USING OSEE FOR SELECTING AMONG ALTERNATIVE SURFACE CLEANLING PROCESSES

Mantosh K. Chawla, Photo Emission Tech., Inc.
3255 Grande Vista Drive, Newbury Park, CA 91320

1 Abstract

Industry faces a dilemma in trying to select the "right" cleaning process. Evaluating alternative cleaning processes requires the answer to two questions: (1) is the new cleaning process as effective as the one being replaced? (2) Does the new cleaning process leave behind any residue that could be detrimental to subsequent processing or performance? This paper discusses reasons for monitoring surface cleanliness, factors affecting the selection of cleanliness monitoring method and a simple-to-use technique for quantifying the level of surface cleanliness to help answer both of these questions. The technique can be used to; Establish, quantitatively, the cleanliness level achieved by an existing cleaning process; Measure the cleanliness level achieved by the alternative cleaning processes to help select the most effective and cost efficient alternative; Monitor the effectiveness of the cleaning process on an on-going basis.

2 Why Monitor Cleanliness

Presence of contamination can degrade the performance of parts, components and systems, results in non-conformance and, in the worst case, product failure. Molecular contamination of surfaces can drastically affect the performance of the parts. Thin film contamination on surfaces can result from inadequate or incomplete cleaning methods, from oxide growth during the time between cleaning and performing the next operation, or from failure to properly protect cleaned surfaces from oxide growth during the time between clearing and performance of next operation, or from failure to properly protect cleaned surfaces from oils, greases, fingerprints, release agents, or deposition of facility airborne molecules generated by adjacent manufacturing or processing operation.

Cleaning is part of many manufacturing operations. Parts may require cleaning before they can be electroplated or painted, before they can be soldered, or before they can be packaged and shipped for end use. Thus cleaning is necessary for various reasons to assure desirable product appearance or performance.

In most cases, control of cleaning processes is achieved by specifying the operating parameters of the cleaning process, e.g. chemical concentration, temperature, water pressure or the amount of time the parts are washed or rinsed. This approach defines how "clean" a part should be by specifying the process used to do the cleaning (i.e. dip Part A in Cleaning Solution B at Temperature C for X minutes), without regularly checking how clean parts actually are. This approach takes advantage of knowledge gained through experience with the cleaning process or through measurements taken during initial testing of the cleaning process. This method while practical and good most of the time, cannot be consistently relied upon for precision cleaning. This type of procedure generally also specifies the properties of the cleaning solution and replenishment of the chemicals on a periodic basis. This approach does not take into account the number of parts that may go through the process in a given period of time. The more parts go through the cleaning process, the more contamination is removed from the parts, which is mixed in the cleaning solution. It also does not take into account the amount of contamination present on each part. The type and amount of contamination on each part varies from time to time and from vendor to vendor. Thus, this approach to assuring cleanliness works only if the average number of parts and the average level of contamination on each part are consistent during a given period of time. If this condition is not achieved, the part cleanliness level will deteriorate below the acceptable level. Without the use of a surface cleanliness monitoring method, the lower level of contamination will not be detected until there are problems downstream.

Hence, in many cases, it is more effective for a level of cleanliness to be specified and have that level checked by measuring cleanliness on a percentage or all of the parts. This is especially true in precision cleaning applications.

If a level of cleanliness is to be specified, then a method of verification must be specified at the same time for that level to have meaning. This generally leads to the question, what do we mean by “clean”? How clean is clean? Even so called “clean” parts have certain amount of contamination, even if it is microscopic level. With advances in technology, more and more applications are moving towards the need for higher level of cleaning. Increasingly precision cleaning cannot afford to rely on old methods of verifying or assuring cleanliness.

Measuring cleanliness not only helps ensure product quality, it is an essential part of implementing pollution prevention approaches related to cleaning. Cleanliness measurement / verification methods can be utilized to: 1) evaluate performance of any existing or alternative cleaning process, 2) optimize the cleaning process by analyzing parts during initial implementation of a new cleaning process, or 3) determine if better parts handling or other innovation may allow the cleaning process to be eliminated entirely. In addition, measuring cleanliness itself often prevents pollution by reducing rejects.

In order to specify a desired level of cleanliness, it is important to specify a method of measuring surface cleanliness that will help in assuring the desired level of cleanliness. Once a method for measuring cleanliness has been selected, it can be used to establish the level of cleanliness achieved by any existing process. This level of cleanliness can be used as a benchmark to make changes to existing process to see if those changes improve the achieved level of cleanliness. It can also be used to evaluate alternative cleaning processes prior to implementation.

3 Factors affecting the selection of a cleanliness measurement method

There are a wide variety of cleanliness measurement methods. To determine which method is right for a given application, many factors must be considered. Some of the factors that affect the choice of method are:

- **Type of contaminants to be monitored -** The method selected must be able to detect the contaminants of interest. For example, some methods will detect only organic contamination and not inorganic contamination. If there is a need to detect inorganic contamination then such methods would not help. Some methods detect only a certain type of contaminants. Such methods would be good if only certain types of contaminants are always expected to be on the surface. In general, it is better to have a method that can detect both organic and inorganic type of contamination and not be restricted to certain type of contamination. This helps to assure surface cleanliness, even if there is a change in any aspect of the production upstream.

- **Type of substrate being checked -** If the part is being inspected directly, then the method must be compatible with the material being measured, without causing any damage. For example, certain cleanliness measuring methods deposit some type of “measuring media” on the surface to measure the cleanliness. Care should be taken to make sure that the “measuring media” deposited on the surface is not going to effect the surface of the part. Care must also be taken to make sure that “measuring media” does not contaminate the part surface.

- **Level of cleanliness that must be measured -** The method must be able to detect the contaminants at the minimum level of interest. Each measurement method has a certain range of detection, and in most cases the minimum level of contaminant that can be detected is important for precision cleaning applications.

- **Accuracy and precision required -** (i.e. how critical is it that the parts are cleaned to narrow specifications?). Some methods provide gross estimates of contamination, even if they can detect contamination at very low levels, while others provide fairly precise data. The method selected must be appropriate for the application.

- **Features of the measurement method -** Some methods have certain features that may or may not be desirable. For example, some methods have to contact the surface or deposit something on the surface to make a measurement. It may be desirable to not contact the surface or deposit anything on the surface. Whether the method is non-contact, non-destructive and / or non-invasive should be considered in selecting the right method.

- **Speed of measurements –** In most cases, it is not necessary to inspect every part. A statistically representative sample at preset intervals is generally sufficient to track the performance of the cleaning process over time. Hence the number of measurements that each method can complete per unit of time becomes important in selecting the right method. The method selected must be able to make analyses / measurements at the desired rate.

- **Acquisition & Operating Costs -** The more precise and automated measurement methods tend to be very expensive. In addition to acquisition cost the operating costs, such as cost of any disposable supplies or costs of required operating skill, must also be considered. The total cost / benefit of the measurement method must be evaluated.

- **Skill level required.** The required skill level to utilize the technique and interpret the results varies a lot among various methods available. The ongoing cost of operating is higher for the more sophisticated techniques, particularly analytical techniques. The cost of providing the required skill level must be taken into account.

For a given cleaning process, it may be possible that more than one method is required to verify / measure all of the parameters of interest. There are many measurement methods that can be used to evaluate cleanliness in a manufacturing environment.

4 Optically Stimulated Electron Emission (OSEE) Background

OSEE**,** also known as photoemission or photoelectric effect, is a phenomenon in which charge particles are released from a material when it absorbs radiant energy. The photoelectric effect commonly is thought of as the ejection of electrons from the surface of a metal plate when light falls on it. In the broad sense, however, the phenomenon can take place when the radiant energy is in the region of visible or ultraviolet light, X-ray, or Gamma rays; when the material is solid, liquid or gas; and when the particles released are electrons or ions (charged atoms or molecules).

The photoelectric effect was discovered in 1887 by a German physicist, Heinrich Rudolf Hertz, who observed that ultraviolet light changes the lowest voltage at which sparking takes place between given metal electrodes. At the close of 19th century, it was established that a cathode ray (produced by an electric discharge in a rarefied-gas atmosphere) consists of discrete particles, called electrons, each bearing an elementary negative charge. In 1900, Philipp Edward Anton Lenard, a German physicist, studying the electrical changes liberated from metal surface when it was illuminated, concluded that these charges were identical to the electrons observed in cathode rays. It was further discovered that the current (given the name photoelectric current because it was caused by light rays), made up of electrons released from the metal, is proportional to the intensity of the light causing it for any fixed wavelength of light that is used. In 1902 it was proven that the maximum kinetic energy of an electron in the photoelectric effect is independent of the intensity of the light ray and depends on its frequency.

The observation that (1) the number of electrons released in the photoelectric effect is not proportional to the intensity of the light and that (2) the frequency, or wavelength, of light determines the maximum kinetic energy of the electrons indicated a kind of interaction between light and matter that could not be explained in terms of closed physics. The search for an explanation led in 1905 to Albert Einstein’s fundamental theory that light, long thought to be wavelike, can be regarded alternatively as composed of discrete particles (now called photons), equivalent to energy quanta.

In explaining the photoelectric effect, Einstein assumed that a photon could penetrate matter, where it would collide with an atom. Since all atoms have electrons, an electron would be ejected from the atom by the energy of the photon, with great velocity. Originally, most investigations of photoemission centered on the emissive properties of solid metals that are good conductors of electricity. Gradually, with the recognition of the effects of volume and surface impurities, there evolved an interest in the photoelectric emission from insulators, which are nonconductors, and from semiconductors, which conduct electricity only under certain circumstances. The energy distribution of electrons in insulators and semiconductors is different from that of metals. As a consequence, the photoelectric yield (number of electrons emitted for each incident quantum of radiation) versus energy of the incident photon can be different for materials having the same work function.

Albert Einstein received the Nobel Prize for his work with the light quantum and photoelectric effect.

5 OSEE PRINCIPLE

The SQM series instruments are based on the principle known as Optically Stimulated Electron Emission (OSEE), also known as Photo Emission (PE). It is well known fact that when metals or certain other surfaces are illuminated with ultraviolet (UV) light with the proper wavelength (energy), electrons are emitted from the surface. The process by which UV photons interact with the surface to produce electrons is known as OSEE. The emitted and subsequently scattered electrons can be collected across an air gap by a biased collector (located at the end of the sensor) and measured as a current that is converted into a voltage and displayed as a number. By maintaining the surface to collector distance relatively constant, changes in the measured photo current (which is in the order of 10^{-10} to 10^{-12} amps) can provide information about the surface, e.g., electronic structure, composition chemistry. Any contaminant or thin film on the surface, depending on its own photoemission characteristics, can either enhance or attenuate the inherent emission from the clean surface. In simple electronic terms, the clean surface is a current generator and a non-photo emitting contaminant acts as a resistance because the current is attenuated by interactions between the electrons and the contaminants. The thicker the contaminant, the higher is the resistance and consequently the greater the decrease in measured signal.

The sensor utilizes low-pressure mercury vapor lamp with two pre-dominant peaks at 185 nanometers (nm) and 254 nm. These two wavelengths correspond to approximately 6.7 electron volts (ev) and 5.0 ev energy level. The UV light flux provides the energy needed by the material so the electrons emit (escape) from the surface.

The materials/surfaces that emit, when exposed to this UV light, are called photo-emitting materials and the other materials are called non-photo emitting. Both substrate and contaminant/coating can be emitting.

A surface with no contaminant or coating on it usually gives a high signal. A contaminant or thin film, depending on its own emission characteristics, can either attenuate or enhance the signal from a clean substrate.

Presence of thin film, contaminant or coating has two effects. First, it reduces the UV light reaching the substrate and second it attenuates the flow of electrons away from the surface. Within a certain range, the signal attenuation is exponentially proportional to the thickness of the thin film on the surface. Hence, the OSEE technique can also be used to measure thickness of thin films. The range of thickness measurement depends on the emission level of the substrate and the attenuation level of the contaminant/coating.

The materials that emit are those that have a work function of 6.7ev or less. The lower the work function of a material, the more readily it will emit and the higher the emission level will be. Work function of a material is a measure of the amount of energy that is needed to release an electron from the surface. Both conducting and non-conducting materials can be photo emitting. A comprehensive list of work functions may be found in any handbook of physics.

6 Selecting a Cleaning Process

In order to effectively replace an existing cleaning process, a three (3) steps procedure is recommended. First step is to know or establish a benchmark cleanliness level for the existing cleaning process. Second step is to take statistically significant number of samples (a minimum of five for each cleaning process under consideration) and clean them with the cleaning processes under consideration and measure the cleanliness level achieved by each cleaning process. The third and last step is to compare the level of cleanliness level achieved by each cleaning process under consideration with the benchmark cleanliness level achieved with the existing cleaning process. The new cleaning processes that meet or exceed the established benchmark cleanliness level are the ones that should be considered. Other factors such as acquisition cost and operating costs should be considered to make the final selection.

In most cases the new cleaning process is likely to be aqueous or semi-aqueous based cleaning processes. These new cleaning processes are generally less aggressive than solvent based cleaning processes. In most cases the surfactant used is selected for the most common soils found on parts to be cleaned. The selected surfactant is likely to be not sensitive to certain type of soils, hence even though the process qualified initially, it is not going to be very effective for certain soils that may end up on parts as a result of changes to manufacturing or handling processes. In most manufacturing processes it is assumed that the average number of parts processed through the cleaning process in a given period of time and the type and the amount of soil on each part is similar. In reality, the number of parts processed in a given period of time can vary considerably. In addition, the amount of soil on each part or batch of parts can vary considerably.

Most new cleaning processes involve rinsing with water as a final step. Rinsing itself can leave watermarks or spots on part surfaces. In order to prevent poorly cleaned parts reaching downstream processes, it is important to implement on-going cleanliness monitoring / verification to make sure that the cleanliness level is maintained regardless of the factors discussed here that can effect the surface cleanliness level.

6.1 Establishing a Benchmark

In order to establish a benchmark for the existing cleaning process, several parts (statistically large enough sample, minimum of five) should be cleaned with the existing cleaning process. OSEE readings should be taken and recorded for these parts. If the samples have a large surface area then several readings (minimum of five readings) should be taken from each part. The Mean and Standard Deviation should be calculated of all the readings. The Mean reading gives the average level of cleanliness achieved by the existing cleaning process. This should be used as the benchmark to evaluate the effectiveness of new cleaning processes. The Standard Deviation gives a measure of the variability of the existing cleaning process. This measure should be used to evaluate the variability of the new processes. Ideally the variability of the new cleaning process should be equal or less than the existing cleaning process.

6.2 Measuring Cleanliness Level Achieved by New Cleaning Processes

Armed with the knowledge of the type of parts and the types of soils that need to be cleaned, a preliminary selection of the cleaning processes can be made for further evaluation. A statistically large enough sample (minimum five parts) of typical parts with most typical soils should be selected for each cleaning process to be evaluated. After cleaning the parts with each cleaning process, measurements of surface cleanliness level should be made and recorded. Ideally the number of readings and the location of the readings should be comparable to the ones taken for establishing benchmark.

6.3 Comparing new cleaning processes with the benchmark

The Mean and Standard Deviation of the OSEE readings for each set of parts should be calculated. The cleaning processes that have Mean OSEE equal to or higher than the benchmark are the ones that demonstrate a level of cleanliness as good or better than the benchmark. These processes are the ones that should be considered as replacements for the existing cleaning process. In addition, the calculated Standard Deviation for each cleaning process under evaluation should be compared with the Standard Deviation for the existing cleaning process. Those processes that have Standard Deviation equal to or less than the existing cleaning process are the ones that should be considered. In the event none of the cleaning processes are as effective in cleaning as the existing process, more cleaning processes may have to be evaluated. Alternatively a decision can be made to pick the new cleaning process that has the highest Mean OSEE among those evaluated. The established benchmark should also be evaluated to see if the optimal level of cleaning process has to be as high as the benchmark. If the existing process is solvent based, it is probably very aggressive and maybe giving a level of cleanliness higher than needed. “How clean is clean” is a question that may have to be or may be desirable to answer. See the paper titled “How clean is clean? Defining acceptable cleanliness levels” by the same author, published in CleanTech 2000 conference proceedings.

7 Examples of OSEE use for surface cleanliness evaluation

OSEE has been used extensively for establishing benchmark, evaluating and selecting new cleaning processes and monitoring on-going effectiveness of various cleaning processes. Following are a few selected specific applications:

7.1 Effect of Time on Surface Cleanliness

A manufacturer of aluminum sheet wanted to evaluate variations of the existing cleaning process to see how the surface cleanliness is affected by changes in the operating parameters of their existing cleaning process. Sixteen (16) samples, representing two different alloys of aluminum and four different surface conditions, were submitted. Two (2) samples of each alloy and each surface condition were submitted. The surface condition of the samples was identified as “as received”, 2 minutes, 5 minutes, and 8 minutes, representing the time duration of time they were in the cleaning process.

The Mean OSEE readings for both alloys of aluminum show that cleanliness level for parts cleaned for 2 Minutes was better than those cleaned for 5 Minutes or 8 Minutes. The slightly lower cleanliness level for parts cleaned for 5 and 8 minutes indicates something unusual happening in the cleaning process, since one would expect to see the cleanliness level for higher cleaning times to be the same as the lower cleaning times if not higher than the parts cleaned for 2 minutes. The reason for different OSEE readings for different alloys is due to the difference in the work function of the two alloys.

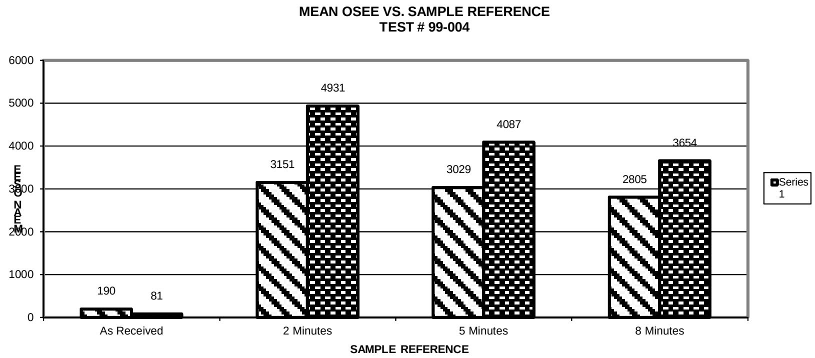

Figure 1

7.2 Evaluation of different cleaning processes

Four samples were tested for surface cleanliness levels using OSEE. One sample was not cleaned and used as a reference of level of cleanliness. One sample each was cleaned using AK225ES, Trichlroethylene and Lenium ES.

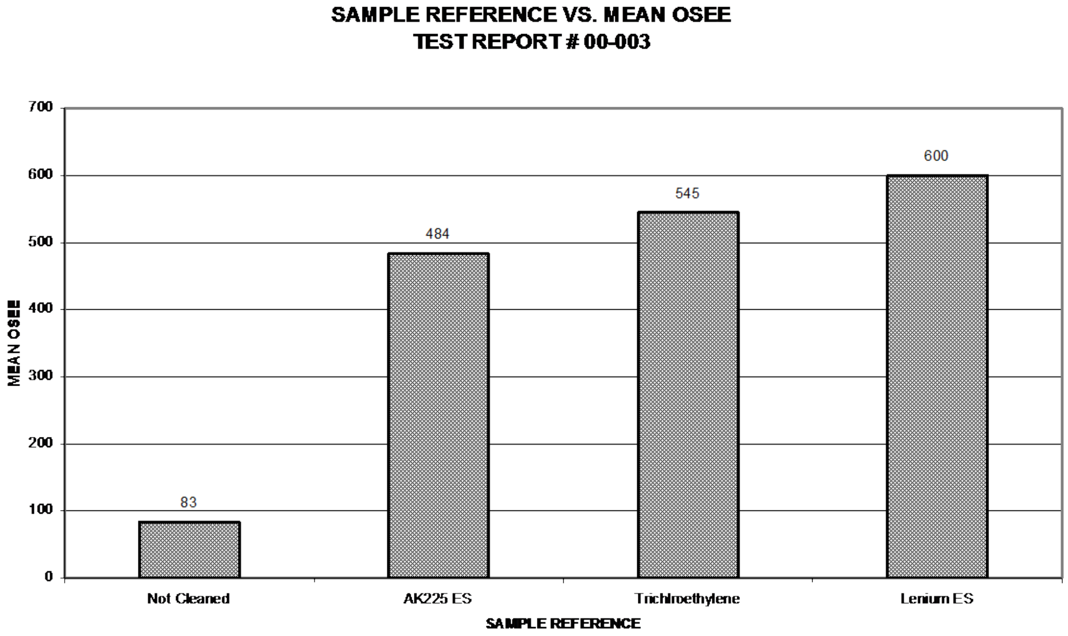

Figure 2

Lenium ES gave the highest level of cleanliness with a mean OSEE of 600, followed by Trichlroethylene with a mean OSEE of 545 and followed by AK225ES. **Caution: The results of this test should not be used to conclude that these cleaning agents would give the same results for other parts, materials and soil types. This simply shows that in this case Lenium ES gave better cleanliness results than the other two cleaning agents.** The purpose of this presentation is to show how OSEE measurements have been and can be used to evaluate different cleaning processes. A word of caution, when comparing samples from different cleaning processes or different settings of the same cleaning process it is important to make sure that the time elapsed between cleaning and taking cleanliness measurements is similar. A wide variation in time lapsed can distort the results, since the surface cleanliness can change with time after cleaning.

7.3 Evaluating cleanliness levels for different concentrations and different processing time

Samples were cleaned using a standard process using two different levels of concentration (10% and 25%) and two different cleaning times (30 Seconds and 3 Minutes). Additional samples were cleaned using 36% concentration of Hydro Choleric Acid for the same two cleaning times and the results were compared to draw conclusions as follows:

First the test results showed that 3 minutes cleaning resulted in higher level of cleanliness when compared with 30 seconds cleaning. For example, samples cleaned with 10% solution concentration for 3 minutes had a mean OSEE of 702 as compared with 376 for samples cleaned for 30 seconds, whereas the samples cleaned with 25% solution concentration for 3 minutes had a mean OSEE of 886 as compared with 512 for samples cleaned for 30 seconds. Second, the standard cleaning process was much more effective in cleaning surface when compared with surface cleaned with 36% Hydro Choleric acid. Samples cleaned for 3 minutes with 25% concentration of the standard cleaning process had a mean OSEE of 886 as compared with 265 for samples cleaned for 3 minutes with 36% concentration of Hydro Choleric acid.

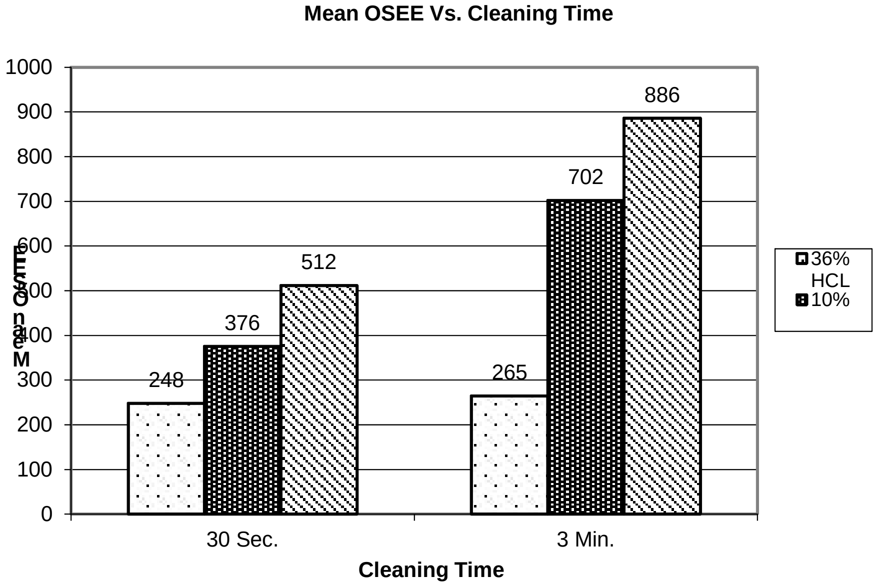

Figure 3

7.4 Different Contaminants, Cleaning and Time Effect on Surface Cleanliness

Eight (8) samples of steel plate approx. 4" x 4" in size were submitted. Each sample had a different surface condition. Each sample was wrapped in household aluminum foil. The surface condition of each sample was identified and is listed below. Tests were conducted to see the effect of different contamination, hand cleaned vs. cleaning process and effect of time on the surface cleanliness.

F	**Contaminated with Oil**
H	**Contaminated with Acid Rinse Solution**
E	**Contaminated with finger prints etc.**
G	**Hand Cleaned**
D	**Cleaned 2 weeks ago exposed to Environment**
B	**Cleaned 2 weeks ago wrapped in foil**
A	**Cleaned surface, Freshly prepared**
C	**Cleaned 2 weeks ago wrapped in foil**

Figure 4 shows graphically the mean OSEE readings for different samples. As expected the contaminated samples have much lower readings than any of the cleaned samples. The results also indicate that hand cleaning is not as efficient for surface cleaning as the cleaning process. Sample D, when compared with samples A, B or C shows the effect of the exposure to the environment after cleaning. The samples that were cleaned two weeks ago and wrapped in Aluminum foil seem to have protected the surface from the environment. The surface of those samples is comparable to freshly cleaned samples.

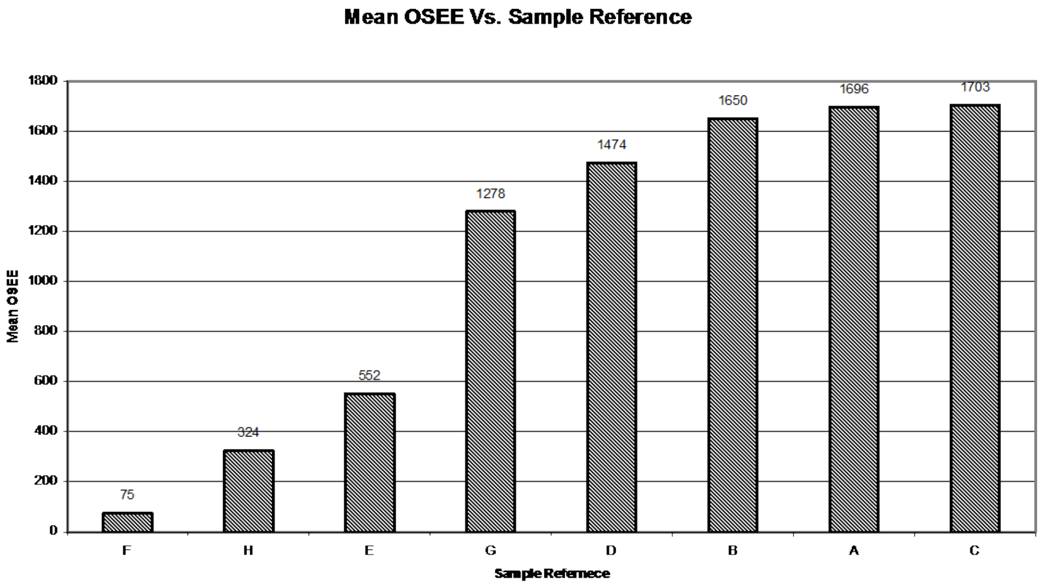

Figure 4

7.5 Summary

OSEE has been used for many years for measuring and monitoring surface cleanliness levels in a wide variety of applications. This technique is most sensitive to the change in the chemical state of the surface. It provides a quick, non-destructive and non-contact means of measuring surface cleanliness for a wide variety of materials and geometric shapes. It is not sensitive to surface finish.