Liquid Photoresist and Soldermask Processing
The Real Environmental Impact

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Abstract
Since the early days of PWBs, liquid photoresists and soldermasks have played indispensable roles in the manufacturing process. From the introduction of the original Kodak Photo Resist (KPR) and PC 301 soldermask, development has sought to keep pace with the improved resolution, processing speed, and advanced substrates demanded by the industry. Similar to the path taken in micro lithographic processing, PWB photoresist and soldermasks have evolved on solvent based coating platforms.

In the new millennium, point-of-manufacture and downstream health issues have come to the fore. Water, soil and air pollution are key drivers and preventative measures have a real economic impact on the manufacturer. Further, as global warming is a reality and oil prices continue to rise, manufacturers are looking for ways to decrease their environmental impact *and* reduce cost without sacrificing performance. But what are the environmental impacts of liquid photoresist and soldermask? And what are the associated costs?

This paper will analyze the following in relation to both the environmental, health and related cost impacts:

- Current photoresist and soldermask formulations
- Application methods
- Medical and health concerns
- Hidden costs such as insurance, shipping and handling

In addition, the paper will describe the environmental, performance and cost impacts associated with utilizing a new water-based photoresist platform.

Introduction
While the importance of global warming is still being debated for political reasons, scientists continue to chart the effects of mankind's expansion in the industrial, transportation and agriculture sectors. In particular, since the mid 1800's, the industrial revolution and population explosion have brought unprecedented changes to the environment we live in. Governments have responded by enacting environmental policies to limit air, water and land pollution to protect the Earth for present and future generation. For the purpose of this discussion we will consider one class of pollutants Volatile Organic Compounds (VOCs).

VOCs combine with oxides of nitrogen (NOx) in the presence of sunlight to produce ozone (O_3). While ozone in the upper atmosphere is beneficial for life by shielding the Earth from harmful UV radiation from the sun, this is not true of ozone located around Earth's surface. Ground level ozone is the major component of smog and is a major health and environmental concern. Evidence indicates that ozone is responsible for a host of respiratory problems. Of increasing concern is that VOCs also make their way to the atmosphere, thickening Earth's insulating blanket, preventing heat from escaping.

Nonmethane volatile organic compounds (NMVOCs), commonly referred to as "hydrocarbons," are the primary gases emitted from most processes employing organic or petroleum based solvents. They are classified as NMVOCs to differentiate them from methane, a VOC emitted mostly from livestock production. As shown in Table 1, solvents in surface coatings accounted for approximately 41 percent of NMVOC emissions in 2003 (most recent compiled EPA data)[1]. Overall, solvent use accounted for approximately 28 percent of total U.S. emissions of NMVOCs in 2003. These solvent emissions occur mostly when the coatings are dried. It is encouraging to note that NMVOC emissions from solvent use have decreased 21 percent since 1990.

Photoresist and Soldermask fall into the general surface coating category that also includes paints, varnishes anti corrosion coatings etc. It is estimated that in 2003, photoresist and soldermask accounted for 47, 000 tons of solvent emissions globally.

Table 1 – US VOC Emissions by Category (x 1000 Tons)

NMVOCs	1997	1998	1999	2000	2001	2002	2003
Degreasing	556	337	363	316	331	310	301
Graphic Arts	266	272	224	222	229	214	208
Dry Cleaning	148	151	267	265	272	254	247
Surface Coating	2,228	1,989	1,965	1,767	1,863	1,744	1,695
Other[A]	1,893	1,922	1,849	1,814	1,852	1,735	1,686
Total	**5,100**	**4,671**	**4,569**	**4,384**	**4,547**	**4,256**	**4,138**

[A] Includes cutback asphalt, pesticide application adhesives and other miscellaneous applications.

Overall, VOC emissions have been reduced significantly since 1970. Reduction has come from process improvements in petroleum and related industries. In addition, large scale reductions of VOC emissions from surface coatings have been achieved by reformulating solvent-based coatings to waterborne and high solids formulations, high performance and architectural applications. Clearly, the trends in formulation design are being driven by the need for lower VOC emissions. When one looks at the data for electronic manufacturing there is significant room for VOC reductions.

One area for potential VOC reductions is photoresist coatings. This group can be further subdivided into photoresist for primary imaging and soldermask coatings for permanent board protection. Emissions generally stem from use of solvents in the manufacture, application and clean up of the coatings.

The current technology of photoresist, whether applied by dry film or liquid, uses large amounts of solvents. This is because at the point of use the photoresist must have a tack-free surface to allow for handling and contact imaging. Dry films achieve this goal by using a cover sheet over a relatively soft film that has been applied to a carrier sheet. The dry film is formulated as a low solid, high % organic solvent solution of polymers, monomers, photoinitiators and pigments. As part of the coating process, the solvents are flashed leaving the carrier sheet coated. The solvent is typically collected in a closed loop system but this abatement process is a major cost component. Handling the large volume of often flammable solvents involved with dry film manufacture necessitates the use of explosion proof equipment. Operator contact with solvents requires the use specialized ventilation, protective clothing and breathing equipment. In addition frequent exposure to these solvents poses definite health issues.

Liquid photoresist has been replacing a large volume of dry film for primary imaging because of the lower cost of liquid resist. As shown in Table 2, as with dry film, these photoresists are a high % organic solvent solution of polymers, monomers, photoinitiators and pigments. They are applied generally by roller coating and the solvent is then removed in an oven during a drying step to yield a tack-free coating. To meet VOC regulations in some parts of the world, PCB manufacturers have had to put in expensive solvent abatement and recovery equipment such as Gas Fired Thermal Oxidizers (GFTO) that can cost $150,000 per year to operate. In this technology, natural gas is added to the VOC laden exhaust stream. Combustion reduces most VOCs to CO_2 and water. Regenerative Catalytic Oxidizers (RCO) accomplishes the same without the use of natural gas but use electric heaters and catalytic beds to oxidize the VOCs. Newer systems can reclaim the heat in the vapor stream. Though these technologies are becoming more efficient to operate, they still release large amounts of CO_2 to the environment contributing to global warming.

Clean up, especially in the case of roller coaters, involves the use of large quantities of solvents. In the best case, these solvents are recycled at a high cost upwards of $300 per drum. A roller coating operation may spend several thousand dollars per month recycling clean-up solvent. In the worst case they are poured down the drain. In most locales, handling the large volume of flammable solvents also necessitates the use of explosion proof equipment. Operators deal with large volumes of solvents that require the use specialized ventilation, protective clothing and breathing equipment. As with other solvent based coatings, health issues arise from frequent exposure to these solvents.

These costs can add up to 25% to the liquid photoresist process cost making the use of liquid photoresist prohibitive. In some localities, new VOC emissions will not be allowed even if abatement equipment is in place. Unfortunately, in some areas, manufacturers may emit these VOCs directly to the environment. Thus, these manufacturers can be more competitive by using the solvent based liquid resists but the environmental burden can be quite high.

Table 2 – Formulation of Solvent Based Liquid Photoresist (%)

Polymers	32
Monomers	5
Photoinitiators	3
Fillers	10
Solvent	**50**

Soldermask, (or solder resist) is applied to the circuit board to protect conductor patterns during application of various surface finishes and downstream assembly operations. The first soldermasks were 2-part solvent based products composed primarily of epoxy and a hardener. They were applied by screenprinting through a stencil and then the coating was cured in a convection oven. Needless to say, large amounts of VOCs were released with this technology.

In the mid 1980s, in response to a need for better resolution, liquid photoimageable soldermasks (LPI) were developed. Similar to solvent based liquid photoresists, these are high percent organic solvent solutions of polymers, monomers, photoinitiators, curing agents and pigments (see table 3.) Applied by blank screen printing, curtain coating or spraying, liquid photoimageable soldermask has become the standard. Solvent is removed during a drying step in the oven, to yield a tack-free coating. The same health, safety and environmental concerns exist because of the solvent contained.

Table 3 – Formulation of Solvent Based Liquid Photoimageable Soldermask (%)

Polymers	40
Monomers	5
Photoinitiators	5
Fillers	10
Curing Agents	10
Solvent	**30**

In addition, as noted above, there are significant costs incurred in the handling and abating solvents which typically make up between 30-70% by weight of photoresist and soldermask. There are also hidden costs that come in the form of higher insurances during photoresist and soldermask manufacture. Shipping of flammable solvent containing material is markedly higher and requires specialized packaging. Also the increased medical costs from worker exposure during manufacture and use of these coatings must be factored in.

As stated above, large-scale reductions of VOC emissions in other types of surface coatings have been achieved by reformulating from solvent-based to waterborne and high solids type formulations. These new technologies can reduce or even eliminate solvents and still achieve comparable performance. In response to VOC, as well as other safety concerns, a unique waterborne technology has been developed that permits 100% solvent-free (VOC-free) liquid photoresist and photoimageable soldermask, without a loss of performance. These innovative liquid chemistries can be applied using conventional equipment.

Formulating Technology

The current process for liquid photoresist and soldermask dictates that after application, a tack free surface must be achieved for contact imaging with a film. Newer technologies such as laser direct imaging use off-contact imaging but the panel must be held in place on a vacuum table and hence a hard tack free surface is still required.

This requirement has traditionally been met by dissolving solid or high Tg polymers and oligomers in an organic solvent. UV curable monomers, oligomers, photoinitiators, pigments and fillers are added according to the application. Generally the polymers and oligomers are only soluble in organic solvents. Still, this provides the formulator with a high degree of latitude. Even the highest Tg polymers can be dissolved in solvent under heat and shear. Insoluble materials such as inorganic fillers can easily be suspended in the polymer matrix.

However, in the paint and coatings industry, waterborne technology is now well established and has led to major VOC reductions. The primary waterborne polymers used include alkyd, acrylic, esters, epoxies, urethanes, PVA etc. In many cases raw material suppliers have worked hand-in-hand with formulators to tailor waterborne polymers per specific use. Because of these factors, waterborne technology for general coatings has enjoyed explosive growth and competes well in terms of performance and cost.

It would seem that a logical step in the development of PWB resist coatings would be a waterborne approach. In fact, efforts have been made since 1990 to commercialize this technology. But formulating waterborne photoresist and soldermask poses many unique challenges. First, there is the multi-step nature of the photoresist process; coating, tack dry, imaging, development and final cure. Each step puts particular demands on the coating. In addition, most proven raw materials, used in solvent-based chemistry are water-insoluble. An additional hurdle is the inherent wetting problems associated with waterborne coatings. The high surface tension of water, 72 dynes/cm relative to the copper substrate at 35 dynes/cm causes beading, fish-eyes, de-wets and other flow problems. Special surfactants can be employed to reduce the surface tension but these are also difficult to control. Further difficulties are encountered when trying to adjust flow properties for roller coating and curtain coating processes, each with a unique set of dynamic forces.

New Technology

To overcome these problems a new waterborne technology platform has been developed. Functional groups have been designed into the polymer backbone, eliminating the need for complicating additives. The polymer morphology contributes to a tack-free coating after soft-bake. The innovative chemistry permits 100% solvent-free formulation of liquid photoresist and soldermask. Further, the technology can be applied using conventional coating methods. The technology drastically reduces VOCs, and offers a process with little odor that is cleanable in soap and water.

Waterborne Liquid Photoresist

Using the new technology a waterborne photoresist was formulated for acidic inner layer processing. Table 4 summarizes the formulation and processing highlights compared to a widely used solvent based liquid photoresist. The environmental advantages are readily apparent in the fact that the photoresist can be formulated 100 % VOC and solvent free. The coating is not classified as flammable or hazardous, thereby drastically reducing shipping, insurance and safety costs. The need for solvent abatement equipment can be eliminated. The waterborne technology is extremely user friendly with low odor. Equipment and spills can be cleaned up with soap and water, further eliminating the need for clean up solvents. Large roller coaters can be cleaned by circulating soap and water through the entire system drastically reducing clean up and downtime.

Additional advantages are seen in the process capabilities. Viscosity can be adjusted and fine-tuned by simply adding water. Drying time for the waterborne technology has been reduced to 2-4 minutes, increasing throughput greatly. If necessary, dried panels can be stored up to 3 weeks prior to exposure, increasing manufacturing latitude. Typical liquids and dry film must be exposed within 72 hours.

Perhaps the greatest process advantage is the exposure requirements. Although sensitive in the same spectral range, the waterborne photoresist can be imaged at 20-30 millijoules, which is 5-6 times faster than solvent based photoresists. This allows ultra fine resolution down to 12 microns as shown in figure 2. Further, the low millijoule requirement enables laser direct imaging, to take advantage of the higher yields, accuracy and reduced phototool cost permitted by LDI.

Table 4 – Formulation and Process Highlights Waterborne vs. Solvent Based Photoresist

Parameter	Waterborne[2]	Solvent Based
Type	1-Part	1-Part
Color (unexposed)	Blue	Blue
Color (exposed)	Faded Blue	Faded Blue
Viscosity (Roller coating)	1800-2000 cps.	1000-1700 cps
Density	1.04 g/cm^3	1.05 g/cm^3
pH	7-8	3 (mixed w/ water)
Solvent %	0	58 (1-methoxy-2-propanol acetate)
Solids %	42	42
Thinner	Water	Solvent
Working Thickness	8-12 microns	8-12 microns
Dry Time/Temp	2-4 minutes @ 120C	10 min @ 85C
Stackable	Yes 72 hours	Yes 72 hours
Hold time after Drying	4 weeks	Not available
Spectral range	300-450 nm	300-450 nm
Photosensitivity (Stouffer 21-step)	7-8 Solid @ 20 millijoules	4-5 Solid @100-120 millijoules
LDI Compatible	Yes	No
Resolution	12 micron	25 microns
DES Process	Standard	Standard
Clean Up	Soap and Water	Solvent

Figure 1
Clean Up of Waterbased Photoresist with Soap and Water

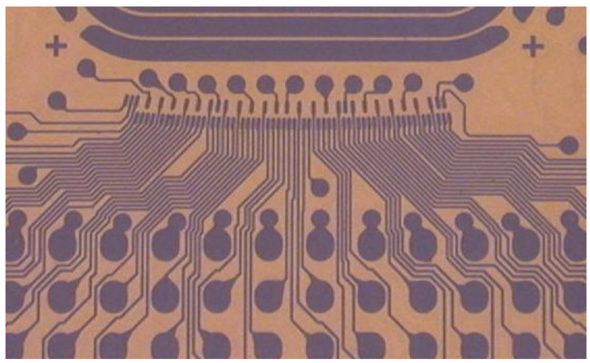

Figure 2
Waterbased Photoresist 16 Micron Resolution

Waterborne Photoimageable Soldermask

Using the new technology platform, a waterborne soldermask was also formulated. Table 5 summarizes the formulation and processing highlights compared to a widely used solvent based liquid soldermask. The environmental advantages are readily apparent in the fact that the soldermask can be formulated at 0% VOCs for curtain coat and only 1% VOC for screenprint and spray applications (Development is underway for a 0% VOC version for screenprint.) The coating is not classified as flammable or hazardous, thereby drastically reducing shipping, insurance, safety and ventilation costs. The extreme low level of VOCs can eliminate need for solvent abatement equipment. As with the photoresist, the waterborne technology is extremely user friendly with low odor. Equipment and spills can also be cleaned up with soap and water, further eliminating the need for clean up solvents. The Part A Resin and Part B Hardener are easily mixed and can be reduced with water if necessary, again eliminating the use of solvents.

A total of 80 ppm chlorine (40 ppm hydrolzable chlorine and 40 ppm bound chlorine) and no bromines, means the waterborne soldermask is classified as halogen free. It is also RoHs compliant. This combination of VOC free, halogen free and RoHs compliance provides the user with an excellent option to meet Green Initiatives at the fabricator and OEM levels.

Additional advantages are seen in the process capabilities. Although sensitive in the same spectral range, the waterborne photoresist can be imaged at 100 millijoules, which is 2-4 times faster than many solvent based soldermasks. This allows the high resolution needed for fine solder dams (see Figure 3.) Further, the low millijoule requirement enables laser direct imaging to take advantage of the higher yields and reduced phototool cost permitted by LDI.

Finally, the use of specialized epoxy polymers and crosslinkers results in mechanical, chemical and electrical properties that are comparable with solvent based soldermasks (see Table 5.)

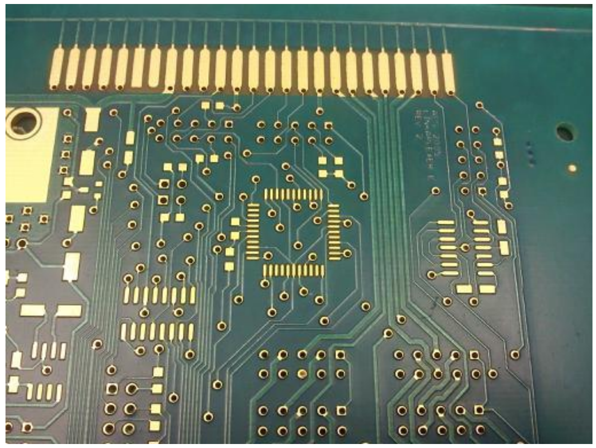

Figure 3
Waterborne Soldermask

Table 5 – Formulation and Process Highlights Waterborne vs. Solvent Based Soldermask

<table>
<tr><th>Parameter</th><th colspan="2">Waterborne[3]</th><th colspan="2">Solvent Based</th></tr>
<tr><td>Type</td><td colspan="2">2-Part</td><td colspan="2">2-Part</td></tr>
<tr><td>Color</td><td colspan="2">Green Semi Gloss</td><td colspan="2">Green Semi Gloss</td></tr>
<tr><td>Viscosity Screenprinting</td><td colspan="2">55,000 cps.</td><td colspan="2">60,000 cps</td></tr>
<tr><td>PH</td><td colspan="2">7-8</td><td colspan="2">N/A</td></tr>
<tr><td>Solvent %</td><td colspan="2">1%</td><td colspan="2">30</td></tr>
<tr><td>Solids %</td><td colspan="2">55</td><td colspan="2">70</td></tr>
<tr><td>Halogen Free</td><td>80 ppm Chlorine</td><td colspan="2">IEC Requirement: 900 ppm max Chlorine</td><td>N/A</td></tr>
<tr><td>RoHs Compliant</td><td colspan="2">Yes</td><td colspan="2">Yes</td></tr>
<tr><td>Mix ratio Resin: Hardener pph</td><td colspan="2">100:18</td><td colspan="2">100:43</td></tr>
<tr><td>Thinner</td><td colspan="2">Water</td><td colspan="2">Solvent</td></tr>
<tr><td>Working Thickness</td><td colspan="2">25 microns</td><td colspan="2">25 microns</td></tr>
<tr><td>Dry Time/Temp</td><td colspan="2">1^{st} 20 minutes @ 85C/2^{nd} 45 minutes @ 85C</td><td colspan="2">1^{st} 20 minutes @ 85C/2^{nd} 45 minutes @ 85C</td></tr>
<tr><td>Spectral range</td><td colspan="2">300-450 nm</td><td colspan="2">300-450 nm</td></tr>
<tr><td>Photosensitivity (Stouffer 21step)</td><td colspan="2">13 @ 100 millijoules</td><td colspan="2">10-12 @500-700 millijoules</td></tr>
<tr><td>LDI Compatible</td><td colspan="2">Yes</td><td colspan="2">No</td></tr>
<tr><td>Resolution</td><td colspan="2">25 micron</td><td colspan="2">25 microns</td></tr>
</table>

Developing Process	Standard	Standard
Final Cure	1 hour @ 150C	1 hour @ 150C
Clean Up	Soap and Water	Solvent

Test Results Snapshot	**Waterborne**	**Requirement**	**Solvent Based**
Pencil Hardness	8H	F Min	8H
Insulation Resistance Before Solder	$2.0X10^{12}$ ohms	$5.0X10^{8}$ ohms	$1.3X10^{13}$ ohms
After solder	$1.4X10^{13}$	$5.0X10^{8}$ ohms	$3.3X10^{13}$ ohms
M and I Resistance	Pass	$5.0X10^{8}$ ohms	Pass
Electrochemical Migration	$8.6X10^{8}$ ohms	$2.0X10^{6}$ ohms	$1.4X10^{12}$ ohms
UL Flammability	94 V-0	94 V-0	94 V-0
Hydrolytic Stability	Pass Class T/Class	Pass Class T/Class	Pass Class T/Class
Dielectric Strength	2200 VDC/Mil)	500 VDC/mil min	2800 VDC/mil
Compatible All Final Finishes	Yes		Yes

Conclusion

Recent advances in polymer design and formulating methods have enabled the development of a workable VOC free liquid photoresist and very low VOC LPI solder mask. These products are not only significant in reducing or eliminating VOCs, but they are compatible with LDI imaging and are halogen free and RoHS compliant. The advantages of this breakthrough are many and include a greatly reduced environmental impact in the manufacture of PCB’s and a much safer and cleaner work environment. This advanced in technology should be welcomed both by government agencies such as air quality regulators as well as OEM’s in helping them make their products greener.

References:

[1]EPA, Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2003
[2]GENESIS Material Technology, Technical Data Sheet AQ 2000 G-SP
[3]GENESIS Material Technology, Technical Data Sheet AQ 3000 RC