As originally published in the IPC APEX EXPO Conference Proceedings.

Low Surface Energy Coatings, Rewrites the Area Ratio Rules

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Abstract
Paste release characteristics are driven by the Area Ratio formula, which is based upon conventional stencil foil materials such as a variety of stainless steel alloys, nickel, *etc.* The surface energy or "phobic" characteristics of these materials are significantly greater than the newer chemistries used to coat stencils and therefore effectively limits the conventional Area Ratio formula in its ability to predict transfer efficiency in ultra-fine pitch devices.

Introduction

With today's consumer technologies driving the need for denser and more compact devices, the assembly process for surface mounted devices has becoming increasingly more difficult. With the mixture of components requiring a broader range of print deposition volume, various techniques are in use in an attempt to ensure consistent and appropriate paste volume is achieved.
Some of these techniques include step etching a stencil locally on a targeted device, promoting electroformed smooth wall nickel stencils, through to laser cutting newer grade stencil materials.
This paper focuses on the relevant attributes that affect the properties of solder paste release and introduces the effects of surface free energy with respect to key elements that make up the stencil printing process.

Area Ratio

Increasingly, todays stencil aperture designs, typically utilizes the Area Ratio as a guideline which is specified in IPC 7525B. A value of > 0.66 is a threshold which has been established to ensure a high consistent release of the solder paste from the stencil known as Transfer Efficiency. This is the percentage of solder paste released from the stencil aperture compared to the theoretical (not actual) aperture size.

The Area Ratio formula is stated as:
Aperture Area/Aperture wall surface

The Transfer Efficiency has been generally accepted in the industry to be 80% or greater as the threshold for "good" effective solder paste deposition. We have researched extensively throughout the available literature and have been unable to establish the origin of this figure. Almost all the historical data has been captured since the early 90's and would have been experimented with the materials of the day. These include aperture filling with unique/novel squeegee designs to paste deposition using Electroform stencils with their "unique" cusps to trapezoidal apertures due to the inherent nature of the lasers of the day.

As can be seen by the following discussion, there is more to this simplistic formula that affects the transfer efficiency and therefore, a more complex formula is required to accurately determine the transfer efficiency threshold for each individual process.

Aperture Filling

As previously mentioned, the Area Ratio formula assumes a 100% aperture fill. Aperture fill is achieved by a combination of squeegee type (angle of attack, blade flex *etc.*), print speeds and the make-up of the solder paste being printed. There has been many experiments published on effective aperture filling, however, verifying that the aperture is 100% filled prior to being released from the stencil has not been typically established. Studies such as squeegee angle of attack, squeegee material type, edge treatments and ultrasonic/vibrating squeegees have been tested, claiming to enhance the paste deposition/transfer

efficiency. It would stand to reason that packing more material into a cavity, may lead to other problems associated with the release characteristics. Forced aperture fill and/or poor gasketing with non-mask defined pads, will create a small amount of leaking of flux around the perimeter of the aperture on the contact side of the stencil. With the newer surface chemistries, the flux build up can transfer to the pad with more ease and reducing the flux build up on the stencil surface. This in turn will lead to less stencil cleaning wipes.

Solder Mask Defined Pad (SMDP) and Non Solder Masked Defined Pad (NSMDP)

Recent work has also been uncovering the effects of transfer efficiency on both SMDP and NSMDP. From our perspective, the effects of transfer efficiency can be related to the additional surface energy derived by the SMDP versus the lack of additional surfaces by the use of NSMDP.

Surface Related Properties

The printing of solder paste *via* stencils onto PCB surfaces from the standpoint of surface/interface chemistry is extremely complex. Successful printing of solder paste through stencil apertures is a function of multiple different phenomena, some of which can be considered issues of surface/interface chemistry rather than bulk material properties. The following is a list of surface-related properties that can potentially have an impact on solder paste printing and adhesion to surfaces:

1. Surface chemistry of the stencil surface(s), especially the side of the stencil facing the PCB and the sidewalls of the stencil aperture.
2. Surface chemistry of the surface being printed on.
3. Surface chemistry of the flux mixture.
4. Surface chemistry of the solder balls (can usually be ignored unless the particle size is <1 micron).
5. Surface tension of the flux mixture.
6. Presence of surface-active agents in the flux (reducing agents, surfactants, *etc.*).
7. Total contact area of the stencil surfaces with the solder paste.
8. Total contact area of the solder paste with the surface being printed on.
9. Surface topography/roughness.
10. Gravity.

We should mention that when we (and others) use the term ‘surface free energy’ to describe a particular material’s surface, what we really are speaking of is its surface chemistry. Molecules and atoms interact with each other in many different ways, including covalent, ionic, hydrogen and Van-Der-Waals type bonding mechanisms and it is these interactions which define not only the bulk properties of materials, but also their surface properties. Attraction/repulsion of complex materials like solder paste to surfaces can be considered consequences of the relative strengths of these forces. In other words, these basic forces are also responsible for determining the surface and bulk chemical interactions of materials in general. In order to assist the readers to understand how variances in surface/interface chemistry relate to printing of solder paste on printed circuit boards, we will attempt to explain each issue separately then bring them all back together again in order to provide more general guide to assist in selection of materials.

Points 1-6: Surface chemistry

When a liquid (or semisolid) material is brought in contact with a solid surface, the interaction between these two phases will be controlled by the forces listed above; we will focus on the important considerations of these forces towards governing the interaction(s) between solder paste and various materials. An excellent guide to wetting of liquids on surfaces has been written by Gao and McCarthy[1]. Figure 1 is a schematic illustrating a basic example of solder paste being printed onto a PCB surface. As you can see, there are multiple forces acting that control how solder paste behaves when being printed.

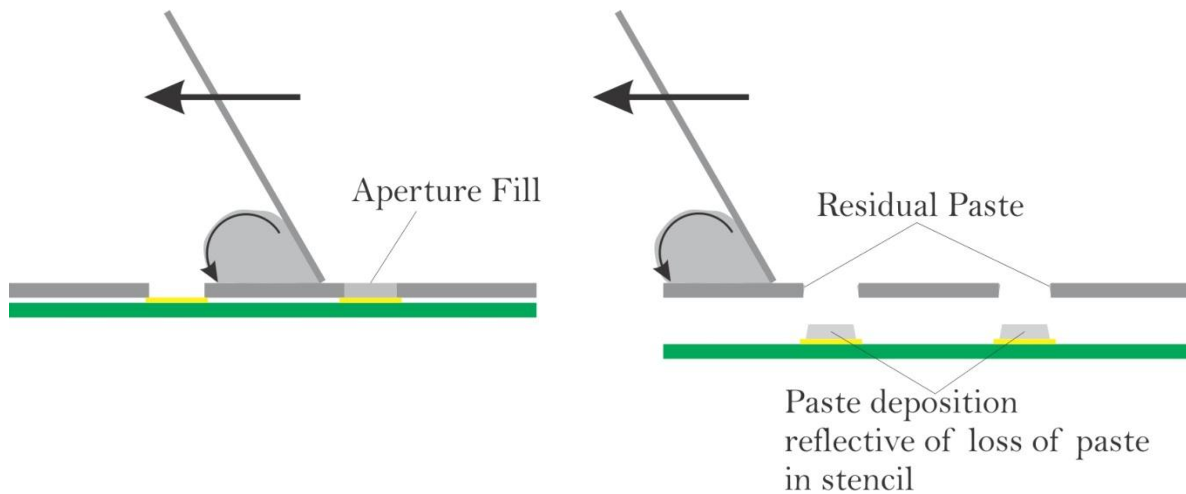

Figure 1

The first things to consider are the surface free energies of all the components in the 'system'. We have used a copper pad as an example to illustrate. Estimated surface free energies of the various components in this system compared to a few low surface energy substrates are in Table 1. An important thing to notice first is that the surface free energies of both copper and stainless steel are lower than one might expect. Metal oxides typically possess surface free energies of at least 70 dyn/cm^{2}, however almost all surfaces exposed to a typical laboratory environment will rapidly be contaminated and therefore the surface energy lowered as a result[2]. Furthermore, metals which have been exposed to processing with organic materials, for example cutting fluids, etching chemicals, fluxes, fingerprints and even plasticizers from plastic shipping containers or tape will have even more surface contaminants present that can be difficult to remove. Most metal surfaces which have not been specially prepared will behave like a hydrocarbon as far as wetting phenomena due to the presence of these contaminants.

Table 1

Substrate	**Surface energy**
Stainless steel (clean)	>70 dyn/cm^2
Stainless steel (contaminated*)	30-40 dyn/cm^2
Copper (clean)	>70 dyn/cm^2
Copper (contaminated*)	30-40 dyn/cm^2
Nickel (clean)	>70 dyn/cm^2
Nickel (contaminated*)	30-40 dyn/cm^2
Amine-cured epoxy	40-50 dyn/cm^2
Polypropylene	~30 dyn/cm^2
Teflon	18-24 dyn/cm^2
Fluorocarbon self-assembled monolayers	14-20 dyn/cm^2

*surface energy of contaminated surfaces depends on the nature of the contaminant(s)

Regardless, due to the fact that organic-based fluxes are mainly hydrocarbon-based they will readily spread out on all surfaces except those which have extremely low surface free energies such as fluorocarbon-based materials. This is due to the fact that hydrocarbon-based molecules interact via weak Van Der Waals forces and are therefore not strongly attracted to each other. Hexadecane (a decent surrogate for organic fluxes) has a surface tension of ~27 dyn/cm and will have contact angles of <10 degrees (extremely wetting) on everything from metal oxides to polypropylene. Furthermore, fluids with low surface tensions are likely to separate into droplets more readily than high surface tension fluids when force is applied to

them. Comparing the surface energies of the materials in Table 1, it can be estimated that solder paste will likely transfer to each surface similarly. While a small amount of surface transfer to the stencil apertures is not much of a problem for large openings, it becomes a significant issue when area aspect ratios drop to <0.66. So far, fluorocarbon films are the only materials on which liquid hydrocarbons will not spontaneously spread. The ability of fluorocarbons to repel other molecules rests in their extreme nonpolar behavior at the molecular scale. While the high electronegativity of fluorine compared with the relatively low electronegativity of carbon does result in a dense distribution of electron density away from the center of mass of each CF_2 segment, in perfluorocarbons ($-[CF_2]_n-$) all of the local dipoles tend to cancel out across a molecule, resulting in no net dipole[3]. Also, due to the extreme difference in electronegativity between carbon and fluorine, there tends to be a bit more resistance to creation of transitory dipolar attraction of neighboring molecules. In addition, while solder paste is far more viscous and less 'liquid' than a simple organic solvent it should still be repelled more readily from fluorinated surfaces in comparison to untreated surfaces.

However, it is dangerous to simply use surface free energy to determine the degree of repellency of a particular surface treatment. It must be taken into consideration the nature of what materials are contacting the surface and any potential they have to chemically react or form surfactant-like layers at interfaces. Solder paste typically contains reducing agents which are used to remove surface oxides during soldering so that intermetallic contact can be made between the solder metal alloy and the PCB trace[4]. Although these reducing agents are usually formulated to react at higher temperatures they will still react with the metal oxides at lower temperatures, albeit at lower rates. If a fluorinated surface treatment is present on the stencil surfaces, it must be stable to continuous contact with the flux's reducing agent(s) for an acceptable time otherwise it will be etched away from the surface. This also means that in the case of a thin treatment (<1 um) the underlying metal oxides should be stable towards chemical attack by the reducing agents, as there will inevitably be some pinholes present in very thin films (or molecular diffusion through the layer itself). In some cases, surfactants are used to lower the surface tension and surface free energy of solder pastes in order to achieve more uniform wetting on surfaces[5]. These pose a particularly difficult problem, as surfactants can essentially defeat even fluorinated films by lowering surface energy/tension too far. Fluorinated surfactants are almost guaranteed to achieve good wetting of formulations on fluorinated surfaces. We would suggest that formulators looking to make solder pastes that print at high fidelity with surface-treated stencils may need to avoid the use of surfactants for the reasons stated above. They may also want to avoid aggressively-reducing formulations to avoid damage to the underlying metal oxide on the stencil surface.

Points 7-10: Surface area and gravity

Obviously, the relative contact areas of the solder paste with the stencil surfaces compared to the PCB surface is of high importance when printing small areas. Table 2 lists the relative surface areas for various packages (data reproduced from IPC 7525-B). Even in the case of the largest average aperture device, PLCC, the stencil sidewall surface area is still quite large when compared to the surface area of the printed section. This should result in a significant amount of material transferred to the sidewalls of the stencil. However, gravity and a lack of opposing attractive force on the other side of the stencil opposite the printed area results in most of the solder paste being transferred correctly. As the area ratio of printed patterns begins to drop, the amount of material transferred becomes increasingly important; the generally accepted rule is that manufacturing problems begin to arise as the area ratio drops below 0.66.

Table 2

Part Type	Pitch	Land Footprint Width	Land Footprint Length	Aperture Width	Aperture Length	Stencil Thickness Range	Aspect Ratio Range	Area Ratio Range	Solder Paste Type
PLCC	1.25 mm [49.2 mil]	0.65 mm [25.6 mil]	2.00 mm [78.7 mil]	0.60 mm [23.6 mil]	1.95 mm [76.8 mil]	0.15 - 0.25 mm [5.91 - 9.84 mil]	2.4 - 4.0	0.92 - 1.53	Type 3
QFP	0.65 mm [25.6 mil]	0.35 mm [13.8 mil]	1.50 mm [59.1 mil]	0.30 mm [11.8 mil]	1.45 mm [57.1 mil]	0.15 - 0.175 mm [5.91 - 6.89 mil]	1.7 - 2.0	0.71 - 0.83	Type 3
QFP	0.50 mm [19.7 mil]	0.30 mm [11.8 mil]	1.25 mm [49.2 mil]	0.25 mm [9.84 mil]	[1.20 mm] 47.2 mil	0.125 - 0.15 mm [4.92 - 5.91 mil]	1.7 - 2.0	0.69 - 0.83	Type 3
QFP	0.40 mm [15.7 mil]	0.25 mm [9.84 mil]	1.25 mm [49.2 mil]	0.20 mm [7.87 mil]	[1.20 mm] 47.2 mil	0.10 - 0.125 mm [3.94 - 4.92 mil]	1.6 - 2.0	0.69 - 0.86	Type 3
QFP	0.30 mm [11.8 mil]	0.20 mm [7.87 mil]	1.00 mm [39.4 mil]	0.15 mm [5.91 mil]	0.95 mm [37.4 mil]	0.075 - 0.125 mm [2.95 - 4.92 mil]	1.2 - 2.0	0.52 - 0.86	Type 3
0402	N/A	0.60 mm [19.7 mil]	0.65 mm [25.6 mil]	0.45 mm [17.7 mil]	0.60 mm [23.6 mil]	0.125 - 0.15 mm [4.92 - 5.91 mil]	N/A	0.86-1.03	Type 3
0201	N/A	0.4 mm [9.84 mil]	0.45 mm [15.7 mil]	0.23 mm [9.06 mil]	0.35 mm [13.8 mil]	0.075 - 0.125 mm [2.95 - 4.92 mil]	N/A	0.56 - 0.93	Type 3
01005	N/A	0.200 mm [7.87 mil]	0.300 mm [11.81 mil]	0.175 mm [6.89 mil]	0.250 mm [9.87 mil]	0.063 - 0.089 mm [2.5 - 3.5 mil]	N/A	0.58 - 0.81	Type 4
BGA	1.25 mm [49.2 mil]	CIR 0.55 mm [21.6 mil]		CIR 0.52 mm [20.45 mil]		0.15 - 0.20 mm [5.91 - 7.87 mil]	N/A	0.65 - 0.86	Type 3
Fine-pitch BGA	1.00 mm [39.4 mil]	CIR 0.45 mm [15.7 mil]		SQ 0.42 mm [13.8 mil]		0.115 - 0.135 mm [4.53 - 5.31 mil]	N/A	0.65 - 0.76	Type 3
Fine-pitch BGA	0.50 mm [19.7 mil]	CIR 0.25 mm [9.84 mil]		SQ Overprint 0.28 mm [11.0 mil]		0.075 - 0.125 mm [2.95 - 4.92 mil]	N/A	0.56 - 0.93	Type 3
Fine-pitch BGA	0.40 mm [15.7 mil]	CIR 0.20 mm [7.87 mil]		SQ Overprint 0.23 mm [9 mil]		0.075 - 0.100 mm [2.95 - 4 mil]	N/A	0.56 - 0.75	Type 4

Note 1: It is assumed that the fine-pitch BGA lands are not solder mask defined.
Note 2: N/A implies that only the area ratio should be considered.

There is some controversy whether the roughness of the stencil sidewalls plays a role in determining the amount of solder paste transferred. Some solder paste will obviously be trapped in any grooves/pores on the stencil sidewalls; whether solder balls or flux alone is trapped will depend on the size of the defects *vs.* the solder balls' diameter. A variety of techniques have been used to minimize the amount of exposed stencil surface (electro polishing, using thinner metals, more precise cutting methods, *etc.*), however attention must eventually be turned to modifying the surface chemistry of the stencil by incorporating a low surface energy treatment such as a fluorocarbon film (for the aforementioned reasons).

The choice of surface treatment type and methodology to create such a surface treatment is dependent on several factors, including:

1. Three-dimensional nature of the stencil (has an impact on coating techniques that can be used).
2. Ability to bond to metal oxides such as nickel and chrome/iron oxides (stainless steel).
3. Stability to chemical attack and physical abrasion.
4. Additional thickness imparted to the stencil apertures by the coating.
5. Flexibility/fracture toughness of the coating.
6. Slipperiness of the surface treatment (can impact performance of the solder squeegee).
7. Surface free energy of the treatment and it's relation to the chemistry of solder pastes that will be used.
8. Surface roughness of the stencil apertures (will need to be smoothed out by the surface treatment).

Currently, there are vast multitudes of ways in which surfaces can be coated and insulated from the surrounding environment. However the ways in which surfaces can be rendered oleophobic are few. In this section we will attempt to explain the most relevant methods for making stencils oleophobic and the benefits/detractions associated with them. It must be noted that while true 'oleophobicity' is a technically valid term only when the static oil contact angle of a surface is $>90^o$, most coatings manufacturers in this arena describe materials with oil contact angles in the $60\text{-}70^o$ range as 'oleophobic' due to the fact that most surfaces have oil contact angles of $<10^o$, resulting in a significant change in the oil repellent properties of a treated *vs.* untreated surface. There are three general classes of surface treatments to modify the oleophilicity/phobicity of surfaces, including single molecular layers of fluorocarbons bound to the surface (hereinafter simply called 'monolayers'), multilayered or oligo/polymeric fluorocarbons, and traditional organic coatings (what one would normally describe as a paint or varnish). In the next section we will attempt to compare and contrast all three approaches in consideration of the eight factors illustrated in the preceding paragraph.

Monolayers: If solution-applied they are easy to use on complex surfaces, and can be readily applied from solution and work in large scale operations unless special chemistries are used. Monolayer-based treatments can achieve some of the lowest surface free energies due to the inherent nature of these systems to form organized structures. Abrasion resistance of these

treatments on stencil materials is typically good. There are two main chemistries used to form monolayers on metal oxide surfaces, siloxane and phosphonates. Generally speaking, the chemical stability of silicon-oxygen-metal bonds (other than Si or Sn-based oxides) are poorer than phosphonates due the fact that Si-O-M (M = Cr, Fe, Ni, *etc.*) bonds are readily hydrolysed in the presence of weak acids/bases whereas P-O-M bonds are only hydrolyzed in the presence of strong base[6]. Siloxanes typically form monodentate bonds to surfaces whereas phosphonates will form bi- or tridentate species with most metal oxides[7], giving them even more resistance to hydrolysis. Furthermore, the overall quality of siloxane monolayers are dependent on the amount of surface hydroxyls present; most metals are in the range of 10-15% M-OH functionality, meaning that true monolayers of siloxanes will be inherently limited to submonolayer packing densities[8]. Phosphonate-based treatments do not suffer from this limitation due to their capability of bonding to μ-oxo (M-O-M) groups as well as metal hydroxides. Chemical bond strength of monolayer systems to the substrate is very high compared to organic coatings, though phosphonates are significantly better than siloxanes on Ni/SS due to the aforementioned issue of hydrolytic stability. Proper cleaning of the stencil prior to coating is of critical importance, as contaminants must be completely removed, exposing metal oxide that the monolayers can covalently bond to. In a typical application, the stencils will be cleaned with a heated caustic solution, followed by rinsing then dipping into the active solution for some period of time. Phosphonate-based systems are generally tolerant to changes in operating conditions (dip time, temperature, humidity, *etc.*), whereas siloxanes will need careful control of the ambient environment to avoid dimerization/polymerization of active materials. The impact of how much water is adsorbed on the stencil surface (in the 1-10 monolayer regime) will affect the end performance of siloxane monolayers; in contrast phosphonates will be unaffected. In addition, phosphonates do not typically need a post-curing step whereas siloxanes will need a 100-150 ^{o}C cure for up to an hour, depending on the siloxane used. Monolayer-based treatments are an optimal choice for very low aperture sizes (they will only narrow the apertures by 2-5 nm) where print quality is critical yet cost per coated stencil is of some concern.

Multilayered surface treatments: Typically, these types of treatments are only applied via vacuum-based techniques as they are very difficult to apply homogenously on complex surfaces from solution. They are generally derived from multifunctional reactive silanes/siloxanes[9] and require control of surface water content, deposition rate, substrate temperature, *etc.* and therefore need tight process monitoring in order to be performed successfully. Flexibility can be an issue, as these systems are heavily crosslinked to achieve good surface coverage. Cost and manufacturing speed are obvious weak points when vacuum-based systems are used due to the batch-wise nature of the process and the rather expensive equipment needed. If performed correctly, they can have very low surface energy, moderate chem/abrasion durability and a small impact on aperture narrowing (they are typically in the 50 nm thickness range). Adhesion of these treatments can be difficult to achieve without developing a system for priming the surface. Proper cleaning of the stencil prior to coating is extremely critical to achieving a good quality treatment for the same reasons outlined for monolayers. Overall, these may be equivalent performance to solution-based monolayer systems but with significant added cost.

Organic (thick coatings): More traditional organic (thick) coatings can be difficult to homogenously apply to complex surfaces due to the difficulty of preparing <1 um thick polymer coatings. A classic example of this type of treatment would be the Teflon® coating applied too cookware. These types of treatments typically have very good adhesion, chem/abrasion stability and flexibility. However, they will have higher surface energies than monolayers/vacuum coatings and can easily clog small apertures. Any roughness on the stencil surface should be homogenized by the thicker coating, allowing for some benefit in reducing adhesion of solder paste to stencil sidewalls that have been roughened during cutting. There are potential issues with some coating particulates flaking off into the solder paste over time as the coating ages. The use of thicker organic (polymer) treatments is probably the best choice for ultra-high throughput, medium-large aperture size (>0.66 area ratio) stencils.

In all three cases, post-analysis can be performed through contact angle goniometry, as well as more traditional coatings testing procedures (hardness, cross-hatch/tape peel, *etc.*), though in order to get a more accurate measure of the properties of the last few nanometers at the surface of a treatment it is necessary to use surface-sensitive analytical techniques such as x-ray photoelectron spectroscopy, specular reflectance infrared spectroscopy, and the like. Since contact angle goniometry is (rather unfortunately) used by many as an analytical method to give pass/fail ratings to oil and water repellent treatments, we believe it is necessary to provide readers with some advice on using such measurements to ‘define’ a specific surface or coating.

Contact angle goniometry: a brief warning.

There are precious few methods to analyze ultrathin films on surfaces; most of the available techniques for characterization of nanometer-scale films are very expensive. An instrument capable of performing X-ray photoelectron spectroscopy (one of the best surface analysis techniques) is usually $100,000+ whereas a basic contact angle goniometer can be purchased for less than $10,000. The comparatively low cost and technical skill required to perform contact angle goniometry are likely the main reasons why this technique is by far more widely used than any other technique for characterization of nanometer-scale films. The use of contact angle goniometry, which is characterization of a (typically) solid surface by measuring the contact angle of droplets of various fluids (predominantly water) on it can be a very useful tool to experienced practitioners, however it is also a technique that is rife with misunderstandings, poor experimental design, and misinterpreted results. We have observed time and time again that using only static water or oil contact angles to associate a specific performance metric of soil-repellent films can be problematic. We do continue to use oil and water contact angles as a method for comparing treatments or process improvements to treatments, however only in the case where the substrates have been from the exact same piece of metal (typically we use many small pieces cut from a larger panel) and the treatment processes have been previously standardized using more careful analytics on model substrates. Otherwise, the true best method to compare different coatings or different coating methodologies is best carried out by preparing samples and testing them in their actual intended application. For those who would like a bit more information on the topic of wetting and surfaces, we once again direct readers to the excellent surface wetting primer by Gao and McCarthy[1].

Conclusion

The purpose of this paper is to break down the components of the stencil system and to highlight and understand the phenomenon of interacting surface free energies. Solder paste printing clearly has an intense set of complex interacting parts that does not lend itself to having a one fix for all. From a stencil specific perspective, stencil materials and surface treatments will play a vital role in successful deposition control, especially with the surface mount assemblies that have greater densities of miniaturized components.

From our perspective, as stencil aperture size decreases, the importance of addressing the issue of surface energy becomes more critical. At the moment, fluorocarbon-based surface treatments are the best method to reduce surface energy, and therefore soiling of the stencil surfaces by solder paste fluxes. Of these treatments, we believe that monolayers of phosphonate-based treatments are likely the optimal balance of performance and cost (from the considerations described above) and the fact that the innate thinness of these treatments creates very few risk factors (they do not appreciably 'crack' or leach into paste and if they are damaged there will be no change to the aperture sizing).

The use of the Area Ratio formula is basic in its approach to understanding deposition capabilities. Highlighting the complexities of the various interacting surfaces and their levels of wetting/repellency to the solder paste, more studies will be needed to establish a true formula that will take in to consideration the variables.

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