COMPATIBILITY OF CLEANING AGENTS WITH NANO-COATED STENCILS

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ABSTRACT
High density and miniaturized circuit assemblies challenge the solder paste printing process. The use of small components such as 0201, 01005 and µBGA devices require good paste release to prevent solder paste bridging and misalignment. When placing these miniaturized components, taller paste deposits are often required. To improve solder paste deposition, a nano-coating is applied to laser cut stencils to improve transfer efficiency. One concern is the compatibility of the nano-coating with cleaning agents used in understencil wipe and stencil cleaning. The purpose of this research is to test the chemical compatibility of common cleaning agents used in understencil wipe and stencil cleaning processes.

Key words: Nano-coating, cleaning, under-stencil wipe, stencil cleaning, chemical compatibility

INTRODUCTION
The natural progression of innovation is the driving force behind the miniaturization and increased density of circuit assemblies. With this drive towards smaller, more complicated devices, an increase demand is placed on the manufacturing process. Unfortunately, the relative decrease of component size is not uniform for all components. Passive components have decreased in size more readily than components like RF shields. This, non-uniform decrease in component size, coupled with the overall size reduction of the finished assembly has forced large and small components into close proximity. This discrepancy between large and small components adds to the challenge of designing and manufacturing such assemblies.

While the industry has advanced from the 1206 to the 01005 resistors and from BGA to µBGA devices the basics of printing remain unchanged. Stencil printing is the dominant method of depositing solder paste due to its cost-effective nature and its reliability. As it stands now, further reductions in component size, as well as the presence of multiple component sizes, threaten to wreak havoc on the assembly process. In order for stencil printing to remain the dominant method for these more difficult assemblies, new technology has had to be incorporated into this process.

One of these technologies, nano-coated stencils, uses an extremely thin coating of a material on the stencil that has shown promise in prolonging the viability of the stencil printing process [1] [2]. A systematic evaluation of the chemical compatibility between the nano-coating and cleaning agents used to clean stencils and squeegees has not yet been conducted. Additionally, there is as paucity of literature detailing effective ways of measuring the performance of the coating.

In the stencil printing process there are numerous variables that one must control in order to yield a robust process. There are two basic steps in the stencil printing process. First, the stencil is filled with solder paste. Then, the paste is released from the stencil onto the printed circuit board (PCB) as the stencil is lifted away from the PCB. In the first step, squeegees transport solder paste over what is known as the "squeegee side" of the stencil. This squeegee forces paste into the apertures with the intent of filling them uniformly. Some of the variables that impact this step include the construction of and pressure applied to the squeegee, the paste roll, the orientation of the aperture relative to the direction of the printing and the solder paste. After the paste has been applied to the apertures, the paste release begins.

In the squeegee transfer process, the goal is for the solder paste to have a stronger attraction to the PCB than to the walls of the apertures. This process is affected primarily by the stencil's design, although the solder paste and the speed of the board separation also have influence. The design of the stencil introduces many factors. The material used to construct the stencil of and how the stencil manufacture creates the stencil affect this process. A number known as the *area ratio*, which is defined as the ratio of the aperture opening on the PCB side to the area of the aperture walls, is commonly used as a measure of the adhesive forces. As the area ratio decreases, the force applied to the paste by the aperture walls increases, causing a decrease in the transfer of the solder paste from the stencil to the PCB. The very definition of the area ratio underscores the importance of another key variable, the wall smoothness. A smoother wall will exert less adhesion to the paste than a rougher one. The roughness can be controlled by various methods for forming the apertures (e.g. laser cutting and electroforming). A new method of modifying not only the smoothness of the aperture but also the chemical interactions between the paste and the stencil uses a nano coating.

Nano-coated stencils represent a relatively new technology. These stencils work in two complementary ways to reduce the adhesive force between the paste and the aperture. First, by adding the extremely thin coating, the roughness of the aperture is reduced [2]. Additionally the coating fills in some of the "valleys" in the surface topology. This process, as noted above, decreases the adhesion. However, the primary mode of improving solder release is the way in which the coating chemically modifies the surface of the aperture and decreases the chemical attraction that the paste has to the metal surface.

Surfaces can be characterized as being either high or low surface energy, terms that denote how liquids interact with the surfaces. Unmodified metal surfaces are typically high surface energy. Surfaces with high surface energy are held together by strong or high energy chemical bonds (ionic, covalent, or metallic). High energy surfaces are typically able to be wetted (a liquid can readily spread over the surface of the material) by most liquids due to the interaction of the surface and the liquid being stronger than the interaction between liquid molecules. Low energy solids, on the other hand, are held together primarily through physical interactions, such as hydrogen "bonds" or Van der Waals forces. Since these surfaces interact with liquids via weaker methods, the surface tension of the liquid is too great for the surface to overcome, and the liquid does not spread.

Nano-coatings profoundly influence this process, as they are low energy molecules which, when applied to a metal surface, chemically bonds with that surface, forming a low energy coating. This coating decreases the interaction between the paste and the aperture, allowing for a cleaner release.

Currently there exist two nano-coating stencil options, one offered by LaserJob GmbH, NanoWork stencils and one offered by DEK, Nano-ProTek. While they work similarly, their primary differences lie in method of application. The NanoWork stencil's nano-coating is applied by LaserJob during the manufacturing of the stencil. This process creates a strong chemical bond between the coating and the metal of the stencil. DEK's Nano-ProTek is a two part wet wipe system that can either be applied during the stencil manufacturing or used in the field to coat an existing stencil, rendering it a nano-coated stencil, or to repair a nano-coated stencil with damaged coating. The first part of the system is essentially a primer in a wipe that prepares the metal surface in order to improve the bonding of the metal to the nano-coating, which is contained in the second wipe. The current method of assessing the presence and performance of the nano-coating is qualitative in nature.

There are two suggested methods by which to evaluate the performance of the nano-coating, both of which are subjective. The first method is the least subjective and consists of placing a drop of water on the stencil and observing whether it beads up. If it fails to do so, then the coating is absent or damaged. The other, more subjective method entails marking the coated surface and seeing how easily the marking is removed [1].

Currently, no special recommendations for cleaning nano-coated stencils exist. The cleaning process typically involves three steps that take place in the order listed: wet, vacuum, dry. The wet cleaning involves running the PCB side of the stencil over a cleaning wipe that has been wetted with a cleaning agent. This process is then followed by running the same side of the stencil over a dry wipe while a vacuum is applied to the other side of the wipe. This step helps to dry the residual cleaning agent on the stencil as well as to remove solder balls. Finally, the stencil is passed over a dry wipe.

A second cleaning step involves placing the stencil into a stencil cleaning machine at the end of production or when the apertures become clogged with solder paste. This machine sprays cleaning agents onto the stencil to dissolve the flux residue and physically remove solder balls.

METHODOLOGY

The goal of this study is to determine the chemical compatibility of the cleaning agents with the nano-coating previously applied to the metal stencil foil. As noted previously, no quantitative methods for measuring this compatibility are detailed in the literature. Upon reviewing literature and attempting to measure or quantify both DEK and LaserJob's coatings with optical metrology methods, scanning electron microscopy, and Fourier transform infrared spectroscopy to no avail, a method for measuring compatibility was devised using the basic principles noted in the introduction.

A common way of characterizing wetting ability and surface energy is by using contact angles. When a drop of liquid is introduced to a surface of a material, it flows outward until it reaches equilibrium with the forces that are interacting upon it, namely the surface tension of the liquid and the interfacial surface tension, also known as free energy. At this equilibrium, the curvature of the drop forms a characteristic angle with the substrate, which is known as the contact angle or θ (more technically, this angle is known as the equilibrium contact angle or θ_{eq}, but it is commonly called the contact angle and it is assumed to be the equilibrium contact angle unless otherwise stated).

There are three sets of these interfacial surface tensions which, when combined give rise to the contact angle: the interaction between the solid and the liquid (γ_{sl}), the interaction between the solid and the surrounding medium, which is usually air (γ_{sv}), and the interaction between the liquid and the surrounding medium (γ_{lv}). These forces are shown in Figure 1. Young's equation, Equation 1, shows the mathematical interaction between these three forces and how they give rise to the contact angle.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta$$

Equation 1: Young's relationship [4]

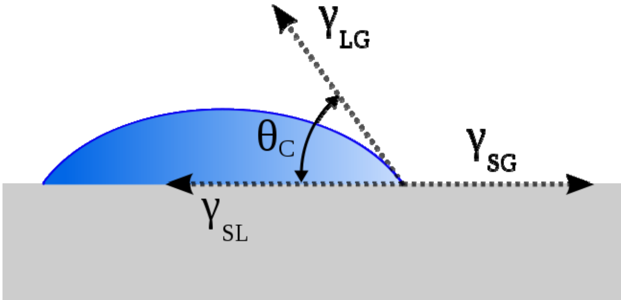

Figure 1: The three forces that give rise to contact angles, adapted from [4]

While it is possible to calculate these three values for any given unknown, this step is usually not performed. Instead, the contact angles are used to imply the nature of the interactions and to rate the strength of the interactions. In general, with other variables being held constant, as the contact angle becomes larger, the wettability, adhesiveness, and surface energy decrease. Thus a low contact angle results in an increase in adhesion.

A more familiar use of contact angles is in describing the hydrophobic/hydrophilic nature of a surface. A hydrophobic surface is typically defined as a surface with a contact angle with water of greater than 90°. Other descriptors used are also lipophilic and lipophobic, which describe the contact angle of oil and a surface. A lipophobic surface is typically a hydrophilic surface, and a hydrophobic surface is usually lipophilic.

Research Hypothesis

The hypothesis for this study is that the nano-coating will produce a high contact angle and that, if it is removed, the contact angle will decrease until it reaches the contact angle of the substrate.

Measuring Contact Angle

Typically the contact angle is measured on a goniometer. A goniometer contains a syringe or a pipette positioned perpendicular to the sample to deliver a control volume of water. The sample is illuminated either from behind a camera or by the camera. The camera is positioned with an angle of 0-5° to the plane of the sample. The camera is used to take images which are then transferred to imaging software to measure the angle. In the imaging software, a line originating at the intersection of the air/liquid/surface interface and tangent to the drop is created. The angle that this line forms with the surface is the contact angle. A schematic of a goniometer is shown in Figure 2.

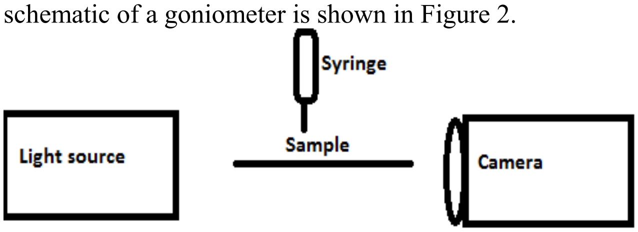

Figure 2: Schematic of a Goniometer

Due to a lack of access to a goniometer, a goniometer was fashioned from a Keyence VHX-1000 microscope set to 90° (corresponding to a 0° angle with respect to the plane of the sample), a 5µL GC syringe, and a light source placed behind the sample. The creation of an "improvised" goniometer is not without precedence [5]. This apparatus is shown in Figure 3. In an effort to minimize operator error, only two individuals measured the contact angles.

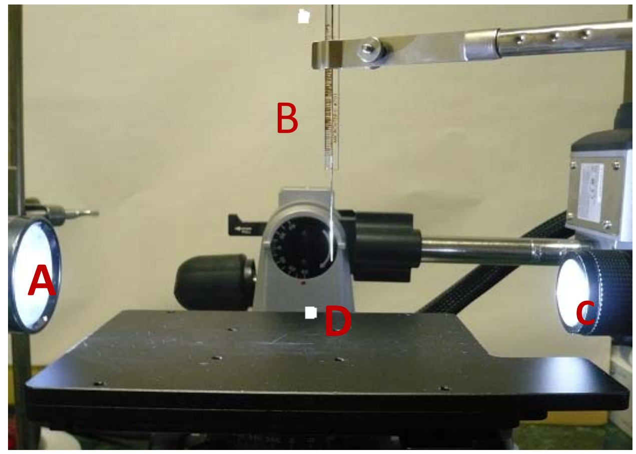

Figure 3: Goniometer, A- Light Source, B - 5µL GC syringe, C-Keyence VHX-1000 Camera, D-Sample

Verification of the Goniometer

After the goniometer was set up, its performance was verified. A commercially available reference was purchased from Ramé-Hart Instrument (part number 100-27-0). This reference sample is a piece of virgin polytetraflouroetheylene (PTFE) for which the contact angle was measured by the manufacturer. Five contact angles were measured and compared to this range.

Compatibility

For compatibility testing, a set of test coupons was obtained for each material. Both sets of test coupons were approximately 1"x4" inches with the treatment on one side. The NanoWork coupons were obtained directly from LaserJob and were individually numbered on the side without treatment. The coupons obtained that were coated with DEK's Nano ProTek wipes were from Sten Tech. These were not individually numbered, so a unique number was inscribed on the non-treated side in order to avoid disturbing the coating. The contact angle was measured on the treated side ten times for each coupon using the equipment described above. On approximately half of the samples the non-treated side was also measured ten times to serve as a control.

Next, a test coupon from one manufacturer was paired with a test coupon from the other manufacturer for compatibility testing, so that one coupon from each manufacture was tested with each cleaning agent. The cleaning agents that were selected were: Cybersolv 8622, Cybersolv 3418, Cybersolv 3400, Cybersolv 3412, Ionox BC, Lonox 5611, and Lonox 5611D. All testing was performed on undiluted cleaning agents at ambient temperature with no agitation, with the exception of Lonox5611D, which was gently rotated to keep it well mixed.

Each pair of test coupons was placed in the cleaning agents. At intervals of 15 minutes, 1 hour, 4 hours, and 24 hours, the coupons were removed, and dried, and the contact angle was measured ten times on the treated surface and recorded.

RESULTS

Verification of Contact Angle Accuracy

Five replicate measurements were made under the experimental conditions specified by the standard's documentation. The range was determined to be 100.4° to 104.29°, which is within the range measured by the manufacturer (100.1-104.8°) and validates that the method selected yields accurate contact angles. Two images of the contact angle, one of which shows its measurements, are presented in Figure 4.

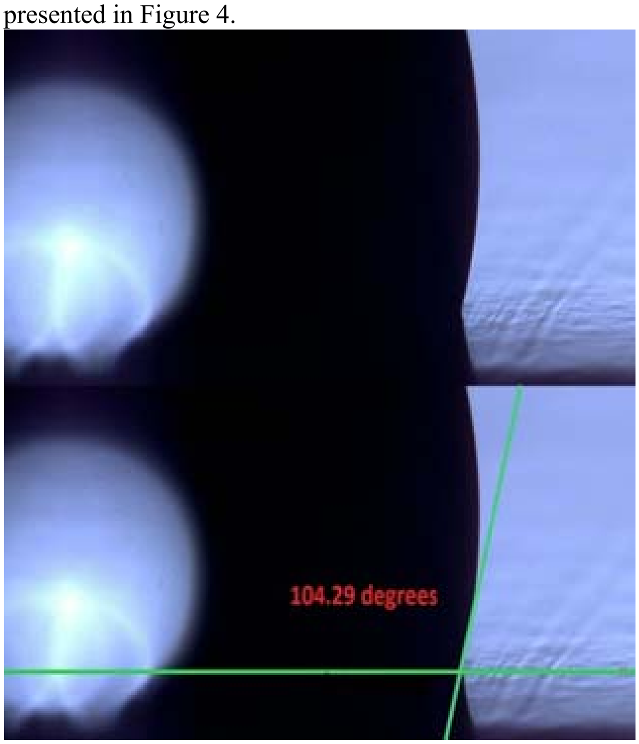

Figure 4: Top Half of the Image is the Contact Angle on the Reference Sample – The Bottom Half of the Image is the Contact Angle after Exposure to the Cleaning Agent

Chemical Compatibility Data Findings

Table 1 shows the mean contact angle for all manufacturers, chemistries, and time. Box plots showing the variability of the data are presented in Figure 5 and Figure 6 for DEK and LaserJob, respectively. A mean interaction plot for DEK is shown in Figure 7 and LaserJob in Figure 8. The reference lines, from top to bottom are, one standard deviation above the mean for all contact angles at time zero for that coating, the mean contact angle at time zero for that coating, and one standard deviation below the mean for that coating.

DEK Nano ProTek					
Cleaning	Time (hr.)				
Agent	0.00	0.25	1.00	4.00	24.00
C 3400	111.41°	112.37°	108.90°	103.84°	103.69°
C 3412	94.71°	111.56°	107.33°	108.63°	85.77°
C 3418	100.04°	108.44°	111.73°	113.60°	109.54°
L 5611	112.78°	107.54°	109.78°	108.41°	105.04°
L 611D	92.41°	105.03°	105.50°	106.27°	107.19°
L 8622	96.66°	108.82°	109.35°	115.01°	104.48°
I BC	102.58°	106.89°	108.47°	101.46°	108.30°
LaserJob NanoWork					
Cleaning	Time (hr.)				
Agent	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C 3400	105.08°	102.68°	108.03°	103.47°	107.29°
C 3412	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C 3418	109.84°	104.61°	106.72°	107.30°	106.18°
L 5611	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
L 611D	104.48°	105.06°	106.43°	106.35°	105.44°
L 8622	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
I BC	108.24°	105.54°	105.44°	106.71°	106.02°

Table 1: Mean Contact Angle Measurements

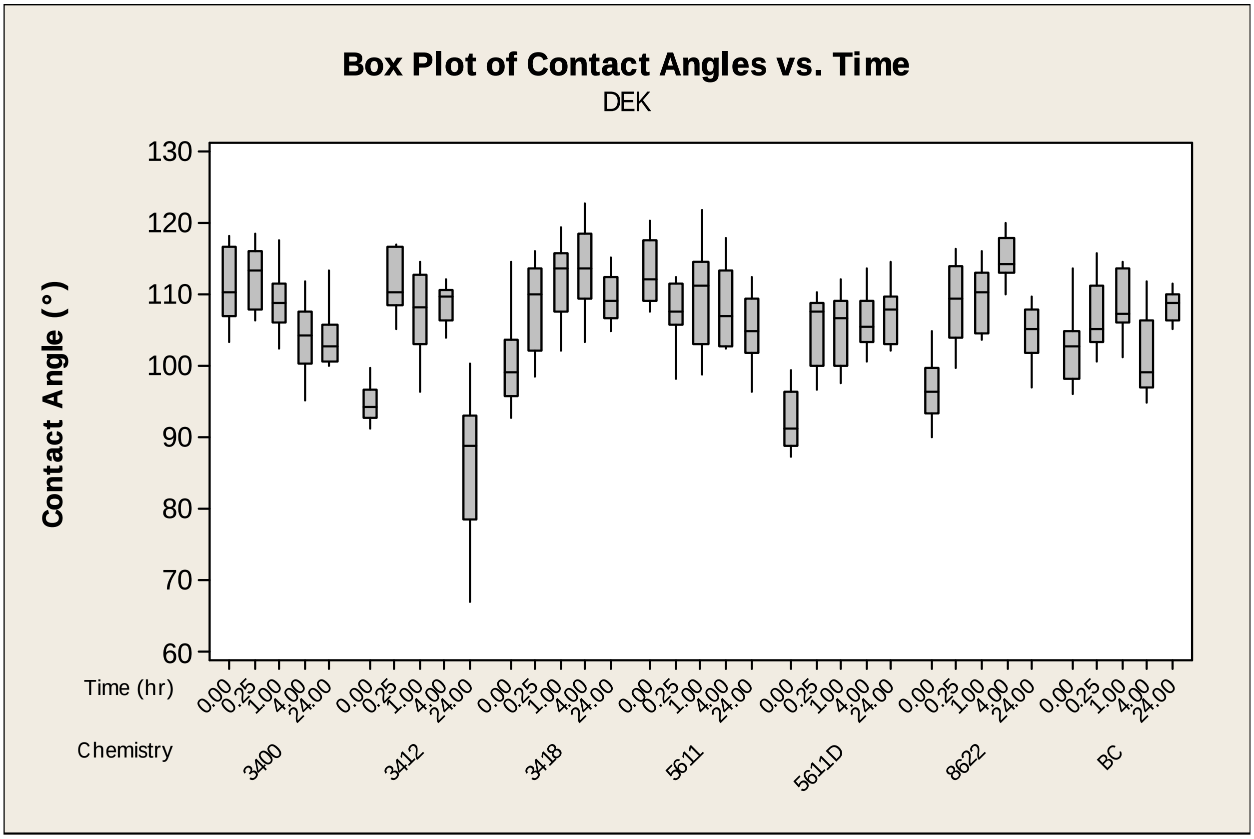

Figure 5: Box Plot of contact angle vs. cleaning agent and time.

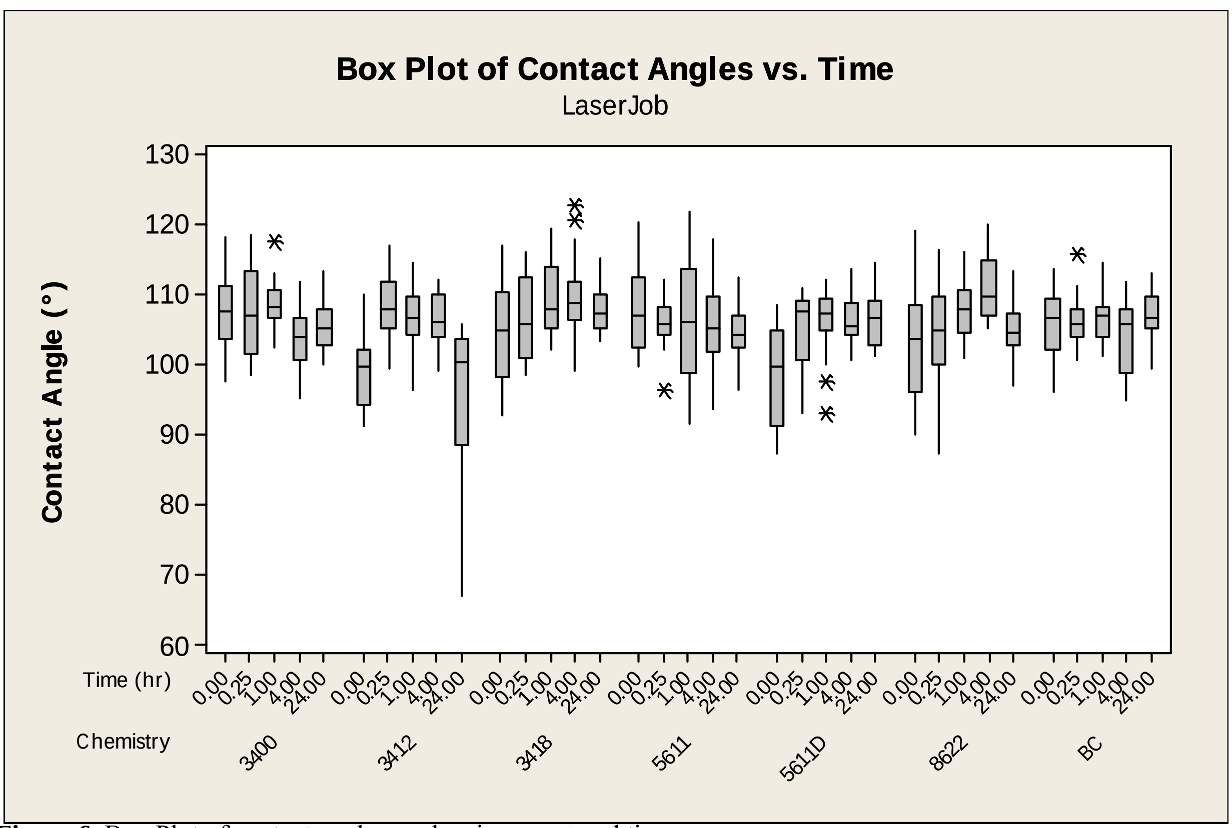

Figure 6. Box Plot of contact angle vs. cleaning agent and time.

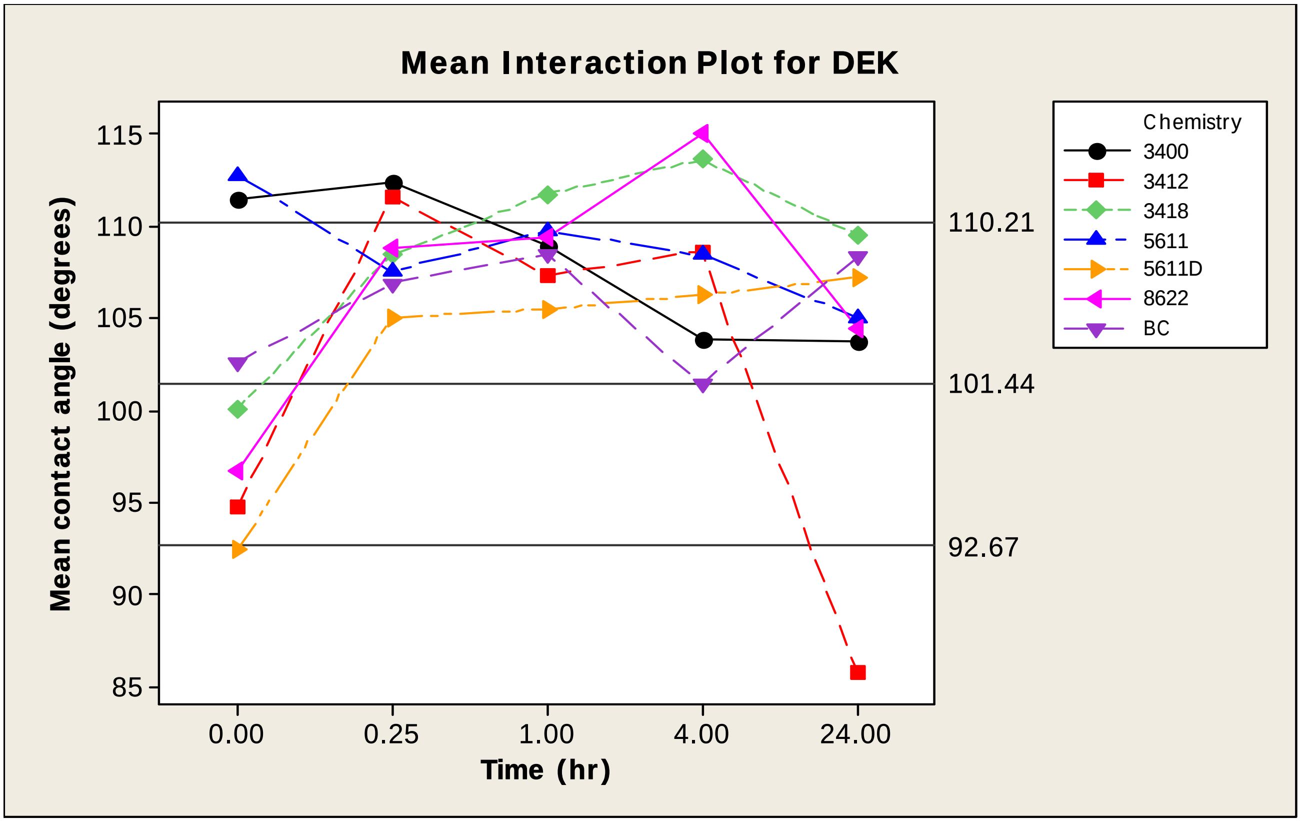

Figure 7: Mean interaction plot for the exposure of DEK nano-coated stencils to various cleaning agents. The lines at 110.21°, 101.44°, and 92.67° represent mean starting contact angle +1σ, mean starting contact angle, and -1σ from mean starting contact angle.

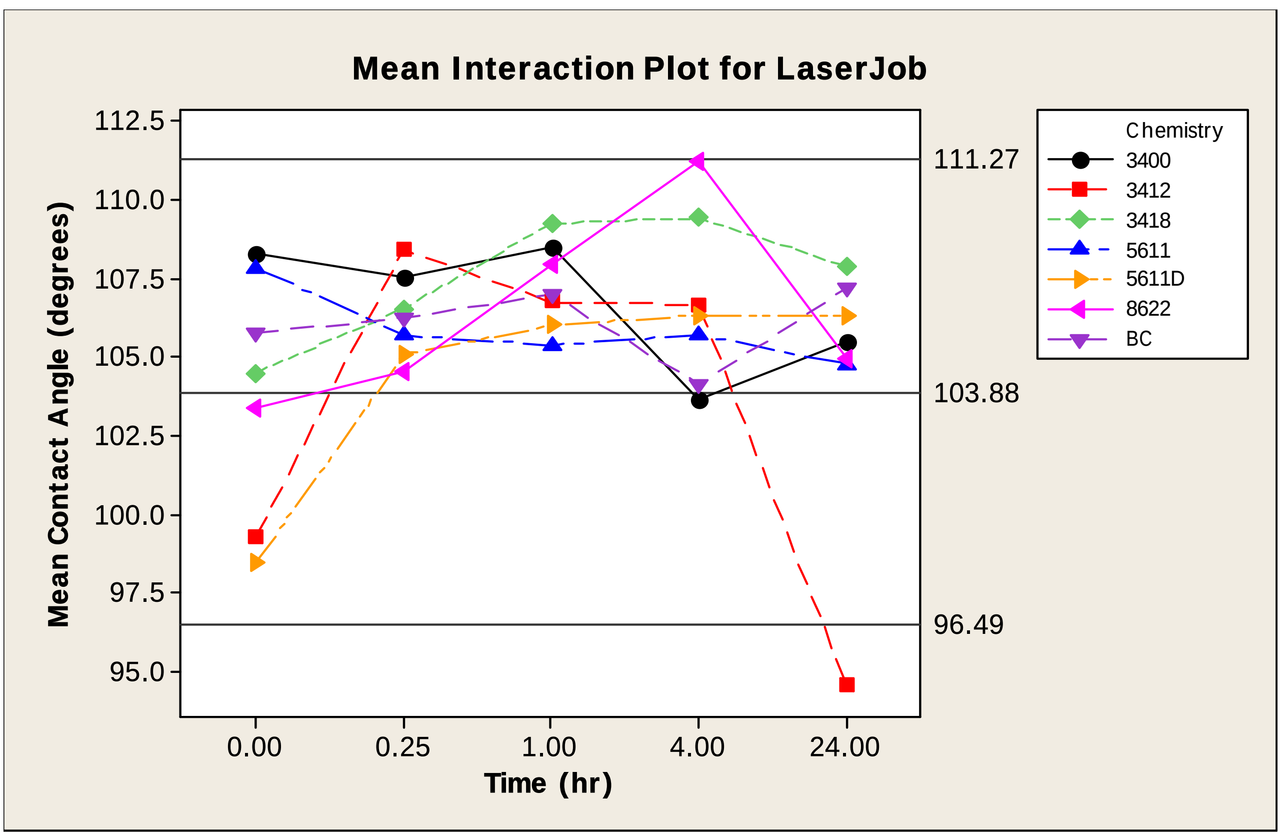

Figure 8: Mean interaction plot for the exposure of LaserJob nano-coated stencils to various cleaning agents. The lines at 111.27° 103.88°, and 96.49° represent mean starting contact angle +1σ, mean starting contact angle, and -1σ from mean starting contact angle.

INFERENCES FROM DATA FINDINGS

The data indicates that under the experimental conditions all cleaning agents were chemically compatible with both the DEK Nano ProTek and the LaserJob NanoWork nano-coatings. There appears to be no statistically significant change in the contact angle. According to the hypothesis if the material was not chemically compatible the contact angle would decrease as the coating is removed. This effect was not observed.

One interesting observation is both the DEK and LaserJob nano-coatings showed a sudden decrease in contact angles between four and twenty-four hours with Cybersolv 3412. Although this decrease was not statistically significant it would be reasonable to infer that over a longer period of time under these conditions chemical compatibility may be an issue for Cybersolv 3412.

RECOMMENDATIONS FROM DATA FINDINGS

It appears that the cleaning agents tested are compatible with the nano-coatings tested for up to one day of static immersion, at ambient temperature. As noted above it would be reasonable be cautious when submerging a nano-coated stencil to Cybersolv 3412 for over one day, which is not likely to occur in any process. A future study will examine the effects of mechanical and chemical action on the nano-coated stencils. In that study a more detailed characterization of the surface energy of the nano-coating will be performed.

Contact angle is a viable option for those who wish to confirm their nano-coating's performance in their facilities. While a microscope was used, it is possible to use a typical digital camera and free or commercially available imaging software. One should measure the contact angle at several locations to minimize the effect that surface topology and contamination has on the recorded value.

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