# **Liquid Resists for Photo Chemical Machining**

Diethard Kapp-Schwoerer, Dr. Kurt Meier, Charles Gantner (HTP HiTech Photopolymere AG, Basel, Switzerland)

### 1. Introduction

This article focuses on liquid photoimagable etch resists for the production of functional or decorative metal parts. Since its beginning the PCM industry used liquid resists in the patterning process of metal sheets.

In the following the chemical nature of the different resist types will be described and characterized in respect to their benefits for this particular application. In addition an overview on the various application methods is given.

## 2. Common Processing Condition

In contrast to dryfilm, liquid resists need specific processing conditions in the pre-clean and exposure step.

Almost without exception, liquid resists contain an organic carrier solvent, even though they may be fully aqueous processable. In fact, all commonly used resist formulations are solutions rather than dispersions. Depending on the type of resist and application method, the formulation contains 50 - 80% solvents. The typical viscosity of a resist is rather low (100 - 1000 mPa·s).

### 2.1. Pre-cleaning

Some resists contain highly non-polar solvents. The wetting characteristics of liquid resists are good to excellent. Chemical pre-cleaning processes generally are sufficient. For the various metals and alloys specific cleaning methods have been established (Visiting Photochemical Machining, Karl Dietz; PCMI Journal No.66 & Continuos Cleaning of Metallic Strips for Photochemical Etching, Dr Kenneth Abate, PCMI Journal No.67).

If proprietary pre-cleaning solutions are used, it is important to check their specific effect on resist adhesion and ease of stripping. Most likely the results will vary from metal to metal, whereby copper containing alloys (e.g. BeCu, Brass) often show a different behavior than steel and stainless steel substrates. Liquid resists will interact more likely with a chemically pre-cleaned metal surface, than laminated dryfilm. This can be an advantage as far as adhesion is concerned. The stripping chemistry and conditions must be selected (tested) to match the particular pre-cleaning process.

### 2.2. Exposure

After drying the target thickness of all liquid etch resist is  $5-10 \, \mu m$ . The resist can be exposed by contact printing. In this case the artwork is in close contact with the thin photoresist layer, allowing using less expensive and often more powerful, non-collimated printers. In a negative acting resist material, the solubility of the film is significantly reduced on exposed areas (polymerization), whereas positive resist become more soluble at the exposed sites (decomposition).

#### 2.3. Developing

With the exception of dichromated resists, most liquid resists can be developed choosing a fairly aggressive break-point <sup>1</sup>. Aqueous processable positive and negative resists are developed in conveyorized developing equipment as used for the innerlayer manufacturing of printed circuit boards (PCB). Solvent developable resists can be processed in stainless steel developing equipment, commonly used to develop solvent processable soldermask. It is imperative to confirm the equipments durability (e.g. gasket, pumps etc.) against a specific developing solvent. Data can be obtained from the

Break-point: Percentage of total active developing chamber length required for complete wash-off of resist, leaving a clean metal surface.

equipment manufacturer. In the PCM industry many users of solvent developable resist employ simple tank developing machines. A conveyorized developer is rather costly.

## 3. Common Advantages over Dryfilm

### 3.1. Wetting Characteristics

Good wetting characteristics are the reasons that the resist coats the metal surface regardless of the actual topography. This holds true for the microstructure (e.g. Grain structure, micro roughness) as well as macro-structures such as dents or scratches.

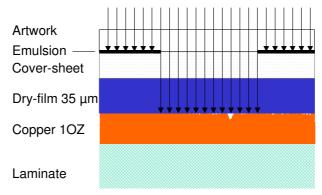
The fact that liquid resists have a superior wetting compared to laminated dry-films does not automatically conclude that these liquid resists have a better adhesion.

The adhesion of resists is strongly influenced by the chemical nature of the photoresist and the interaction with a particular surface of the substrate. Different resist chemistry as described in section 5 show significant difference as compared to each other on the same substrate and different adhesion to different metals.

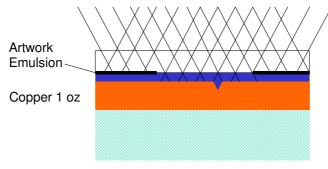
In the development of liquid resist formulations the "know-how" has been used to achieve the best possible adhesion. Even this argument is not true in all cases. Generally speaking, it is true, that liquid resists exhibit superior adhesion than dryfilm because they intrinsically have a better surface wetting to start with.

#### 3.2. Resolution

The contrast between exposed and non-exposed areas is significantly better than with dryfilm, which is many times thicker than a liquid resist coating. The emulsion of the artwork is positioned on top of the protective Mylar film. The relevant dimensions are shown in picture 1 and 2



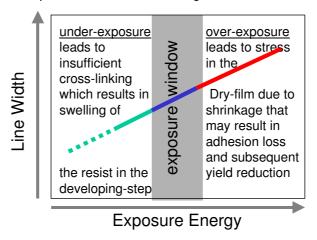
Picture 1: Imaging dryfilm using collimated light to overcome the geometric effects



Picture 2: Imaging liquid resist using non-collimated light

With only a few exceptions, all liquid resists are exposed with non-collimated light. This imaging technique results in more than adequate resolution capabilities in the subsequent developing step.

In practical applications, negative working liquid resists, often are over-exposed. The reason for this, is that dust, present between the artwork and the phototool, can be "burned-out". By increasing the exposure energy the amount of pin-holes can be drastically reduced. Since the phototool is in close contact with the resist (as shown in picture 2) the dimensions of features and gaps (slots) are hardly affected. Exposing a dryfilm is much more delicate. If a dryfilm is over-exposed, the dimensions of the features will change measurably, even though collimated light is used to minimize this effect. Picture 3 highlights the boundaries of the process window discussing the effects of under and over exposure.



Picture 3: Limited process window of dryfilm exposure

The resolution after developing is not only governed by the quality of the imaging, but by the behavior of the resist in the developing step. After drying the liquid resist, it retains only marginal quantities of solvents (<0.5%). In contrast, dryfilm contains a considerable amount of solvent (up to 3%). This is required to positively influence the "flow" during lamination. As a consequence, the side walls of the dryfilm will swell in contact with the developer solution. This has a negative impact on the resolution capability. In order to minimize this effect, it is necessary to tightly control the recommended breakpoint (commonly  $50 \pm 5\%$ ). Under highly confined conditions one can achieve an opening (space) of 25 µm with a 25 µm thick dryfilm. Under production conditions it is rather complicated to achieve such resolutions. Under the same production environment some 10 µm thick liquid resists can safely and repeatability produce 20 µm openings. Next to the low profile, the superior adhesion and the tolerability of aggressive developing parameters are the reasons for this superior performance.

The above, does not hold true for liquid resists based on cyclic poly-isopren and dichromated resists. The latter will swell during the developing due to their chemical nature. Specifics are given below.

#### 3.3. Etching Tolerances

Among many parameters in the etching process, the "rate of etchant exchange" is a dominant factor. In practical terms this means that the etching speed is slowed down in small channels. In this respect the profile of the resist is significant. A liquid resist with a coating thickness of 10 µm or less allows a substantially higher "rate of etchant exchange". This is the reason, why some PCM parts, featuring small dimensions, can only be successfully manufactured in large scale production using liquid resist. Shadow-masks, suspensions for recording-head and leadframes are typical products manufactured with liquid resist technology requiring tight tolerances and small features.

### 4. Common Shortcomings compared to Dryfilm

#### 4.1 Carrier Solvent

The coating solutions of all liquid resists contain a carrier solvent as already outlined in point 2. Waterborne liquid resists, using water as the carrier solvent, are described in numerous publications and patents, but have no practical relevance. In many cases, these so-called "waterborne" systems often are not solutions, but emulsions. The pot-life of these experimental resists is restricted and the end properties fall short, as compared to conventional photoresists using an organic solvent.

In any case the organic solvent should be judged from different perspectives such as: Toxicology, long term exposure limits, flammability, evaporation rate and other critical properties.

By correctly addressing the above issue, necessary precautions and safeguards can be taken to safely process the particular photoresist.

### 4.2 Etching of thick sheets (>500 µm; 20 mil)

For etching thick plates the resolution capabilities are secondary since the corresponding feature size is well within the capability of dryfilm. In this case the thickness of dryfilm is an advantage. The etch profile on thick plates, where substantial under-etch is taking place, dryfilm is more suitable, since the thicker resist offers a better mechanical stability as compared to thin resist layers. The trade-off point, at which resolution is of minor importance and the benefits of a mechanically more stable overhang are required (to achieve straight edges) is at a substrate thickness of about 20 mil. This trade-off point may vary according to the actual artwork (design) and material selection.

Some liquid resist users extend the thickness range of the substrates by double coating ( $\rightarrow$  twice coating/drying). This technique extends the capabilities of liquid resist for thicker plates and may well be the best compromise between resolution and increased mechanical stability of the overhang.

### 4.3 Sensitive to oxygen during exposure

Some negative working resists, particularly thin coatings of cyclic poly-isopren based resists (5.2) and acrylate resists (5.5) show a reduced sensitivity, if oxygen (air) is present during exposure. The difference in photo sensitivity can easily be demonstrated by exposing such resists under hard contact and off-contact conditions (projection mode) at the same exposure energy. The sensitivity guide (e.g. Stouffer Step) will show different readings indicating the reduced sensitivity caused by the presence of air during the exposure.

For PCM hard contact printing is standard. Therefore the negative impact of oxygen is not really significant. Nevertheless, the printing times under hard contact of the two resists mentioned, is longer, as compared to an oxygen free exposure under a nitrogen blanket.

Acrylate dryfilm resists show less impact of oxygen inhibition, since they are exposed through the polyester-coversheet. It functions as a diffusion barrier for the oxygen.

## 5. Different liquid Resist Types

### **Dichromated Resists**

These are the oldest type of photoresists used. Water soluble polymers are combined with a photosensitive dichromate salt. Historically this polymers were of biologic origin, such as gelatin, proteins from eggs (egg albumin), milk (casein) or starch (gum arabic). In the the 1930s, the sensitization of PVA (polyvinylalcohol) has been studied.

As of today shadow masks are produced with photoresist composed of casein and sensitised with ammonium dichromate. Also application for etching steel and electroforming with PVA are still known today.

The principal photoreaction is the same: The dichromate ion absorbs light. Subsequently the  $Cr^{6+}$  species undergoes an electron-transfer reaction with the polymer matrix to form a polymer radical. These undergo further reactions to form for the  $Cr^{3+}$  and a crosslinked polymer matrix.

Crosslinked Poly(vinyl alcohol)

Figure 1: Crosslinking of PVA

The resist is developed in water. The solubility difference between the crosslinked polymer matrix and non-exposed matrix is small. Therefore, unlike all other liquid resist discussed, the breakpoint has to be carefully monitored. Since the non-exposed resist coating undergoes a "dark reaction" (starts to crosslink without light) the difference in solubility can diminish to the extend, that developing becomes impossible. This can happen if:

- 1) The coating solution is to old
- 2) The time between coating and development is too long
- 3) The drying temperature/time is too high/long

In order to achieve the final properties, the resist may have to be rinsed after developing with water containing ammonium dichromate. In any case a burn-in at high temperatures is required to achieve the desired properties. After the burn-in step, the resists exhibits extraordinary adhesion. The cured resist tolerates etching in ferric chloride at fairly high temperatures (e.g. 60 °C) but cannot be etched with protic oxydizing acids like nitric acid. The shortcomings as listed below make it not feasible to use this type of resist, if the production requires flexibility in hold-time and multiple choices of materials.

#### Advantages:

- Superior adhesion on steel after baking
- Developing in water
- Inexpensive resist

#### Shortcomings:

- Limited shelf life of sensitized formulation (only a few days)
- Lot to lot variation
- Short hold-time of coated boards (dark reactions)
- Drying temperature has to be controlled in tight tolerances
- Rinse with water, containing ammonium dichromate, is needed after developing to achieve optimum results
- Burn-in at temperature exceeding 200 ℃ is required
- Presents of Cr<sup>6+</sup> in the resist, developer (water) and rinse needs specific attention
- Due to low resist thickness (< 8 μm) only thin steel panels can be processed</li>

#### 5.1 Cyclic poly-Isopren based Resists (cyclized rubber)

Negative acting resist compositions, which combine an unsaturated hydrocarbon polymer, derived from polyisopropene, with an organic acromatic bis-azide were introduced in the 1960s.

The raw material for the "cyclized rubber" can either originate from natural rubber (latex) or synthetic polyisoprene.

During the exposure of the formulated resist, azide groups in the sensitizer "ABC" undergo sequential loss of molecular nitrogen. Each fragmentation produces highly reactive nitrogen with two unpaired electrons. Crosslinking results when nitrogen intermediates add to residual carbon-carbon double bonds or insert into carbon-hydrogen bonds thereby converting the matrix into an insoluble network.

Figure 2: Crosslinking of partly cyclized Polyisopren

The nitrene intermediate also reacts with oxygen to form azoxy and nitrose products. This oxidation competes with the addition and insertion reaction reducing the extent of the polymer–polymer crosslinking. This phenomenon is called oxygen inhibition

This type of resist was successfully used in the semiconductor industry when printed in "hard contact", minimizing the effect of the oxygen inhibition. With the introduction of soft contact (proximity mode) and

off contact (projection mode) the resist showed severe film thinning (scalping) as a direct consequence of the reduced crosslinking density near the air–polymer interface. Today Cyclic poly-Isopren based resists play only a minor roll in the semiconductor industry.

Since hard contact printing is the dominant printing method in PCM, this weakness of the resist has no significant impact.

Another inherent characteristic however, cannot be overlooked also for PCM applications. The crosslinked resist has a softening temperatur below 80 °C. As a consequence the developed structures may "flow" during drying, impacting the resolution capabilities. In some case a heat bump is used to optimize the adhesion but additionally increasing the "flow".

#### Advantages:

- Highly non polar solvent: easy to coat
- Good adhesion on all metals
- Resistant to many enchants
- No negative impact of hold times (resist & coating)

#### Shortcomings:

- Xylene as carrier solvent
- · Developing and stripping in solvents
- Limited resolution compared to other liquid resists
- Expensive

#### 5.2 Diazo naphto quinone based resists

This group of resists are positive working resists based on the dissolution inhibition of diazo naphto quinone (DNQ) in a matrix resin. This matrix is a low molecular weight condensation product of formaldehyde and a cresol isomer known as novolac. During the exposure DNQ undergoes photolysis that destroys its inhibitory effect of film dissolution. The photolysis causes the DNQ to undergo a reaction forming a base-soluble carboxylic acid that can be rapidly developed in aqueous solution of hydroxide ions (e.g. 1% NaOH). The dissolution of the non-exposed resist area is very slow. In contrast with crosslinked resists the film solubility is controlled by chemical and polarity difference rather than molecular size.

Figure 3: Acid generation scheme from DNQ

This type of resist has some unique characteristics: Unlike radical based systems, it shows no oxygen inhibition and therefore can be exposed off-contact without negative effects. In the developing no swelling will be encountered.

In PCM this type of resist are mostly used for manufacturing suspensions for recording heads. For this kind of parts the resolution capability is of highest importance.

The exposure energy is dependant on the resist thickness. In most cases the targeted resist thickness is  $\sim 5 \ \mu m$ .

The resist can be used for multiple exposures, different areas of the board surface may be imaged with one single resist coating in sequential exposure, develop and etch steps.

### Advantages:

- High resolution, no swelling
- Hard surface (Scratch resistant)
- No oxygen inhibition
- Developing and stripping in aqueous chemistry
- Dissolves in the stripper (can also be a disadvantage)
- Multiple exposure possible

### **Shortcomings:**

- Exposure energy increasing with resist thickness: Thickness limitation
- Hold time after imaging required (The acid forming reaction requires water, which comes from humidity present in the environment)
- · Specific artwork required

### 5.3 Poly(vinyl cinnamate) type resist

In 1953 this type of resist was introduced commercially by Eastman Kodak, still known today as KPR.

The material is a crosslinking system based on the photo-dimerisation (poly-addition) of poly(vinyl cinnamate) chains.

Figure 4: Crosslinking reaction scheme

The resist originally was used in circuit board- and semiconductor manufacturing and then abandoned for this applications by more advanced photoresists. Dryfilm took over circuit board patterning and positive resists were introduced within the semiconductor industry in the 1960s.

Today these type of resists have still some specific use in the PCM. For manufacturing parts the use is restricted by the cumbersome processing, involving solvents for developing and stripping (similar to processing cyclic poly-isopren based resists).

High-end photoengraving plates, for embossing and foil-stamping or as masters to produce rubber plates for flexographic printing, are dominantly manufactured with poly(vinyl cinnamate) type resists.

The photo engraving plates are copper, brass, zinc or magnesium. The single side etching is accomplished in specifically designed etching equipment (paddle etcher) using nitric acid. Especially when etching magnesium, the poly(vinyl cinnamate) resist demonstrates superb etch resistance in the highly exothermic etching process.

Without this particular field of use, one may speculate, that the expensive, synthetic polymer would have disappeared from the market.

### Advantages:

- Stable in nitric acid
- Good adhesion on phosphate magnesium
- Good hold times of pre-coated plates

#### Shortcomings:

- Developing and stripping in solvents
- For some application a "burn-in"-step above 120 ℃ is required
- Expensive

#### 5.4 Epoxy based resists

Many epoxy based photopolymers have been developed for the PCB industry as solder masks and more recently as photo-definable dielectrics. Another rather new application of epoxy based resists is the building of high aspect ratio microstructures used as electroplating molds for micromechanical parts (MEMS) and other electronic applications. This last application needs resists which can be structured in thick layers up to one millimeter. The most frequently used resist in this category is called SU-8 because it is based on Shell's epoxy resin SU-8.

Figure 5: Crosslinking reaction of carboxy functional polymer with di-epoxide

However, full epoxy resists are not well suited for the PCM industry because the cured resists are very difficult to strip. Another disadvantage is that the SU-8 and other full epoxy solder masks have to be developed by organic solvents.

On the other hand, the conventional aqueous processable resists do not withstand the aggressive chemicals used in the etching of metals such as titanium, tantalum and others.

For these difficult-to-etch metals HTP has developed a resist in which the chemistries of the conventional aqueous are combined with those of the epoxy resists. The epoxy resin does not participate in the photoreaction, but reacts after development in an additional process step induced by heat. This yields a polymer network which is crosslinked by acrylic and additionally enhanced by epoxy groups. The higher crosslinking density of this resist type now allows the use of more aggressive chemicals in the etching. Stripping is still possible with caustic solution, but needs higher temperatures and a longer dwell time.

## Advantages:

- Good adhesion on all metals
- Resistant to many enchants
- Developing in aqueous sodium carbonate
- Still possible to strip in aqueous caustic solution

### Shortcomings:

- Two component system
- Limited pot-live when mixed
- Need to be cured after developing (60 min @ 150 ℃)

### 5.5 Acrylate based resists

The radical initiated polymerization of multifunctional acrylates is the base photoreaction in the imaging transfer process of most soldermasks and etching and plating resist.

The initiation of the acrylate polymerization by radicals is a complex reaction sequence. It starts with the absorption of a photon by a photoinitiator or sensitizer molecule. The photoexited sensitizer can transfer

the energy to the photoinitiator. The exited photoinitiator decomposes under formation of two radicals. These are active enough to attack a carbon-carbon double bond present in the acrylate monomer and oligomers. Radicals formed by this reaction add to other double bonds and herewith start the chain reaction, ending up in a polymer network. The average chain length is restricted by recombination reactions of two radicals (including oxygen). The level of crosslinking strongly influences the solubility of the carboxy functional resist matrix in alkaline, aqueous media. The carboxylic acid groups form a "soluble" salt in the alkaline environment of the developer.

Figure 6: Acrylate polymerization scheme

In 1968 DuPont was first to market this chemistry as a dryfilm for lithographic applications under the trade name  $Riston \, ext{@}.$ 

In the 1990s liquid etch resists for the production of innerlayers increasingly became popular. It addressed the challenging requirements for the emerging fine line technology.

For the PCM this liquid innerlayer resists were of limited use, since they were formulated to perform on electro deposited copper only (ED-copper). Many of these resists showed poor adhesion on steel, stainless steel and lock-in on brass and other cooper alloys. Depending on the substrate composition, e.g. presence of Ni, acrylate resists can chemically interact with the metal surface. Even the surface treatment (e.g. acidic- versus alkaline cleaning) can have an effect on the resist performance.

In 1998 HTP HiTech Photopolymere AG, Switzerland introduced a fully aqueous processable acrylate resist, which was specifically developed for the PCM industry (A New Etch Resist For Photo Chemical Machining, Collin Bird Tecan Components Ltd. PCMI Journal No. 69)

This resist combines the processing and cost advantages, such as horizontal processing in aqueous developing and stripping chemistry and showed equally good performance on all commonly etched metals, including stainless steel. It first was introduced for dip coating and subsequently formulated for roller-coating and airless-spraying.

### Advantages:

- Fully aqueous processable
- Simplicity of processing
- Can be developed and striped in the same equipment as dryfilm
- Wide processing windows

### Shortcomings:

Relative soft surface (handling)

## 6. Coating Methods

In the following application technologies are described, which have a particular relevance for the PCM.

#### 6.1 Bar-Coating

The principal of this method is rather simple. To apply a wet coating thickness between 4 and 120  $\mu$ m a wire-wound-bar is used. It is produced by winding precision drawn steel wire onto a stainless steel rod resulting in a pattern of identical shaped grooves as shown in picture 4. The grooves precisely control the coating thickness.

The substrate is placed on a planar coating bed. Depending on the properties of the substrate this bed could be magnetic, heated or feature a vacuum hold down.

This coating technique allows coating virtually all metal thickness', including metal foils. The only restriction being that the substrate must be flat; respectively the foil needs to be free of wrinkles.

With this single sided application method, resists can be efficiently applied with a minimum effort. It is possible to use this method for low volume production, where a particular liquid resist offers the required benefits. An example would be the coating of a special resist to manufacture parts of a difficult to etch metal such as titanium.



Picture 4: Schematics of a wire-bar

Bar-coating can be implemented with a minimum investment as a hand coater or in a slightly more sophisticated version in which the movement of the bar is motorized, allowing to select various, constant coating speeds.



Picture 5: Sophisticated bar-coater (courtesy of RK Print-Coat Instruments Ltd., England (<u>www.rk.print.com</u>).

Using an adjustable applicator instead of a wire-bar, the wet weight can even be extended into the mm-range. This applicator has a micrometer adjustable blade. The resist is coated moving the applicator over the substrate with a specific setting of the blade opening to achieve the desired wet-film thickness. This coating method is of interest to apply thick resist coatings for some electroforming processes.

### 6.2 Dip-coating

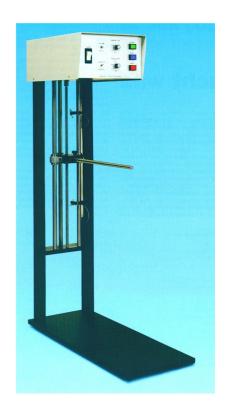
For low production volume dip-coating is the most widely used application method for liquid resists. Originally cyclic poly-Isopren based and poly(vinyl cinnamate) type resists have been coated by this method. Even today, this application technique is the method of choice.

With the introduction of a fully aqueous developable acrylate based resist, developed for PCM applications in 1998 (see 5.5), this coating method again has become applicable for medium size production. The reason being that the new photoresist offers the benefit of using inexpensive and highly productive horizontal developing and stripping equipment. Production volumes of up to  $30^{\circ}000 \text{ m}^2$  can be realized.

The benefits of dip coating are obvious. As a double-sided coating method all type of formats can be coated. It allows coating thick plates as well as thin sheets. Simultaneous coating of multiple sheets increases the productivity significantly.

A high and consistent coating quality can be ensured, since the few and basic coating parameters can easily be maintained. These parameters are the withdraw speed, the resist viscosity and the solid content of the photoresist.

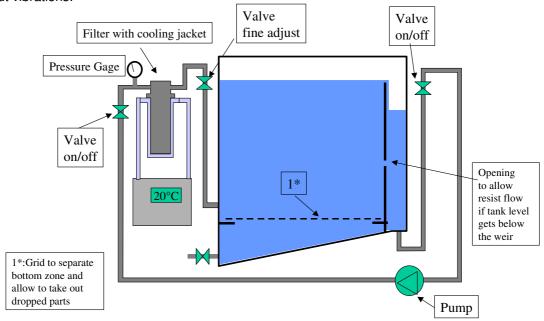
The investment barrier for implementing dip-coating is small. In some cases the PCM manufacturers have custom built their own dip-coater to suite their specific production needs. The equipment consists of two parts: The withdraw unit and the dip-tank.



Picture 6: Withdraw unit

Picture 6 shows a small commercially available withdraw unit. In this design electrical controls and the motor are mounted on top. The movement is accomplished by a general purpose trapezoidal screw thread. Two sliding bushing are mounted on vertical guiding rods to accept the weight.

The withdraw unit has to be designed to provide constant withdraw speeds in the range of 5 to 15 cm per minute. A particular construction design is necessary to ensure, that the load (metal sheets) is lifted without vibrations.



The dip-tank should be made out of stainless steel. The flow rate over the weir turns over the tank volume once per hour. The standard design incorporates a filter and a temperature control. For safety reasons an air driven diaphragm pump is a good solution. The schematics highlight the features of a tank design.

Since dip-coating is used in other industrial applications, different types of machines are offered. Some sophisticated equipment is shown in picture 7 incorporating the dipping and the drying step in one compact unit. The process in this machine is highly controlled, including air cleanliness (Class 1000). Since dip-coating is a vertical process it is rather costly to fully automate the loading and un-loading.



Picture 7: Semi-automated Dip-coating and drying equipment (Picture courtesy of IDC, Israel)

#### 6.3 Roller-coating

There are two different roller-coating methods: The reverse roller-coating and the roller-coating using a grooved roll:

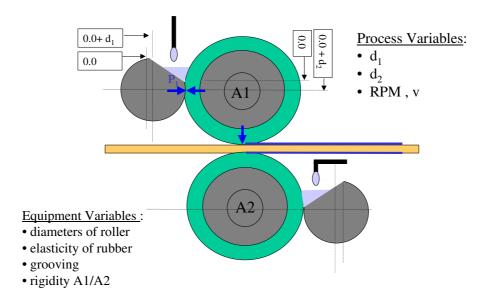
#### Reverse roller-coater

In this technique, the application roller is a smooth metal roll, rotating opposite to the movement of the substrate. The application roll itself is in contact with a second roll. This rubber lined roll also has a smooth surface. The lacquer is filled in between the rolls. Some lacquer adheres to the application roll and is transferred by proximity contact to the substrate. In order to gain a desired coating thickness the rotation-speed of the dosing-roll can be multiple times faster than the movement of the substrate underneath. Changing the rotation speed and proximity gap can vary the coating thickness in a wide range.

Being a single-sided coating technique, it is mainly used for decorative wood coatings. Varnish used in this application technique typically employs a low viscosity.

### Roller coating using a grooved or structured application roll

Photoresists commonly are coated with this method. The grooved rubber-lined roll is pressed against a smooth metal roll (dosing roll). The application roll is pressed onto the substrate and thereby transferring the resist. The rotation speed of the application roll exactly matches the speed of the substrate. In most cases the application is double-sided. Therefore the substrate is transported by the top and bottom application roller during the coating process. Picture 8 shows the working principle of a double sided roller-coater.



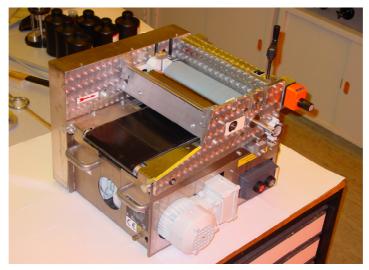
Picture 8: Working principle of double sided roller-coater

This type of roller-coating is the liquid resist application method of choice for applying primary imaging resists for PCB's.

For PCM a few high volume producers use this application. Combined with a specifically formulated resist, roller-coating provides highly uniform coatings with an excellent thickness distribution variation of less than 10% throughout the entire coating area. This is demonstrated by one company, who recently has selected roller coating for the application of a plating resist to manufacture precision electroformed parts using the "overgrow method". By overgrowing the metal a constant thickness of the photoresist is imperative to achieve consistent feature dimensions.

The dry coating thickness can be varied by a specific roller grooving (deeper grooves = higher wet weight) and/or the solid content of the photoresist. 5 to 15  $\mu$ m are the standard dried lacquer thickness'.

For a small scale production some companies manufacture stand allone roller coater units. As shown in picture 9 these systems are single sided units.



Picture 9: BLK Lab Roller-Coater (Bürkle, Germany)

Commercial roller-coating- and dying-systems have been presented to the PCMI community (Rollercoater Application of Liquid Photoresist JPCMI Journal No. 77, June 2000).

### 6.4 Spin-coating

This application method dominantly is used for coating silicon wafers to manufacture integrated circuits. Similar to dip-coating, there are only two parameters, which influence the final thickness of the resist coating: The resist solution itself and the spinning speed. By selecting the correct settings, uniform coating thicknesses from 1 to 500  $\mu$ m can be achieved. Particularly the thicker coatings are of interest for plating applications used in the manufacturing of microstructures. Besides being flat, there are no particular requirements on the substrate. Therefore metal sheets, metalized glass or wafers can be used.

For coating etch resists for PCM, this application method is not attractive. The reason being, is that it is single sided and wastes a lot of photoresist.

### 6.5 Spray-coating

Spraying photoresist can be accomplished by different spraying methods:

### 1) Electrostatic Spraying

The heart of this application is a spray bell rotating in excess of 20'000 rpm. This bell is charged (e.g. 20 kV). The rotating action of the charged spray bell forms so called "atomized droplets". The design of an electrostatic spray-cabinet is further complicated by the safety requirements for spraying a flammable resist. Since the droplets follow the electric flux lines, the amount of overspray can be minimized. The same electrical effect can lead to an undesired "grip-over" of the coating onto the back side.

### 2) Airless-Spraying

The heart of this application is a spray gun, similar to the ones used in the automotive industry.

The resist is pushed out of a pressurized tank via a supply pipe to the spray-head. The spray-head has a defined aperture where the spray mist is formed. The shape of the spray-pattern can be modulated (formed) by a secondary air-cushion.

Compared to electrostatic spraying, the droplets formed in the spray-mist are not as small. This can lead to problems in the coating. In order to avoid the undesired overspray the spray-gun must be kept close to the board (e.g. 5 cm compared to 30cm in electrostatic spray).

For PCM spraying can be of interest for 3D parts. As an alternative to roller-coating, it is also used to coat photoengraving plates. To coat sheets or plates, integrated coating and drying systems, conceptually similar to roller-coating systems for innerlayers, are available today. Picture 10 shows a double-sided spray-coating system with integrated dryer, which has been developed to apply solder masks for PCB.



Picture 10
Double sided horizontal spray coating system SC 1800 (Systronic GmbH, Germany)

#### 6.6 Curtain-coating

The coating takes place by passing the substrate under a free falling resist-film (curtain). The viscosity of the resists for curtain coating ranges between 500 – 3000 mPas.

Before the innovation of the double-sided-vertical screen printing process, curtain coating was the dominant high volume application method for soldermasks, perfectly conforming to the topographic structures of the PCB. In the 1990s the coating method was competing in the USA against roller coating to coat liquid etch resists for innerlayers.

For PCM, this coating technique is of no interest. In the future it may become interesting for the application of liquid resists for electroforming, since resist thicknesses between 10 and 200  $\mu$ m can be obtained.

### 7. Conclusion

New techniques and technologies are constantly being introduced to our industry. In order to build upon a rich history of imaging for PCM applications, HTP is committed to carry on the tradition of supplying new and innovative photoresists to address new demands set upon us by our customers.

## 8. Literature consulted (References)

- [1] PCMI Journal, No 69 Summer 1997: "A New Etch Resist for Photo Chemical Machining"; Colin Bird (Tecan Components Ltd., UK)
- [2] PCMI Journal, No 67 Winter 1997: "Continuous Cleaning of Metallic Strip for Photochemical Etchting"; Dr. Kenneth Abate (BMC Industries, USA)
- [3] PCMI Journal, No 69 Summer 1997: "Semiconductor to PWB: Bridging the Imaging Gap"; Ken Bridges (Morton Electronic Materials, USA)
- [4] PCMI Journal, No 77 June 2000: "Roller-Coating Application of Liquid Photoresist"; Diethard Kapp-Schwoerer / Charles Gantner (HTP HiTech Photopolymere AG, CH)
- [5] PCMI Journal, No 76 March 2000: "Visiting Photochemical Machining"; Karl H. Dietz (DuPont Printed Circuits Materials, USA)
- [6] Dryfilm Photoresist Processing Technology; Karl H. Dietz (Electrochemical Publications Ltd., 2001)
- [7] Kirk-Othmer: Encyclopedia of Chemical Technology / Supplement Fourth Edition 1998 pg 233-280
- [8] D M Allen: The Principles and Practice of Photochemical Machining and Photoetching, Adam Hilger, IOP, Bristol, 1986