiolabeling was a technique very widely studied and favored from the 1950s onward, when radioactive isotopes first became available. There are probably hundreds of publications (see, e.g., Chapter 21 in ref. 29) in which the adsorption of organic species on a metal surface has been studied. If the first such studies were made in the United States in the 1950s, the great bulk of subsequent work emanates from the Eastern European countries, and although the method appears to have fallen out of favor in the West, it continues to be used in Eastern Europe. The increasing availability of radioisotopes explains the rise in popularity of the method. The subsequent tightening of legislation and regulations governing the use of radioisotopes in laboratories and in industry explains why the method has largely fallen from favor. Indeed, it would not be far from the truth to suggest that for these reasons the method is now only of interest for historical reasons and for very specialized research. As a method for routine industrial use it is fair to state that the procedural requirements involved in the use of radioisotopes make the method more trouble than it is worth. In this spirit, it is worth reproducing the data shown in Table I.²³

Radiotracer methods had a brief revival in popularity in the form of the evaporative rate analysis method used to characterize the cleanliness of razor blade edges. The essence of the method was to determine the rate at which a test liquid containing a radiotracer element evaporated from the metal surface. As little as 0.02 µg/cm² of oil could readily be detected in this way. Typical radiotracers were *n*-tridecane (with carbon-14) or 1,1,2,2-tetrabro-

moethane. Solvent carriers were cyclopentane, straightforward freons or freons with 10% chloroform. The essence of the method is that, by interactions and mutual solubility, the presence of grease on the surface can inhibit the rate of evaporation. A method was described at length by Andrade³⁰ and earlier by Hamilton.³¹

Measurement of Contact (Surface) Potential Difference

Guttenplan³² describes the surface potential difference method, which, unfortunately, once again uses a radioactive source. In this case, the radioactivity is used to initiate ionization. The probe is placed some 1–10 mm above the test surface in air, and the potential difference is electrometrically measured using a high-impedance instrument. The basis for the method is the effect that surface films have on the electronic work function of a metal (energy required to withdraw an electron). In his report, which also cites use of the method to characterize aluminum after conversion coating, Guttenplan compares its sensitivity with the water-break test, finding it easily capable of detecting films that were not shown by the water-break test. The report describes plans to develop a commercially available instrument, but it is not known whether this was ever produced.

Another variant of this method—electrostatic charge decay—measures this quantity and also contact potential difference. It was developed for use on the space shuttle to check the cleanliness of the aluminum surface on the fuel tanks and has been described by Cibula et al.³³

Combustion Methods

By introduction of a sample of metal to a furnace and passage of oxygen over the surface, oily matter is oxidized to carbon dioxide and water. The former species is determined by one of a number of analytical methods. To ensure complete combustion to carbon dioxide rather than the monoxide, a

catalytic stage is included (e.g., using silver wool and barium chromate). A description of the method with typical data, including reproducibility, was published by Kresse et al.³⁴ The technique is not overly sensitive; 5–25 mg/m² was used in this particular work. Oxidation times are typically 15 min and oxidation temperatures approximately 600°C. The criticism has also been made that soils not containing carbon pass undetected by this method.

Cohen³⁵ describes a variant of the method used by the Ford Motor Co. as follows. A fiberglass cloth saturated with 50% hydrochloric acid is used to mop a 4-in. × 12-in. steel panel. After appropriate drying, the carbon content is determined by combustion in oxygen at 400 and 600°C, the carbon dioxide being determined in one of the usual analytical procedures.

Contact Angle Measurements

Related to the spreading wetting tests above, but more sophisticated in its approach, is the actual measurement of the contact angle of a sessile drop, which has been mentioned by several authors, including Cohen³⁵ and Rice.³⁶

Washing Tests

A family of tests have been developed, mainly by the electronics industry, in which the surface to be tested is washed with an aqueous or nonaqueous solvent. The washings are then subjected to analysis. A trenchant criticism of this approach is that it detects only soil that has been removed, not that remaining on the surface. In a sense, it is precisely the latter rather than the former that is of greatest concern. A full treatment of this class of test is given by Ellis.¹⁴

Analysis of Washings

The simplest method for washings analysis is conductimetric, and this, as Ellis describes, has formed the basis of several commercial instruments; however, it should be clear that the presence of ionic species (acids, alkalis and salts, mainly inorganic) is of greater concern to the electronics industry than to the majority of surface treatment processes. That said, such contaminants can interfere with other surface treatment processes, for example, phosphating.

OTHER METHODS

Space does not allow more than a brief mention of other methods. Perhaps the most useful for practical purposes is the optically stimulated electron emission method in which light in the visible or UV region irradiates the surface, and the current resulting from emission of the stimulated electrons is recorded. The method has been described by Chawla³⁷ and is of special interest because it is the only "modern" instrumental method not involving major financial investment. The use of attenuated total reflection in the infrared region can lead to identification of the actual contaminants. The surface insulation resistance method is best carried out using a standardized "maze" pattern of electrically conducting tracks on an insulating substrate. This is formed by the normal methods used in fabrication of PCBs. Then, too, there are the methods using scanning electron microscopy (enabling density of resident particles to be counted) as well as analytical methods such as Auger electron spectroscopy or electron spectroscopy for chemical analysis. These can, of course, allow inferences to be drawn as to the nature of the surface contaminant, but their use is limited to the largest organizations that have such equipment in house.

CONCLUSIONS

This report will serve to give some idea of the wide range of test methods for assessing surface cleanliness developed over the years, although it does not claim to be exhaustive. How is a prospective user to choose among them? Clearly, they can be ranked in terms of the cost of equipment or instruments required to carry out such tests. Then, too, the nature of contamination will affect the choice. Particulate soils are not suited to some of the methods described above, and even in terms of oily layers the nature of the oil can be important. The same questions affect the issue of test sensitivity. Linford and Saubestre carried out tests in which the sensitivity of some of the simpler methods was compared. What is undoubtedly true is that the ever-decreasing cost of computer-linked optical scanners or cameras should prompt a reassessment of the methods

that previously relied on superimposition of grids to derive a quantitative result. And, most certainly, such is the diversity of methods available that no metal finisher should be able to offer any excuses for processing poorly cleaned work.

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Biography

After majoring in chemistry at Oxford University and receiving a PhD in electrochemistry there, Anselm T. Kuhn worked as an electrochemist for Leeson Moos in New York and then with John Bockris at the University of Pennsylvania. In the United Kingdom, he was a researcher with ICI before starting a career as a university teacher at Salford University and then London University. He is the author and editor of several books and over 100 research publications. Currently he is Managing Director of Finishing Publications Ltd. and Metal Finishing Information Services, both based in Stevenage, U.K. MF

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