Photochemical Machining by Ink Jet. A Revolution in the Making?

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Abstract

Ink jet (IJ) printing has advanced to a point where etch resist imaging can be achieved at the required resolution for many segments of the photochemical machining (PCM) or chemical milling industry. This advance together with the development of suitable etch resist inks for this application has made it possible for the introduction of IJ printing in commercial PCM manufacturing environments. This paper describes attributes that affect the IJ printed resist resolution, novel inks suitable for jetting, the advantages that are gained and the resist performance obtained.

Introduction

Photolithography is the predominant method of imaging in PCM production. This technique has served the industry well as it provided the desired image resolution at an acceptable cost. It suffers from the drawback of being an analogue processes and requires production of a phototool. This adds cost and delays to the preparation of metallic items particularly for prototype and short run production. This traditional process using dry film resist materials is summarized in Figure 1.

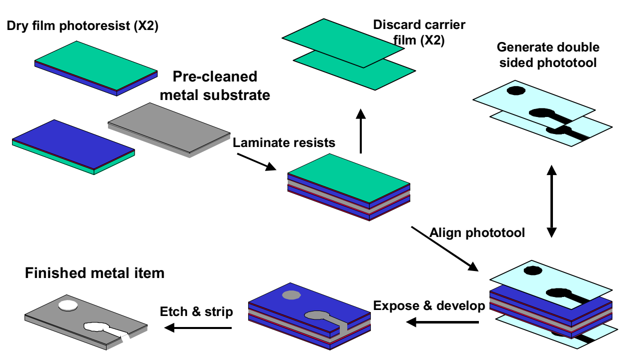


Figure 1. Traditional PCM Dry-film Resist Production.

The benefits of digital imaging methods are known as a way to simplify, speed up and add flexibility in production. Laser direct imaging (LDI) was developed in part to address this problem. LDI writes the design on a special photoresist layer with a laser and thus eliminates the need to prepare a phototool. Additionally it provides excellent resolution but market acceptance has been limited by both capital and consumable costs associated with this technology.

IJ printing is well known in desktop and graphic arts printing and is increasingly moving into industrial applications[1] as exemplified by the recent introduction of IJ manufacturing of printed wire boards in a fast and efficient way.[2] IJ printing has advanced to a point where primary resist imaging can be achieved at the required resolution for many segments of the PCM (or chemical milling) industry. This advance together with the development of suitable etch resist inks for this application has made it possible for the introduction of IJ printing in commercial PCM manufacturing environments.

This paper discusses the ink approaches and advances in both image resolution and ink performance to enable IJ technology to become commercially viable for direct etch resist imaging. It highlights the advantages to be gained by adopting IJ approaches in PCM manufacture and some of its current limitations.

Why Use Ink Jet in PCM?

IJ technology has been widely adopted in many printing, patterning and related processes for three principal reasons: 1. It is a direct method to accurately place material in one step, 2. It is a digital process and thus affords the ability to write data and continuously change the output, without the need of any intermediate stages and 3. It provides a non-impact method to deposit significant quantities of material. IJ printing has not been used for PCM yet, however, these advantages mean that IJ has considerable potential provided that the remaining technical challenges can be overcome because the input has already been standardized as digital Gerber files and the translation of this data to the final product involves conversion to analogue imaging processes. Simplified IJ processes can be designed for many of today's industry requirements and Figure 2 depicts a possible PCM process employing direct IJ writing of the etch resist to manufacture etched through metal objects.

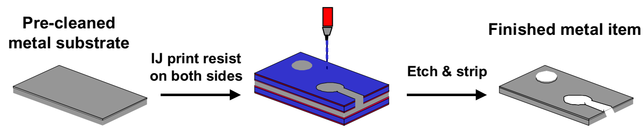


Figure 2. Ink Jet Process for PCM Manufacture.

Existing obstacles to the adoption of IJ technology in this application have been predominantly caused by two factors, the lack of available IJ printing heads capable of delivering the image quality and functional etch resist inks to perform the job. Substantial progress has now been made enabling IJ driven PCM production in an industrial environment.

Resolution Requirements in the Current Market

An analysis of the existing PCM market has recently been published[3] and highlights the considerable variation in run length, product use and resultant feature size requirements.

Most of the large volume applications, particularly suspension head assemblies and shadow masks require both high resolution and high accuracy, features of 100 microns with an accuracy of around 10 micron[4] and this is approaching the current limits of etch technology.

IC Leadframes are less exacting and can tolerate 200 micron resolution, low enough to enable stamping as an alternative manufacturing technology for high volume designs.

The majority of job-shop work is less demanding. While feature sizes can be as small as 100 microns, the majority is in the 250 micron plus range and accounts for a multitude of items like meshes, springs, gaskets, heaters, scales, jewelry, decorative plaques and boxes with fold lines.[4]

DOD IJ Resolution Capabilities for PCM

Resolutions achievable using DOD IJ printing are determined by a number of factors and any one of these can independently be the cause of image degradation. The most important are: 1. Drop size and drop reproducibility. 2. Drop spread on the substrate. 3. The process used to place drops of ink. 4. Mechanical limitations and 5. Digital factors including the raster image processor (RIP).

1. **Drop Size and Drop Reproducibility.** The relationship between drop volume (in pl) and drop diameter (in microns) is shown in figure 3. Drops sizes achieved by today's leading heads (6-30 pl) are in the right order of magnitude (1-2 mils, 20-40 microns) to meet the requirements of the majority of job-shop applications.

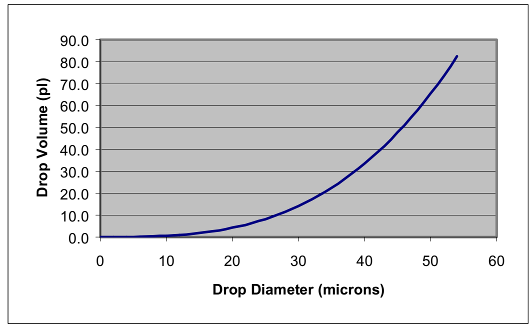


Figure 3. Relationship Between Drop Volume and Drop Diameter.

2. **Drop Spread on the Substrate.** When a drop is fired, the initial spherical shape (diameter d_1 in Figure 4) will deform as the drop hits (diameter d_2) and then settles on the substrate surface (diameter d_3) and this will result in a significant increase in diameter as depicted in figure 4.

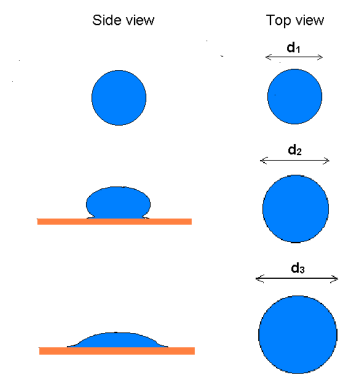
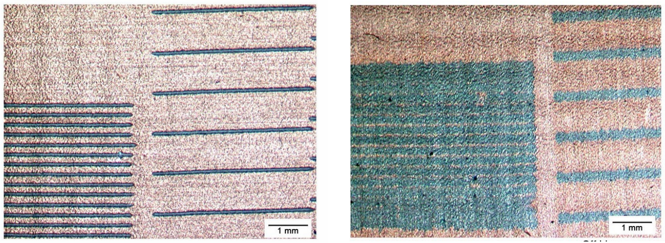


Figure 4. Diameter Increase on Printing.

The extent of increase is dependent on many factors including, ink viscosity and surface tension, surface energy, roughness and absorbency of the substrate and the time taken to 'freeze' the ink. Unfortunately, ink viscosity and surface tension are fixed low values to enable correct functioning of the IJ head and this maximizes ink spread. Control of drop spread is thus achieved by ensuring optimum preparation of the substrate and design of the printer system. By careful control of these parameters it is possible to minimize drop gain to 1.5 (i.e. d_3/d_1). Failure here can result in 10 times diameter increase and give the appearance of rough edges as the ink 'wicks and feather' over surface defects. This is illustrated in Figure 5, showing the effect of UV exposure on image quality for etch resist IJ printed on copper for both rapid exposure (a) and delayed (b) exposure.



(a) (b)

Figure 5. Effect of UV exposure time delay on image quality.

3. **The Process Used to Place Drops of Ink.** Printing a single line of touching dots forms the thinnest features (Figure 6, a). This results in excessively wavy edges and would result in gaps if errors occurred during printing. This problem can be minimised by placing drops on top of existing drops with an offset to smooth out the edges (6, b). IJ printers normally print the image by scanning the head backwards and forwards across the board and this introduces an additional complication that straight edges printed with the direction of the scan, at right angles to the scan and diagonally across the scan are different. This necessitates the need for a more complex and wider array drop pattern to minimize image imperfections (6, c).

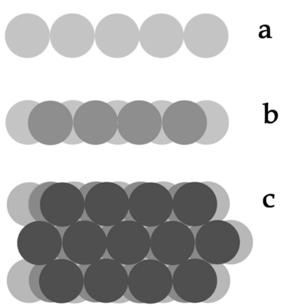


Figure 6. Drop Patterns to Produce Lines.

4. Mechanical limitations arise from both print head or platform movement and alignment. Good design of modern print platforms minimise these errors to the extent that these are not a current performance limitation.
5. Digital factors including the RIP can have a large effect. Computer power is no longer a limitation but RIP software is still advancing to reduce the current rasterisation error of typically 30 microns.

In the real world, all these factors combine. Current state of the art printers use 30 pl drop size. For etch resist printing on a smooth metal substrate, a resolution of 150 micron feature size is achievable in all print directions to produce high image quality and 120 micron features are obtainable with slight decrease in edge quality. This performance is predicted to improve to 75 micron features within the next year as equipment manufactures integrate 10 pl or smaller drop volume heads. This feature sizes place IJ technology as a real contender to compete with all but the smallest feature size sectors of the PCM market.

IJ Ink Design for PCM Applications

Existing materials used in PCM photolithographic or screen imaging range from viscous fluids to semi-solid or solid gels when applied and solid after imaging and cure. This provides a dilemma for IJ where the ink must have a low viscosity and surface tension to be jetted. We have considered several different approaches to deposit material using IJ as summarized in table 1 together with an assessment of some of the resultant strengths and weaknesses of each approach.

Table 1. Ink Types for PCM Using IJ

Ink Type	Strengths and Weaknesses
Resin in volatile solvent with no cure	Easy to design and formulate, good jetting performance but copious amounts of solvent to remove, and low image quality
Resin in volatile solvent with UV or thermal cure	Good jetting performance but copious amounts of solvent to remove and low image quality
Aqueous resin with no cure	Easy to design and formulate, good jetting performance but difficult to remove water, and low image quality
Aqueous resin with UV or thermal cure	Good jetting performance but difficult to remove water and poor image quality
100% Hot melt with UV or thermal cure	Good film quality, improved image quality but difficult ink design and limited IJ head choice
100% UV cure	Good film quality, good image quality but difficult ink design and UV lamp required

Significant problems have been encountered with all ink approaches based on lowering the viscosity of a resin by either making a solution or dispersion in an organic or aqueous solvent, as no successful ways have been found to control ink spread before drying and this gives big drops which wick and puddle around surface energy variations and defects on the substrate resulting in unacceptable image quality.

More recently, a number of approaches have been developed based on '100%' inks. In these systems, all the jettable ink becomes the final film. These approaches enable the deposition thicker films, eliminate the need for solvent removal and could provide the basis commercially viable products. Ink spread control is achieved by one of two mechanisms:

1. Hot melt inks, the viscosity is designed to be low in the IJ head and rise to become a solid on cooling after landing on the board. Additional UV or thermal cure can then be undertaken later to obtain the final film performance if required.
2. 100% UV cure inks work by having a low viscosity ink which is irradiated by UV light after application to the substrate to effect polymerization resulting in solidification of the ink. Additional UV or thermal cure can then be undertaken to further harden the film if needed. An ink suitable for this approach to PCM production has recently been comercalised,[5] which was co-developed to work in an industrial printer.[6]

Advantages and Disadvantages of 100% UV Cure Inks for PCM Etch Resist Applications

The combination of high resolution DOD heads, an etch resist ink and good system integration into a printer is now realizing the following advantages:

- Direct digital processing, provides easy one-off to short run capability with the unit cost of a run length of one equaling that of run length 100 or 10,000.
- IJ print and integrated UV cure eliminates the following stages: screen or phototool generation, screen printing or dry film lamination, exposure and wet development processing.
- Savings on capital for equipment associated with the eliminated steps, reduced running and maintenance costs and space savings of this equipment's footprint.
- Large reduction in material usage as only the final image area is covered versus the total metal item in existing processes, no dry film polyester backing film is used or solvents evaporated to tack the film and chemicals are eliminated from the development stage. Reduced material usage also leads to reductions in effluent disposal costs.
- Direct application of the resist removes the possibility of phototool damage during the set up for exposure and eliminates the requirement to store the tool for future use.

Overall, the above benefits will lead to faster turnaround times at a lower production cost.

Disadvantages stem from using drops of ink to form the image and the consequences of being a different process to what industry currently uses. The main issues are:

- Feature sizes are currently limited to 120-150 microns but this will decrease with smaller drop sizes.
- The image generated consists of wobbly lines and rounded corner, compared straight lines and well-defined right angles when produced using photolithography. This effect will not cause an issue for many applications but will be unacceptable for the finest resolution uses like suspension head assemblies and shadow masks for the foreseeable future.
- Being a new technology, the number of inks and printers that are commercially available is limited. The new ink is general applicable but not optimized for some specific niche applications as described later. This will change as technology adoption and development proceeds.

Etch Resists for PCM IJ Application

The new 100% UV cure etch resist ink[5] is suitable for use in a number of leading IJ heads. The ink can be printed on most pre-cleaned metals used by the industry and then processed through the existing etch, strip and some plating baths. This strategy will enable trial and adoption of this technology by existing players for the cost of purchase or lease of an IJ printer together with the consumables used. Measured properties of the ink are summarized in table 2. Specific compatibilities of the etch resist to different metals and etch conditions are detailed in table 3.

Table 2. Properties of 100% UV Cure Etch Resist Ink[5]

Viscosity	12.4-14 cps at 40°C
Surface tension	25-28 dyne/cm (mN/M)
Cure conditions	Rapid UV cure
Film thickness	5-40 microns
Color	Blue
Metal compatibility	See table 3
Etch chemistry compatibility	See table 3
Plate chemistry compatibility	Resistant to acidic or neutral electroplating e.g. copper sulphate/sulphuric acid
Strip conditions	2.5-4% sodium hydroxide at 40-60°C and some basic solvent systems
Physical form of striped resist	Small/medium flakes depending of film thickness and feature size

Etch resist bath endurance with ferric chloride is excellent for the most important resist coated metals including stainless steel, mild steel, copper and brass which account for in excess of 90% of metals used. The etch resist coating survives well in other acidic baths evaluated with the exception of hydrofluoric acid etching of titanium. Resistance to alkaline enchants is poorer, tolerating the bath for only a few minutes at best as highlighted with copper and cupric ammonium chloride. Caustic etching of aluminum failed totally but is possible with hydrochloric acid and to a lesser extent with an alkaline potassium ferricyanide bath.

Table 3. Metal & Etch Compatibility of the Resist Film[7]

Metal	Etch conditions at 50-55°C	Etch survival	Strip rate
304 Stainless steel (SS)	38 °Bé $FeCl_3$	> 2 hours	medium
Mirrored 304 SS	38 °Bé $FeCl_3$	> 2 h	fast
316 SS	38 °Bé $FeCl_3$	> 2 h	slow
Mild steel	38 °Bé $FeCl_3$	> 2 h	fast
Copper	38 °Bé $FeCl_3$	> 1 h	medium
Copper	33 °Bé acidic $CuCl_2$	> 0.5 h	medium
Copper	cupric ammonium chloride	1-3 minutes	medium
Brass	38 °Bé $FeCl_3$	> 1 h	fast
Beryllium copper	38 °Bé $FeCl_3$	> 1 h	medium
Phosphor bronze	38 °Bé $FeCl_3$	> 1 h	fast
Aluminum	3 molar HCl	> 10 min	fast
Aluminum	alkaline (pH 13) potassium ferricyanide	< 5 min	fast
Aluminum	10% NaOH	fail	N/A
Molybdenum	alkaline (pH 13) potassium ferricyanide	< 5 min	fast
Titanium	10% hydrofluoric acid	fail	N/A

Performance at the strip stage is variable and may require optimization of the industrial strip line used. Strip speed has been shown to depend on the metal type as highlighted in table 3, metal surface finish with smoother surfaces peeling fastest, surface cleaning and pre-treatment, film thickness, the energy used to cure the etch resist and feature size printed.

The ratio between etch resistance and strip speed can be adjusted by increasing the UV dose or incorporating a thermal bake into the process but a point can be reached where the material becomes an immoveable protective coating rather than the required temporary resist material.

Conclusion

Progress that has been made in developing smaller drop size, DOD IJ heads together with a new PCM market specific resist ink, has enabled equipment manufacturers to integrate these technologies and produce viable commercial IJ printing machines for PCM manufacture.

The current state of the art systems enables direct printing of an etch resist film on metal surfaces in one simple step followed by processing using the existing etch and strip tanks resulting in large reductions of lead-time, equipment requirements and chemical usage culminating in substantial cost savings.

Resolutions that are available from today's equipment using the ink jet printable etch resist ink can meet a large proportion of the markets need and this will increase further as the drop size decreases and finer features can be produced using IJ printing.

Acknowledgment

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5. Jetrack™ Etch Resist 001 ink is available from Avecia Ink Jet Printing Materials, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS, UK.
6. New System etch resist printers. New System, Via III Armata, 131, 34170 Gorizia, Italy.
7. Metal etch and strip compatibility was evaluated as follows: The metal sheets (approximately 15X25 cm) were cleaned in acetone and coated with a 10X20 cm solid block of Jetrack™ Etch Resist 001 which was cured with UV irradiation from a Fusion D bulb employing a dose of 0.32J/cm (UVA) and 0.17 J/cm (UVB) to give a 16 micron thick dry film. Etching was undertaken as detailed in table 3 followed by striping in 2.5% sodium hydroxide at 60°C with agitation. Strip rate was then rated as fast (removed in less than 5 minutes), medium (5-20 minutes) or slow (greater than 20 minutes).

Biography

Mark James received a BSc from Durham University and a PhD from University Newcastle upon Tyne, specializing in organic synthesis. After doing postdoctoral research at the University of Southampton he joined ICI and has remained there over the transformation through Zeneca to Avecia. For the past 8 years he has been involved in ink jet projects ranging from colorant design to developing inks suitable for PCM manufacture.