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VERIFICATION OF CLEANLINESS — WHAT DOES IT MEAN?

by

L K Jones

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VERIFICATION OF CLEANLINESS—WHAT DOES IT MEAN?

In the area of contamination control, we are faced with the problem of defining cleanliness and with some answer to the question—"How clean is clean?" For many of us, cleanliness is an intangible term. The degree of cleanliness we wish to achieve lies somewhere between that of an atomically clean surface and that of a surface which causes component failure. In some cases an atomically clean surface is desirable; in others, metal surfaces so clean can lead to galling. From the practical standpoint, atomically clean surfaces are out of the question and we strive for surfaces that are clean enough for our intended purpose. Cleanliness, then, is a degree of controlled contamination in which we know the types and degree of contamination present, the sources of contamination, and the means by which we control the amounts of contamination.

The foregoing statement represents quite a large order. It implies that we must be capable of detecting and identifying contaminants. It implies that we must be completely familiar with the many materials and process variables which are associated with a single part and consequently with our entire assembly. It implies that we understand the absolute necessity of optimum process control, the mechanism and techniques of cleaning for the removal of contamination and manufacturing debris, and the need for protection by recognized clean-room techniques.

James F. Halpin, Director of Quality, The Martin Company, Orlando Division, has defined contamination as follows: "Contamination is when an object is in a place not required by the drawing or specification."¹ We may choose to define it as a material out of place, since the contaminant may be either particulate or thin film in form. A partial list of contaminants encountered may be grouped as follows:

Nonwetable (hydrophobic)

1. Oils, fats, waxes
2. Fatty acids and their salts
3. Some organic solvents
4. Some dusts from the air

Wetable (hydrophilic)

1. Metal oxides
2. Cleaning residues
3. Water soluble acids, bases, and salts

Particulate

1. Lint
2. Hair, fingernail polish, epidermal scale
3. Rosin particles and other process material debris
4. Metallic burrs, solder pellets, wear debris
5. Airborne algae, dust, and other miscellaneous particles

A variety of methods are available for contaminant identification—microscopy, chemical analysis, emission spectroscopy, and infrared spectrometry, to name only a few. In order to solve high contact resistance and other component problems caused by contamination, our group in surface chemistry has been involved for the last seven or eight years in the area of detection and identification of contaminants. Many useful techniques have been employed, and, where applicable, new developments in instrumentation have been evaluated. For example, Dr. R. E. Cuthrell of Sandia Corporation is currently adapting an infrared reflectance technique in order to identify organic films as thin as $200 \text{ \AA}$ (0.02μ) in areas as small as 0.1 mm^2 . A full discussion of various identification techniques, however, is beyond the scope of this paper. It should be obvious that our quest for cleanliness must begin with highly trained technical personnel who may aid us in the identification of the problem contaminant.

A knowledge of the identity permits us to work back to the source. In order to recognize the source, we must be aware of the contributions of the many materials and processes involved in the build-up of the component. We must possess an intimate knowledge of the behavior of materials, the intricacies of manufacturing processes, and the essential variables which must be controlled.

A partial list of contaminant sources (Table I) and of processing faults (Table II) which lead to contamination may indicate the problem we have in tracing our now known contaminants.² It must be emphasized the lists are by no means complete.

TABLE I

Common Contaminant Sources

1. Silicone oil
2. Lubricants
3. Epoxy adhesives
4. Soldering and brazing fluxes
5. Outgassing
6. Sealing compounds
7. Corrosion products
8. Parting compounds
9. Molded parts
10. Paint coatings
11. Plating
12. Machining and finishing
13. Heat-treat processes
14. Wear particles
15. Component and piece-part storage
16. Processing
17. Handling
18. Ovens or furnaces

TABLE II

Common Processing Faults Leading to Contamination

1. Handling or touching parts with bare fingers
2. Touching inside of clean containers with bare fingers
3. Using improper wrapping materials
4. Using uncovered parts containers for storage or transfer
5. Using dirty parts containers
6. Using improper parts containers (sealing methods)
7. Using dirty drying ovens
8. Using improper clothing on operators
9. Using dust catching work areas
10. Using contaminated solvent or overusing cleaning solutions
11. Misusing ultrasonic cleaning machines
12. Using improperly distilled solvents
13. Purchasing solvents in excessive quantities
14. Using the wrong type of solvent containers (allow contamination)
15. Using the wrong solder flux
16. Over-oiling tools and equipment
17. Mixing sealing compounds improperly and over-using or misusing
18. Storing parts in solvent. (The solvent may react to make contaminants left on the part insoluble.)

It can be seen that our materials and process knowledge must be enlarged to include the "contamination potential" inherent in each material and process used for our part or component. Contamination

control, then, becomes quite a complex problem. Great strides have been made in recent years in recognizing the contribution to "dirtiness" by airborne material and in its control by clean-room techniques. We have not made the same giant steps in recognizing many other sources of contamination or in recognizing the necessity of control and removal of nonairborne contamination.

The foregoing discussion has shown what may be present on parts or in components. We now must have a test or a series of tests which will tell us we have observed all the rules, and that we have reached our nebulous goal—our desired level of cleanliness.

Verification of Cleanliness

One of the largest problems is the determination of the relationship between cleanliness and the function of the part or final assembly.¹ Even with a tremendous bank of data, it is difficult to relate degree-of-cleanliness with desired performance. We do not have the background in cleanliness and contamination control that we have, for example, in the determination of the hardness of our metal parts. In this case, we know from past experience (data) that we need a certain hardness because of the function to be performed. We know how to achieve this hardness and how to determine the hardness. We know the effects of not meeting the desired hardness.

The technology of cleanliness (and, hence, verification of cleanliness) is actually in its infancy when we consider the varying functional requirements of single parts and the varying performance requirements of final assemblies. For the time being we know we need cleanliness and would like to know how to verify the attainment of cleanliness.

Verification of cleanliness tests are sensitive detection techniques for contamination. They tell us when something we think we do not want is either absent or at some low value. Mr. G. J. Hof² in a Sandia Memorandum, "Present Practices in the Verification of Cleanliness," has prepared a survey of tests for cleanliness (Table III) which are reported in the open literature (3 thru 7, and others).

It is obvious that many people have looked at this problem of verification, and that a tremendous amount of work has been put forth in the development of applicable tests. Much credit is due these workers for their ingenuity and resourcefulness.

We may stipulate that the ideal test should be objective, should be simple and have a minimum of human factor involved, should be repeatable, and should yield some "number" on our "contamination scale." It should also be capable of identifying all types of contamination (organic and inorganic) on all types of substrates and should be nondestructive to the substrate. In comparison with the ideal test, we find that very few tests available today have even one of these features.

The method reported by Dr. John L. Anderson⁷ in the Journal of the American Association for Contamination Control, June 1963, does appear to have a number of these desirable features. At first glance, it would appear to be directly applicable to organic contaminants on rather simple metal parts. It may also have other applications as the method is investigated further. Like some of the useful tests listed in Table III which have been fully developed, however, it is limited to certain kinds of contaminants.

TABLE III

Summary of Test for Cleanliness

Test										Method of verification available			Limitation
	Any soil	Hydrophobic only	Laboratory	Production	Very sensitive	Sensitive	Relatively insensitive	Expensive	Not expensive	Good quantitative	Visual qualitative	None	
Visual				X					X			X	Visible soil
Tissue paper				X			X		X			X	
Water break		X		X		X			X			X	Hydrophobic contaminants only
Water spray		X		X		X			X			X	
Atomizer		X		X	X				X		X		
Contact angle		X	X			X			X		X		
Rock Island drop		X	X			X			X		X		
Ring test		X	X			X			X			X	
Kerosine		X	X		X				X			X	Laboratory specimens only
Radioactive tracer	X		X		X			X		X			
Gravimetric	X		X			X			X	X			
Fluorescent dye	X		X				X		X			X	
Ferricyanide paper			X				X					X	Ferrous parts only
Mear's (Elm's modification)							X					X	
Copper dip	X			X		X			X			X	
Oil spot				X			X		X			X	Grease type contaminant
Solvent test	X			X		X			X			X	Limited to solvent used

Since tests are generally limited in scope, we must select several tests for various reasons and integrate them into our program of verification. How these tests are selected will depend on the component, the assembly schedule, how well we understand process control, and the kinds of contaminants which must be avoided.

G. L. Wenner⁸ in his recent article in the February 1964 issue of the Journal of the American Association for Contamination Control, illustrates very well the application of several tests to insure that contamination of various kinds is under control. The kinds of contaminants, the sources, the methods of control and/or removal, and the means of verifying that these contaminants are under control have been investigated. It is obvious that quite a comprehensive study has been made of the over-all problem and that he has given proper consideration and emphasis to his program of verification. Obviously other tests and a more complete study may be required where very sensitive small switching and environmental sensing devices are involved. What tests should we select? The pros and cons of the various tests have been discussed many times. However, let us look at a select few of the tests and see what they can do for us.

1. Visual examination.

We tend to underrate visual examination at magnification because we know that, statistically, we can never see all the defects in a visual inspection. It is amazing, on the other hand, how much information can be obtained during visual examination by a thoroughly trained microscopist. Much of what he sees depends on reflected or refracted light from a proper light source. Light which is predominantly blue, green, or red is very effective. Light which is predominantly yellow is very ineffective. Polarized light and long wave length ultraviolet (3660Å) may also be used to a distinct advantage. The limit of such an examination is, of course, the wave length of visible light; hence we are limited to approximately 0.5μ (0.2μ under ideal conditions) film thickness in our detection capability.

The microscopist must be familiar with the material and the fabrication process in order to know what he is supposed to see. He must also be aware of common "things" that may cause trouble. A case in point is the early work in relay contamination. All sorts of contaminants were detected and revisions were made in materials and processes to bring them under control. One of the last culprits to be recognized was solder flux. It had been there all the time in large quantities; and, since everyone knew flux was used, no one looked at it. It was a case of not seeing the woods for the trees.

The method is most subjective, is very tedious, and requires that the microscopist be highly trained. In the hands of a skilled person, it might be rated as one of our most effective verification tests.

2. Water atomizer or advancing droplet test.

This particular test actually has several variations. We may choose to use the test described by Feder and Koontz⁴ in which water is sprayed on the surface in the form of tiny droplets. Or we may choose to place a much larger drop of water or

some other liquid on the surface and observe the contact angle. For example, Dr. W. A. Zisman of the Naval Research Laboratory has utilized this technique in many of his investigations. However, the substrate must be smooth or the contact angle measurement will be misleading on metallic as well as organic polymeric substrates. These tests have been shown to be very sensitive and very effective in contamination control work. Progressive differences may be detected in films from a fraction of a monolayer up to several monolayers in thickness.

Once again we must recognize the kinds of contaminants we look for with these tests. For the most part, only nonwetable film-type contaminants are detected. Residual detergent films (wetable) may yield a false indication of cleanliness in the case of the water test. The test will be useful only if we have some prior knowledge of the history of the surface being tested.

The water atomizer test is also subjective, and requires precise manipulation in the performance of the test. The degree of wetting or spreading of the droplets can be compared with photographic standards for interpretation; however, the degree of wetting can be influenced by failure to adhere to the exact test procedure, i. e., spraying too heavily may show a contaminated surface to be clean. In the hands of a good conscientious operator, the test is very useful; in the hands of a poorly trained one, it is useless.

3. Monitoring solvents (washing or rinsing) for contamination.

Aqueous and nonaqueous solvents are frequently monitored for particulate and soluble contamination removed from the item during the cleaning cycle. When the particulate matter in the liquid falls below a prescribed amount and/or size as cleaning progresses, the article is considered to be clean. The amount of dissolved contaminant is also monitored until a prescribed minimum concentration of contaminant is reached. Ionic cleaners are frequently used, after which the item is thoroughly rinsed in deionized or distilled water. The volume resistivity of the rinse water may be monitored in order to determine when the ionic cleaner has been rinsed away.

We should carefully note that this technique provides an indirect method for verification. Unless we can control the kinds of contamination present on our part to be cleaned, unless we can be sure nothing is trapped in our part, and unless we have some direct backup procedure to use occasionally to tell us we have in fact cleaned the part, we will suddenly be caught short some day with the indirect approach. Failure of this approach usually occurs when our production line introduces a new, different contaminant, or the parts happen to be oriented differently so that the rinsing operation cannot efficiently remove contamination. In some respects the use of the indirect method requires that we have a more thorough prior knowledge of the history of the part than with other tests and a much closer control of the assembly process. Keep in mind we are not testing the part but are testing for the depletion of contamination in the cleaning or rinsing solvents. We are presuming all the contamination has been removed from the part.

This test becomes somewhat objective in that a "number" is obtained by use of the test. Provided the control engineer realizes the importance of correct procedures prior to and during the cleaning operation, the test can be very useful—particularly where large parts or large numbers of parts are involved.

4. Radioactive tracers.

Several methods are available which utilize tracers for the monitoring of cleaning. Most of these involve the use of tagged "synthetic dirt," and either the parts or the cleaning solutions are monitored for residual tracer activity. These techniques are also indirect tests, and for the most part the comments in the previous discussion apply. The novel approach recently described by Dr. Anderson,⁷ however, is a direct test for contamination using the tracer technique. By adding a volatile tracer to the surface and by determining the evaporation rate, we can obtain a "number" which can be related to the degree of contamination present. The method has not been thoroughly investigated; however, it should be applicable for any contaminant that absorbs the tracer compound. It should be noted that porous materials or plastics will also absorb the tracer in a nonreproducible fashion and could yield an erroneous indication of degree of contamination.

It is very likely that this method, with applicable instrumentation, will be quite useful. As mentioned earlier, it has the desirable features listed for the ideal test (certain types of contaminants on certain kinds of substrates). The test does have the possibility of being too sensitive for some devices, i. e., relatively small amounts of contaminant may yield too large a number to be meaningful.

5. Infrared reflectance.

It has been mentioned earlier that Dr. R. E. Cuthrell of Sandia Corporation is evaluating infrared reflectance as an identification technique. Preliminary calculations and a limited number of tests indicate it will be possible to scan the surface and quantitatively detect and identify a wide variety of contaminants at quite low levels, as low as 10^{-4} micrograms.

The absorption spectra for literally thousands of organic compounds have been tabulated in the open literature; work has only just begun in the tabulation of spectra for elements and inorganic substances. Some idea of the possible range of the application of infrared reflectance for elements and inorganic substances is shown in Table IV. It must be emphasized that useful work in this area lies well in the future.

From the foregoing discussion of only a few of the available tests, it can be seen that each test has its limitations, advantages, and disadvantages. We must understand these factors when we choose a test or tests for our purpose of verification of cleanliness.

It is possible we are not ready to talk about a comprehensive program for verification. We are mistaken if we believe verification is easy and that a simple test, simply done, will tell us what we want. Not only our contamination control staff, but our production and management staff also, must recognize

TABLE IV

Infrared (IR)—Elements and Inorganic Compounds⁹

1. Infrared inactive gases (O_2 , N_2 , H_2 , etc.) become infrared active when adsorbed on a surface
2. IR studies have been published on Ozone and sulfur
3. The optical constants of many polyvalent metals show strong wave length dependence above 10μ
4. Borides, carbides, nitrides
5. Halides, hydrated halides
6. Oxides of H, D, T, N, halogens, sulfur, metals
7. XH_3 where $X = N, As, P, Sb$; $H = H, D$
8. XN_3 , XH_4 , digermanes, disilanes
9. Binary intermetallic compounds
10. Boric acid, borates, metal carbonates, metal carbonyls
11. Ternary oxygen and nitrogen compounds
12. Hydroxides
13. Ferrites, manganites, titanates
14. Complex compounds, coordination compounds
15. Oxalates, sandwich compounds, nitrosyls, alkyls, etc.

the tremendous effort necessary in process control and in clean assembly techniques if we are to achieve levels of cleanliness which will pass our tests. And, of course, a prerequisite to a meaningful verification test is the answer to the question "How clean does this part have to be?"

Summary

We have set forth our personal views on some important factors which must be considered if we are to develop contamination control, cleanliness, and the use of verification tests into science instead of black art. The following areas are believed to be of utmost importance if we are to achieve some meaning to our use of verification tests.

1. Contamination—effects, identity and source
2. Materials and processes—contamination potential and control for low contamination level
3. Function and performance of the component
4. Types and level of contaminants to be detected
5. Comprehensive program for verification
6. Control of verification tests

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