UV curable jet-inks for etch resist applications

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Abstract

Ink-jet printing of electronic devices such as photo-voltaics and circuit boards is attractive for a variety of reasons. This includes simplification of the manufacturing process, customization of design and the production of higher resolution prints. Additionally, the non-contact nature of ink-jet printing allows a wide range of media to be used, such as flexible plastics and silicon wafers.

This paper focuses on one class of fluid used in the circuit fabrication process, etch resistant inks. Here, the inks act as temporary masks where they must resist acid but remove readily in alkali, as well as offering mechanical robustness. However, it is difficult for most classes of jet-inks to satisfy these demands, whilst offering reliable jetting, fast dry times and appropriate droplet spread.

Here we show that UV curable formulations can be developed which offer these desirable properties. A discussion is given on how variations of the backbone chemistry, in terms of functionality and cure response, can have a dramatic effect in these properties. By incorporating a surface pre-treatment, we show that it is possible to fine tune the ink spread to give desirable print quality.

Introduction

The typical manufacture of electronic devices and circuit boards is a multi-step process. This may involve a technique such as screen printing where a template is created prior to printing through which ink is passed or the use of photoimaging tools. By switching to an ink-jet process it is possible to print directly onto the substrate, thereby simplifying the process and saving production time. Additionally, if ink-jet printing is chosen it may be tuned to give higher levels of print quality (resolution) compared to screen printing. This can be achieved by varying printing parameters such as drop volume, number of passes and drying/curing regimes.

In the case of etch resist coatings, the printed area is usually a mask which temporarily protects the substrate whilst unwanted material around it is removed (etched) with a fluid (etchant). After this step, the etch is then removed (stripped) to reveal the protected substrate. Figure 1 summarizes the process for an ink-jet printed etch resistant fluid. To perform well in this application the etch coating must resist the etchant, which is typically a very strong acid such as sulphuric or hydrofluoric acid or a buffered oxide etch (BOE), then remove readily in the stripping fluid which is commonly a strong alkali such as potassium or sodium hydroxide. A good degree of film strength is also needed as the prints may be moved around conveyor belts or stacked for a period at different points in the process.

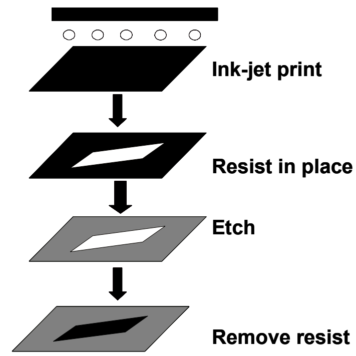


Figure 1
Schematic of etch-resist process by ink-jet printing

Hot melt (or wax based) jet inks have been used in a number of such applications, providing excellent drop definition and high quality prints. Through careful formulation the inks can resist acid and then dissolve in alkali. However, the films are easily scratched or damaged due to their soft, waxy nature. Also, because the inks need to be melted prior to printing, a number of commercial print-heads are excluded from the market. As an alternative to this chemistry, UV curable jet-inks have been identified as candidates in electronics fabrication processes, due to their film toughness, printing reliability and wide range of application properties. Due to good formulation latitude it is possible to create lower viscosity inks. In turn, a wider range of print-heads can be introduced.

There is much challenge in developing UV jet-inks that form a tough film that resists acid yet removes readily in alkali. Particularly difficult is the development of such inks that solubilise or form very small pieces of film in alkali rather than peel off in large strips. This is desirable as the way in which the etch strips is critical to the final usefulness of the coating in the manufacturing process. For example, an etch resist that peels off in alkali might have difficulty removing cleanly enough, leaving strands of film behind (see Figure 2). Additionally, the equipment to separate the stripped films may clog if the strands are large.

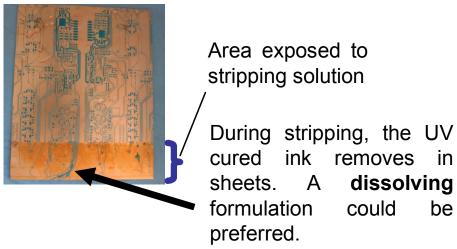


Figure 2
Printed UV etched and stripped copper board

UV jet-ink chemistry

It is well known that UV curable jet-inks can quickly form highly cross-linked films that perform in a variety of demanding graphics markets.[1] This formulation adaptability means they are attractive to numerous electronics applications. But films that are highly cross-linked tend to be difficult to remove in stripping solution. To address this we have formulated towards weakly cross-linked films using a variety of common monofunctional free-radical monomers. We have assessed the resultant film performance in typical etch resist tests. As a comparison, a cationic UV jet-ink was also examined.

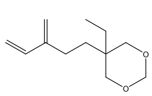
Controlling the spread of UV ink on electronics media is important to achieve the desired image quality. In most cases, the inks tend to spread excessively due to their low surface tension, which is needed to print reliably from most print-heads. Several options are available to address this issue, including pinning with LED lamps, varying printed drop volume and by substrate pre-treatment. In our study we have looked at the latter option.

Experimental

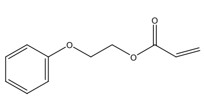
Ink formulations

Key free-radical and cationic monomers were identified and combined with base-line cationic and free-radical UV formulations.

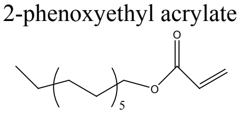
Free-radical monomers – all from Sartomer



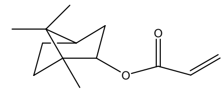
cyclic trimethylolpropane formal acrylate - CTFA



2-phenoxyethyl acrylate – PEA

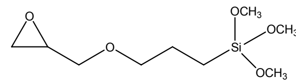


tridecyl acrylate – TDA



isobornyl acrylate – IBOA

Cationic monomers



3-Glycidyloxypropyltrimethoxysilane - GLYMO (Wacker)

Photo-initiators
Irgacure 184 (Ciba)
2,4,6-Trimethylbenzoyl-diphenyl phosphine (BASF)
Omnicat BL550 (IGM)

Pigment dispersion
Proprietary composition (SunChemical).

Etch and strip testing

12 μm films of ink were made on glass slides and cured with an Fe doped Hg lamp (Fusion "D" bulb).

The slides were then placed in beakers using two solutions at 45 ^{o}C as follows:-

Sulphuric acid (5 wt% aqueous solution) as etchant.

Potassium hydroxide (5 wt% aqueous solution) was used as stripping solution.

Control of ink spread

Coatings for circuit boards

A variety of solvent based coatings were applied at various concentrations onto copper board and dried prior to printing.

A Fibrodat was used to deliver 3.9 mL of free-radical ink on to the boards and contact angle measurements noted at 0.2, 0.5 and 1.0 s.

Printing

A Xaar 1001 print-head was used to print free-radical UV ink on copper board.

Results- etching and stripping performance

Table 1 summarizes the results for the free-radical UV jet-inks.

The curing characteristics were described as "fast" or "slow" depending on the number of passes at 200 mJcm^{-2} required to cure the ink film. In the cases of IBOA and CTFA containing inks a comparatively fast cure speed was noted, with the former giving a much harder film than all the other monomers.

Both these formulations gave excellent resistance to the acidic etchant but the CTFA film removed in large pieces in alkali whilst the IBOA based film remained adhered to the substrate.

These brief results indicated that usage of monofunctional monomer could be useful in terms of resisting acid and providing fast cure response. But in doing so, difficulties may be found solubilising the film in alkali. At best, a peeled film forms which is likely to give rise to the issues previously discussed (Figure 2).

Table 1: Summary of free-radical UV ink testing

	CTFA	PEA	TDA	IBOA
General properties	soft film, fast cure	soft film, slow cure	soft film, slow cure	hard film, fast cure
Acid	no damage	damaged	damaged	no damage
Alkali	peeled film	not removed	peeled	not removed

The GLYMO containing cationic UV curing formulation gave fast cure response and readily resisted acid. The cured ink film showed an immediate interaction with the alkali stripping solution and rapidly dissolved (see Figure 3). Notably a very clean interface was observed between stripped and non-stripped areas. It is thought the inherent nature of cationic UV chemistry leads to this promising finding. In other words, the fact that cationic curing is triggered by acid and the propagating species in chain growth is positively charged, are helpful in this application.[2] Therefore, the cured ink film can readily resist acid. In turn, this acid functionality is such that it reacts quickly with strong alkali and is removed from the substrate either as a soluble moiety or in very small pieces.

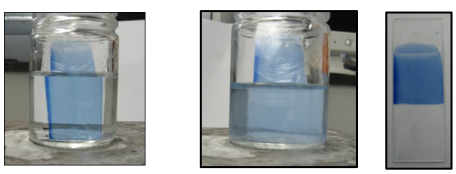


Figure 3 Film of cyan cationic jet-ink on glass in 5% H_2SO_4 (1) and 5% KOH (2) & resultant slide removed from jar after soaking in 5% KOH (3).

Results – control of printed dot size

From the Fibrodat testing (Figure 4), it was clear that drops of free-radical UV jet-ink on copper board could be influenced by a coating pre-treatment. Without this the ink spread excessively, giving a low contact angle in a short time scale. Both treatments 1 and 2 minimize this effect by lessening drop spread.

Whilst pinning the ink with UV light (e.g LED arrays) could control the drop to some degree in the case of untreated and treatment 1, it would have little impact on treatment 2. With this coating there is very little spread with time, as the drop of ink effectively freezes in position upon impact.

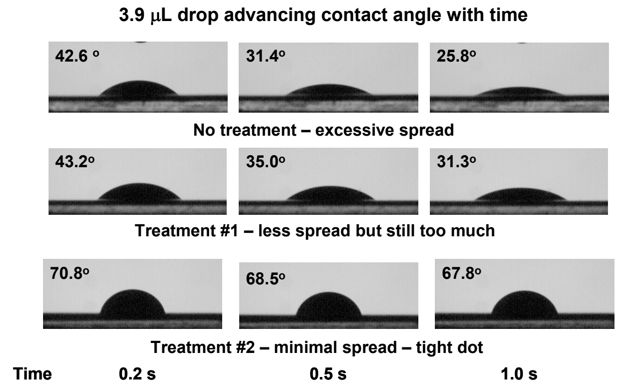


Figure 4: Contact angle from Fibrodat of drops of UV jet-ink applied to copper boards.

Figure 5 shows this finding correlated well with print tests on copper boards, in an analogous manner. A significant reduction in printed line-width with treatment 2 was noted using the same print pattern and ink on the two types of copper board.

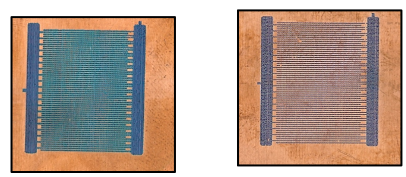


Figure 5: Printed patterns on copper board that is untreated (LHS) and coated with treatment 2 (RHS).

Summary

In summary, there are several options in formulating UV curable etch resistant coatings. Monofunctional free radical monomers can be selected that resist acid and peel off in alkali. If preferred, cationic chemistry may be used to provide an alkali soluble coating.

Good control of ink spread can be achieved by incorporating a suitable surface treatment on copper board prior to printing.

References

[1] A. Grant & H. Allen, Image Quality in UV Curing Ink-Jet Technology (IS&T, Salt Lake City, Utah, 2004) pg. 784-787.
[2] A. Grant, Reactive Silanes in Cationic UV Jet-inks (IS&T, Anchorage, Alaska, 2007) pg. 129.

Author Biography

Hartley Selman is currently Research Manager at SunJet. This followed his position of Project Leader, UV Jet Inks at SunJet, Bath, England UK. In this position he worked on UV curing ink-jet technology for graphics and other applications. He has a BSc from the Open University and holds several patents in UV jet-ink formulations.

Sam Moncur is currently Technologist at SunJet. He started work there as a technician in 2005 having graduated from the University of Loughborough with an honours degree in Chemistry. He has developed numerous jet-inks for both electronics and graphics applications and contributed to several patents in this area.

Alexander Grant was previously Research Manager at SunJet.