CONTAMINANT DETECTION, CHARACTERIZATION, AND REMOVAL BASED ON SOLUBILITY PARAMETERS

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parameter will provide for increased solubility. However, if a solvent is chosen that has a solubility parameter too far away from the target area, the molecules will not match or fit together, and there will be little diffusion, molecular attraction, or solubility. The solubility parameter of a material depends on the polar forces, the nonpolar forces, and the hydrogen bonding potential of each molecule.

Contamination removal is critical in the electronics industry because foreign material on surfaces has the potential of causing electrical surface leakage or failures in encapsulation, coating, or bonding applications. In the past, solvents for contamination removal generally were selected on the basis of adhesion tests and production evaluations. Using the relatively new technologies of evaporative rate analysis and solubility parameter, a new approach to surface cleanliness has been achieved.

Contaminants

An organic residue contaminant is a material which usually occurs on electrical components as a very thin film. These types of contaminants are usually unknown materials. Bacteria and dust particles are also contaminants, but they are not included as part of this study. Identification of unknown contamination is quite often speculative or not possible.

Cleaning solutions, if used over and over, will contain increasing amounts of contaminant that will be redeposited on a surface as it is removed from the solvent. Surface cleanliness requires a technical approach to remove the various contaminants that may be present. The trial-and-error method of evaluation is no longer acceptable.

Solubility Parameter Technology

Solubility parameter technology involves the study of how well materials are compatible with each other. Similar molecules will dissolve more easily in each other than will dissimilar molecules. When the solubility parameter of a material to be dissolved is known, it becomes the "target area," as shown in Figure 1. The selection of a solvent with a solubility parameter value reasonably close to that of the target solubility

Figure 1. Solubility Parameter Solubility-Incompatibility Concept

Evaporative Rate Analysis

Evaporative rate analysis is a relatively new technique for the examination of surfaces. It provides a measure of the presence of contaminants. It involves measuring the rate of evaporation of a carbon-14 tagged radioactive chemical from a surface by a Geiger counter. The degree of retention of the radioactive chemical is a measure of that surface or contamination. The Meseran Surface Analyzer uses this principle and was used for this investigation.

Contaminant Removal by Solvent Selection

It is possible to characterize contaminants so that the exact solvent or solvents can be selected to do an effective job of cleaning. A series of solvents was chosen which represented a major portion of the solubility parameter range of organic material, that is, 7 to 12. Selection was also based on obtaining solvents which represented the weak, moderate, and strong categories of hydrogen bonding.

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After each contaminant was rinsed by the respective solvent, the level of radioactivity counts was determined by the Meseran Surface Analyzer. Bar chart examples are shown for two contaminants in Figures 2 and 3. The most effective contaminant removal is indicated by the lowest Meseran values obtained.

In some cases, complete removal of a contaminant by a solvent is not quite achieved because of insufficient time. Very low Meseran values are obtained by the more effective solvents. According to this analysis, selection of the best solvents can be made for the most effective contaminant removal.

Figure 2. Effectiveness of Alpha 611 Solder Flux Removal by Series of Solvents Characteristic of Solubility Parameter Range

Figure 3. Effectiveness of AZ1350J Photo Resist Removal by Series of Solvents Characteristic of Solubility Parameter Range

Solvents and Solvent Blends

Classification of solvents into three groups of weak, moderate, and strong hydrogen bonding potential increases the accuracy in solvent selection for contaminant removal. It tends to group solvents into their electron charge capability. The strong hydrogen bonding molecules are the alcohols. These have high solubility parameter values. The weak hydrogen bonding solvents are the chlorinated solvents and solvents such as heptane and toluene. These have low solubility parameter values. In between are the moderate hydrogen bonding molecules such as esters and ketones.

Cleaning efficiency of solvents for contamination removal is based on how close the solubility parameter value within a hydrogen bonding class matches that of the contaminant. The relative ease of removal of contaminants by solvents is shown in Table 1. Solvent blends can be formulated from individual solvents to provide polarity and solubility parameter composites. Selection of solvents or solvent blends can be made to remove specific contaminants (organic residues) without damaging plastics. Solvent blending, based on solubility parameter principles, has been demonstrated to be more effective in removing specific groups of contaminants than individual solvents. A specific solvent blend (C), for example, is best suited for various contaminants that might be encountered in electrical component manufacture.

Solvent Blend C	Volume Percent
1,1,1,-Trichloroethane (Methylchloroform)	17
n-Butyl Acetate	33
1,1,2,-Trichloroethylene	33
Isopropyl Alcohol	17

Swell Index of Plastics

Some plastics are not damaged by solvents; other plastics are sensitive to solvents in different ways and in varying degrees. If a polymer is crosslinked, as are plastics derived from thermosetting resins, or is highly crystalline, solvency will be less likely to occur. An amorphous or loosely structured plastic would probably be soluble in several solvents.

Where plastics are used as substrates, solvents selected to remove contaminants must not dissolve the plastic or cause crazing of the surface. Swell index is a measure of these effects of solvents on plastics.

Table 1. Effects of Solvents on Contaminants.* Relative Ease of Removal of Contaminants, by Solvent Series

Contaminants	Weak hydrogen bonding class					Moderate hydrogen bonding class					Strong hydrogen bonding class	
	Hep- tane	2-Ethyl- hexyl chloride	Methyl chloro- form	1,1,2 Tri- chloro- ethane	Vinyl tri- chloro- ethyl- acetate	2-Ethyl- hexyl acetate	n-Butyl acetate	Cello- solve acetate	Ace- tone	Cyclo- hexane	Isopropyl alcohol	
Solder flux types												
Abietic acid	C	C	A	C	A	B	A	B	B	B	B	B
Stearic acid	C	A	A	A	A	C	A	B	B	C	A	A
Photo resist	C	C	C	C	C	C	C	A	B	A	C	C
Spray coating	C	C	A	A	A	C	C	B	B	B	C	C
Fingerprint	B	A	A	B	A	B	B	A	B	B	A	A
Hand lotion	B	A	B	A	A	C	A	A	C	C	C	C
Detergent	C	C	C	C	C	B	B	C	B	C	C	A
Mold Release (carnauba wax)	C	C	C	C	C	C	C	C	C	C	C	C
Grease	B	C	C	C	C	B	B	C	C	B	C	C
Silicone grease	C	C	C	C	C	C	C	C	C	C	C	C

*Levels of contaminant solubility based on Hesteran values after solvent rinsing: A = contaminant effectively removed (16 or less Hesteran units), B = partly soluble, longer rinse times should improve contaminant removal (17 to 99 Hesteran units), and C = limited contaminant solubility in solvent (greater than 100 Hesteran units).

Swell index data on a variety of thermo-plastic and thermosetting plastics, including a glass-filled printed circuit board laminate (Table 2) when used with contaminant solvency (Table 1), provide for solvent selection best suited for a particular application. For example, if the plastic being used is sensitive to moderate hydrogen bonding solvents, then it may be necessary to use a weak hydrogen bonding solvent to remove contaminants.

Characterization of Surfaces

Solubility parameter technology and the evaporative rate analysis technique have been combined to characterize surface contaminants. This technology can be

expanded to include direct characterization of surfaces in terms of their balance of forces based on their polarity and nonpolarity attributes.

Solubility parameter technology is the study of how well materials are compatible with each other. Similar molecules will dissolve more easily in each other than will dissimilar molecules. Applying the same principle to surface characterization, it follows that polar solvents emphasize polar characteristics of surfaces and nonpolar solvents emphasize nonpolar characteristics. A four-quadrant chart analysis technique has been established that can be applied to surface characterization of plastics as well as contaminants.

Table 2. Effects of Solvents on Plastics*, Relative Solvency, by Solvent Series

Plastics	Weak hydrogen bonding class					Moderate hydrogen bonding class					Strong hydrogen bonding class	
	Hep- tane	2-Ethyl- hexyl chloride	Methyl chloro- form	1,1,2 Tri- chloro- ethane	Vinyl tri- chloro- ethyl- acetate	2-Ethyl- hexyl acetate	n-Butyl acetate	Cello- solve acetate	Ace- tone	Cyclo- hexane	Isopropyl alcohol	
Teflon	1	1	1	1	1	1	1	1	1	1	1	1
Polyethylene	1	1	1	2	2	2	1	1	1	1	1	1
Polyvinyl- chloride	1	1	1	2	3	4	2	4	4	3	1	1
Nylon	1	1	1	1	1	1	1	1	1	1	1	1
Acrylic	1	1	1	1	3	5	1	5	5	1	1	1
Polystyrene	1	3	5	5	5	5	5	5	5	5	1	1
Cellulose acetate	1	1	2	2	3	5	1	5	5	5	2	2
Nylart	1	1	1	1	2	2	1	1	2	1	1	1
Polyphenylene- sulfide	1	1	1	1	1	1	1	1	1	1	1	1
Polycarbonate	1	1	3	3	5	5	1	3	3	5	1	1
Phenoxyl†	1	1	1	2	4	5	1	3	5	5	1	1
Bisallylphthalate	1	1	1	1	1	1	1	1	1	1	1	1
Phenolic	1	1	1	1	1	1	1	1	1	1	1	1
Polyphenylene oxide	1	2	5	5	5	2	3	3	3	4	1	1
ABS	3	1	4	4	5	1	5	5	5	5	1	1

*Levels of plastic solubility are based on percent swell in 24 hours. 1 = little or no solvent absorption (swell = less than 1%), 2 = slight absorption of solvent (swell = 1 to 10%), 3 = moderate absorption of solvent (swell = 11 to 49%), 4 = excessive solvent absorption (swell = greater than 50%), and 5 = plastic dissolved partially or completely in solvent.

†Trade name of product of E. I. duPont de Nemours.

‡Trade name of product of Union Carbide.

The relative level of polarity of molecules can be estimated from the electronegativity differences in the functional groups. As the electronegativity differences in the elements of a chemical bond increase, the bond becomes more polar.

Three radioactive chemicals were selected for use with the Meseran Surface Analyzer according to their level of polarity. The radiochemical diethylsuccinate with its C-O and C=O bonds, will have a moderately large electronegativity difference of 1.0. Tetrabromoethane, on the other hand, with its C-Br bonds, will have a small electronegativity difference of 0.3. In these two cases, the electronegativities of the terminal atoms (oxygen and bromine) are more negative than the carbon atom and are considered as being of negative polarity. Diethylsuccinate has a greater charge potential than tetrabromoethane and therefore is more polar. Tridecane, however, with its C-H bonds can be considered as being nonpolar, because the terminal hydrogen atom is less electronegative than the carbon atom.

Because the bulk vapor pressure of the radioactive chemicals is substantially equivalent, the observed amount of measured retained radioactivity results primarily from the ability of a substrate to interact with the functional group of the radioactive chemical. In this regard, the three radioactive chemicals (tridecane, tetrabromoethane, and diethylsuccinate) have similar vapor pressure properties.

The three radioactive chemicals can be used as surface energy probes to determine which one reflects the polarity or nonpolarity condition of a surface. In this manner, the level of polarity or balance of forces that exist on a surface can be ascertained. The largest Meseran number obtained by one of the three radioactive chemicals will show the strongest characteristics of the surface. Thus, if the tetrabromoethane number is largest, the predominant characteristic of the surface will be of weak polarity. If diethylsuccinate provides the largest number, the surface has a moderate to strong polarity. If the surface is nonpolar, the tridecane number will be the largest. Therefore, if A stands for tetrabromoethane, C stands for diethylsuccinate, and B stands for tridecane, then:

A > C > B equals a weak polar surface,

C > A > B equals a moderate to strong polar surface, and

B > A or C equals a nonpolar surface.

Investigators have used 2- or 3-dimensional graphs to identify compatibility of solvents, resins, and polymers based on units of solubility parameter, polarity, and

hydrogen bonding. This technique characterizes materials according to their regions of solubility. In this work, however, the degree of affinity for the surface by each radioactive chemical is expressed by radioactive counts and is the extension of solubility parameter compatibility principles. The radioactivity counts are a measure of the surface and since there is a degree of nonpolarity in every molecule, the nonpolar tridecane data can be subtracted from the Meseran numbers obtained with the polar radioactive chemicals to reveal the relative polarity level present on a surface. Thus, A minus B (Formula 1) equals weak polar data and C minus B (Formula 2) equals moderate to strong polar data.

This principle was applied to known pure organic chemical films on aluminum foil surfaces, to plastic surfaces, and to various contaminants on aluminum foil surfaces. The maximum benefit was obtained by locating the specific data according to Formulas 1 and 2, on a four-quadrant chart (Figure 4). In this manner, surfaces of unknown contaminants can be determined for their relative level of polarity and nonpolarity.

Surface Electrical Characteristics

Since organic contaminants can have varying degrees of polarity or nonpolarity, it can be expected that the electrical properties of these materials would respond to voltage in terms of surface leakage or voltage

Figure 4. Polarity Indications According to Four-Quadrant Chart Analysis

breakdown (arc over). Using a printed circuit board test pattern, electrical tests were made on a known series of chemicals and on contaminants.

The series of chemicals represented the solubility parameter range which should cover most types of contaminants. Surface leakage tests were made over a 10 to 500 applied voltage range. A definite pattern of electrical activity was found based on the nonpolarity and polarity/hydrogen bonding characteristics in terms of solubility parameter values. A summary of the data is given in Table 3, which characterizes chemical type with surface leakage properties.

A large variety of contaminants were similarly measured for their surface leakage characteristics. The principles developed with the known chemicals are also seen with the contaminants according to their level of polarity/nonpolarity.

Table 3. Classification of Organic Residue Chemical Type With Surface Leakage

Types of Organic Residue	Leakage at 250 to 500 V (Amperes)
Aliphatics, Aromatics	1 μ A to 1 pA
Chlorides, Secondary Amines	10 nA
Esters, Ethers, Ketones	0.1 mA to 1 μ A
Alcohols	0.1 A to 0.1 μ A
Primary Amines	>0.1 A

Major arc over problems occur with materials which are primary amines, alcohols (hydroxyls), and ketones. The greater the hydrogen bonding characteristic is of the chemical, the lower the breakdown voltage.

The various levels of polarity of known chemicals are related to surface electrical leakage in a predictable manner. Arc over limits are less sensitive to polarity differences. In both cases contaminants and known chemicals having high solubility parameter values yield greater electrical surface leakage and least arc over (voltage) resistance.

Summary

Surface cleanliness, in the past, has generally been evaluated indirectly by adhesion or electrical tests. As cleanliness requirements for electrical parts increase, contamination detection and removal become more critical. Using the relatively new technologies of evaporative

rate analysis and solubility parameter, a new approach to surface cleanliness has been achieved. Based on the principles of solubility parameters, compatibility of contaminants with solvents is described. Greater accuracy in solvent selection can be achieved when solvents are classed according to their hydrogen bonding potential. Blending solvents according to solubility parameter principles permits specific solubility characteristics to be obtained for specific contaminant removal. The swell index of plastics also follows solubility parameter principles of solvent compatibility. Surface measurements by the evaporative rate analysis technique permit contaminant detection as low as 0.1 microgram for each 1.0 square centimeter of surface area. Using surface energy probes of various polarity levels, surface characterization can be achieved. Application of four-quadrant chart analyses serves as a means of surface characterization. The surface electrical properties of contaminants (surface leakage and arc over) can be shown to relate to the various levels of polarity/nonpolarity of materials. This work now permits actual measurement of surface cleanliness.

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