
Ink Jet Barrier Film For Resolving Narrow Ink Channels

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Abstract

Ink Jet Barrier Film is a photoresist sandwiched between a polyester and a polyolefin. The unexposed photopolymer film instantly adheres to different types of substrates. The film can be exposed with a photographic artwork, and the unexposed area can be developed in non-halogenated solvents. The cured film on a substrate can be laminated on to a top plate at elevated temperatures. The film is highly flexible and resists partially non-aqueous high pH inks. Several factors affect the resolution of the Ink Jet Barrier Film. Chemical composition and process conditions that affect resolution have been identified. It was possible to resolve 10 micron channels with 30 micron thick films. A modern high technology clean room coater is used to manufacture the Ink Jet Barrier Films. Thickness control capability is excellent. A high Cpk has been achieved for a narrow thickness range.

Introduction

Ink Jet Printer business is growing rapidly. A 38% compound growth rate for the Ink Jet Printer Cartridges has been forecasted for the next few years¹. Colored inks and high resolution printing (300×600 dpi) have been recently introduced. Industrial applications of Ink Jet Printing are growing. The ink and quality of the print head affect print quality. The forecasted growth rate is very much dependent on the improvements in print quality.

Ink Jet Barrier Film is a pre-coated, defect free, high quality dry photopolymer film of controlled thickness sandwiched between a polyester base sheet and a polyolefin cover sheet. The polyolefin coversheet is removed and the film is hot roll laminated on to the substrate. The photopolymer film is imagewise exposed through an art work and developed. The top plate is attached and then thermally cured. End use properties of the Ink Jet Barrier film are affected by the photopolymer film chemistry as well as the process conditions.

Originally published in *Proc. of IS&T's Ninth International Congress on Advances in Non-Impact Printing Technologies*, October 4-8, 1993, Yokohama, Japan.

Non-Aqueous Development

One of the stringent properties the Ink Jet Barrier film has to satisfy is ink resistance. Inks are aqueous solutions containing colorant(s), biocide(s), organic solvents and optionally dispersion agents. Alcohols and Pyrrolidones are the commonly used co-solvents²⁻⁴. pH of the ink ranges from 5 to 9. Aqueous developable photopolymer films contain acidic or basic functional groups. During aqueous development, unexposed photopolymer swells in the developer solvent and the swollen film is dispersed using mechanical force. Developed film is thermally and/or photochemically cured to increase cross link density. Even the cured photopolymer film contains a significant number of acidic (basic) functional groups. The acidic (basic) functional groups tend to hydrate in aqueous media and ink resistance of the hydrated films at elevated temperatures is less than satisfactory. Acidic polymer films swell in the basic ink leading to dimensional change and delamination. Pyrrolidones are excellent solvents for most polymers and tend to swell the barrier film. Film deterioration is accelerated at higher (operating) temperatures. One way to improve the ink resistance of the aqueous developable photopolymer films is to start with an acidic polymer film and then remove the carboxylic acid functional groups during thermal cure (Kolbe Reaction). This kind of chemistry calls for a harsh oxidative cure cycle resulting in a brittle film. Adhesion of brittle films to substrates is poor. Also, elimination of carboxylic acid or other functional groups involves liberation of gases during thermal cure. This can result in lifting of the top plate or the bottom plate. Also, liberation of gases make the film porous through which ink can diffuse at high temperature and degrade the film.

Non-aqueous developable films are hydrophobic and do not require polar(acidic or basic) functional groups. In the past, non-aqueous development was done in 1,1,1-Trichloroethane. Trichloroethane has been classified as a toxic chemical and an environmental pollutant. Use of Trichloroethane is to be avoided due to government regulations.

A variety of halogen free non-aqueous solvents are commercially available. A solvent or a solvent blend can be chosen specifically to suit the photopolymer film and process chemistry. The development can be done in a closed system, and it is possible to recycle the devel-

oper solution. Most solvents have freezing points below room temperature and it is possible to develop the Ink Jet Barrier films at low temperature.

Hydrophobic polymers are used in non-aqueous developable photopolymer films. These films swell less in high pH inks, and the integrity of the film is maintained at high temperatures even after extended periods of time. Swelling of the film in organic co-solvents can be reduced further by increasing the cross linking density.

Ink Jet Barrier film end use properties can be divided into two groups; bulk and interfacial. Ink resistance and resiliency are bulk properties. Adhesion to the substrate and top plate is an interfacial property.

Diffusion Co-Efficient of Water

Since diffusion of ink into the film generally degrades the quality of the pen, low diffusion constant and low weight gain are preferred. Aqueous developable photopolymer films show larger weight gain than non-aqueous developable films.

The diffusion coefficient of water can be determined gravimetrically by determining the weight gain as a function of time⁵. A known weight of fully cured Ink Jet Barrier film was immersed in water at 70°C. The film was removed after a set time, wiped clean of any water drops and then weighed again. The weight gain reaches the limiting value in about 2 hours and the maximum weight gain was in the range of 0.3 to 0.8% at 70°C. Water uptake was found to be a function of the hydrophobicity of the film. More hydrophobic films showed less weight gain. The diffusion coefficient was determined to be 1 E-10 cm²/sec. This diffusion constant is about an order of magnitude less than conventional organic photopolymer films. Diffusion of inks is expected to be faster and the net weight gain is expected to be slightly higher than that of water due to the presence of organic co-solvents in inks.

Contact Angle

Contact angle is a measure of wettability. A good wettability improves the rate of refilling of the ink after the ink bubble has been ejected. Refilling of the resistor chamber with ink after bubble ejection is considered to be the rate determining step in ink jet printing⁶. Hence, a low contact angle is preferred. Low contact angle means instantaneous complete wetting of the surface by the ink which comes from high surface energy. Films that wet the ink thoroughly interact with the ink and swell and eventually degrade. Films that do not wet the ink at all result in longer refilling time, limiting the bubble ejection frequency. An intermediate contact angle satisfies the requirements for sufficient wetting as well as ink resistance.

Contact angle is a function of several factors. Contact angle decreases with temperature. Inks containing organic co-solvents and surfactants show lower contact angles. Process conditions also affect the contact angle. At present, it is not possible to develop an Ink Jet Bar-

rier film that will provide the required contact angle with several inks. For best performance a film has to be developed for a set of process conditions, substrate, top plate and ink.

The film surface temperature might reach 75-85°C under standard operating conditions⁷. An ideal Ink Jet Barrier film should not show a significant change in contact angle when exposed to ink at high temperature for several hours.

Table I. Contact Angle at the Interface of Ink I

Film	Fresh Cure Temp.			24 Hour Soak at 70°C Cure Temp.		
	385°F	300°F	Δ	385°F	300°F	Δ
A	31.8	41.6	+9.8	36.8	33.6	-3.5
B	44.8	44.4	- 0.4	32.8	41.2	8.4
C	48.6	36.8	-11.8	33.4	35.2	1.8
D	49.6	42	- 7.6	39.2	37.2	-2.0

Table II. Contact Angle at the Interface of Ink II

Film	Fresh Cure Temp.			24 Hour Soak at 70°C Cure Temp.		
	385°F	300°F	Δ	385°F	300°F	Δ
A	52.8	49	-3.8	46.4	46.4	0.0
B	50.8	52	+1.2	47.6	44.4	-3.2
C	50.6	50	-0.6	46.2	42.2	-4.0
D	56.2	50.6	-5.6	48.2	46.2	-2.0

Depending on the film chemistry cure temperature increases or decreases the contact angle. Ink chemistry also affects contact angle. An aggressive ink and a mild ink were chosen for this study. Ink II contains less Pyrrolidones than Ink I. Soaking in ink at 70°C generally decreases the contact angle. The change in contact angle after the ink soak can be decreased by changing the cure temperature. Initial UV exposure for imaging and development conditions(solvent, temperature, dwell time) also affect the contact angle. Process conditions have to be optimized for each film and ink combination.

Ink Resistance. Irrespective of contact angle, a small amount of ink diffuses into the film under standard operating conditions. More aggressive inks containing organic co-solvents such as Pyrrolidones accelerate degradation. The degradation can be seen as lifting of the film from the substrate or top plate, or swelling and change in dimension of the barrier film. Bubble and/or void formation in film might occur in extreme cases.

Hydrophobic films generally show less ink attack after accelerated aging test at high temperatures. One way to decrease the ink attack of the film is to increase the cross link density. Highly cross linked systems show less diffusion of solvents or vapors. During the cure, low molecular weight fragments (reaction byproducts and solvents) leave the bulk film, making the film porous. It is important to keep the volatile ingredients to the lowest level possible.

Increasing the cross linking density makes the film brittle. Brittle films show interfacial failure after ink soak test. Interfacial failure can be eliminated by the addition of interfacial adhesion promoters.

Adhesion to the Substrate

Adhesion of the unexposed photopolymer film to the substrate is critical for narrow channel resolution. Insufficient adhesion results in lifting and the fine lines wash away during development. Adhesion to the substrate can be improved either by chemical, physical or mechanical means^{8,9}. We will limit our discussion to chemical and physical interactions.

Different types of substrates are used in the ink jet printer industry. Treated single crystal silicon wafer, glass, epoxy, stainless steel and plastics are common. Often, the substrate surface undergoes multiple surface treatments; passivation, coupling agent treatment and metal deposition are common. Photopolymer films generally adhere to epoxy surfaces and the adhesion to epoxy even after cure is high. Adhesion of the Barrier film to other substrates depends on several factors. Chemical composition of the film affect the adhesion to various substrates.

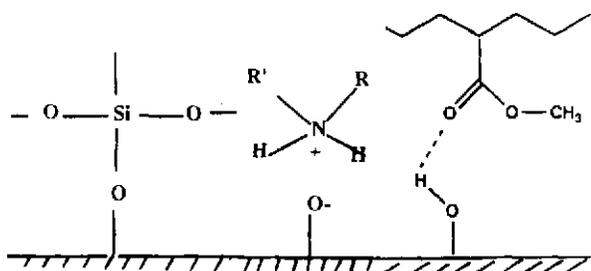


Figure 1. Chemical Interaction between the Substrate and the Photopolymer Film

Three different types of chemical interactions of the photopolymer film on a glass surface are shown in Figure 1. The oxide surface contains a small amount of hydroxyl groups. The amount of hydroxyl groups per unit area depends on several factors such as the environment and the impurities present in the metal near the surface. Glass surface can be made acidic or basic by changing the alkali metal ion concentration near the surface. At high alkali metal ion concentrations the glass surface is basic. The ester groups of the methacrylate polymer film interacts with the hydroxy groups on the silica surface through hydrogen bonding. If the glass surface is basic then the adhesion strength of the methacrylate polymer would be less. Amino compounds abstract a proton from the hydroxy group leading to salt formation. A high adhesion force is observed due to electrostatic interaction between the polymer film and the glass surface. However, such ionic compounds allow inks to diffuse through the interface leading to lifting. Silane compounds react with the hydroxide groups on the surface.

Adhesion promoters in the Barrier film improve adhesion to a specific substrate. Two types of adhesion promoters are available: Polymers containing functional

groups that interact with the substrate or small molecule additives such as heterocyclic compounds (imidazoles) migrate to the interface and chemically bond to the substrates. The nature and the amount of adhesion promoters depends on the type of the substrate surface.

Surface preparation of the substrate plays a critical role in determining the adhesion strength. Often surface treatment generates a specific functional group at the interface which interacts with the ingredients in the film. Surface treatment also often results in roughening of the surface increasing the real surface area per unit geometric area.

The adhesion strength of typical Ink Jet Barrier films on different substrates is given in the following table. An acrylate based dry film was laminated onto the substrate and the unexposed photopolymer film was peeled off along with the polyester.

Table III. Adhesion Strength To Various Substrates Lamination at 103°C at 1.2 m/min.

Substrate	Adhesion, gm./inch			
	A	B	C	D
Silicon Wafer	499	104	586	178
Stainless Steel	18	35	63	12
Copper	61	37	59	15
Glass Epoxy	523	182	491	336
Clear Glass	15	28	21	24
Aluminum	44	63	152	18

Table IV. Lamination at 103°C at 0.3 M/Min.

Substrate	Adhesion, gm./inch			
	A	B	C	D
Silicon Wafer	458	160	666	629
Stainless Steel	15	9	36	43
Copper	44	64	14	12
Glass Epoxy	698	-	802	524
Clear Glass	54	53	260	15
Aluminum	48	121	196	21

Table V. Lamination at 103°C at 1.2 M/Min. Bake at 104°C for 5 Min.

Substrate	Adhesion, gm./inch			
	A	B	C	D
Silicon Wafer	302	91	538	210
Stainless Steel	13	53	18	16
Copper	273	60	351	26
Glass Epoxy	642	-	799	576
Clear Glass	18	10	62	7
Aluminum	37	85	129	19

Two factors are obvious. Chemical composition of the film is important in determining the adhesion to the substrate. Also the type of surface is important. Adhesion strength of film A is only 15 gram/inch on a glass surface compared to 523 gram/inch on an epoxy surface. Adhesion to a silicon wafer is high. The silicon wafer contains a thick oxide layer on the surface. These films were developed for adhesion to a silicon wafer surface. A different type of chemistry is required to improve the

adhesion to clear glass. Adhesion of this photopolymer film to low alkali metal ion glass would be higher. Adhesion to stainless steel also is poor. Addition of heterocyclic compounds to the film composition would probably improve the adhesion to steel.

Adhesion of these photopolymer films to polyester is higher than the adhesion to some of the substrates. Exposed and unexposed film come off with polyester when the cover sheet is removed when adhesion to polyester is higher than to the substrate, and the remaining film on the substrate is washed off during development.

Adhesion to the substrate can be improved by laminating at a lower speed or by baking the film before/after UV exposure at below polymerization temperature. Generally an improved resolution is observed after bake.

Different types of surfaces might be present on the substrate. For example part of the wafer surface might be gold and another part aluminum. Gold does not form oxides on the surface and aluminum readily forms oxides.

Different types of adhesion promoters can be added to improve adhesion to both substrates.

Stereochemistry of the molecule at the interface is important for improved adhesion. For example, heterocyclic molecules can be adsorbed parallel to the surface or perpendicular to the surface depending on the entropy and enthalpy of the interfacial system. Adsorption of adhesion promoters parallel to the substrate surface often results in pi system interactions which are weak whereas adsorption perpendicular to the surface results in a chemical complex formation. One side of the adhesion promoter might be chemically bonded to the surface and the other side may be entangled in the bulk polymer film providing a good interaction between the film and the substrate.

Generally small molecules have a larger effect on adhesion than bulk polymer molecules. Photopolymer films contain photoinitiators, co-initiators, colorants, stabilizers, etc. These compounds may contain amino- or carbonyl group and interact with the surface. Depending on the structure of the additive and the surface concentration, a family of photoinitiators and colorants might be preferred. Interactions of two or more compounds becomes critical for adhesion.

Adhesion To Polyester Base Sheet

Ink Jet Barrier film is laminated with the polyester base sheet and then exposed. The polyester base sheet is removed before solvent development. Adhesion of the photopolymer film to the polyester sheet is in the range of 100-500 grams/inch. Adhesion decreases after UV exposure. Very low adhesion to polyester after UV exposure is preferred. If adhesion to polyester is high, the photopolymer film tends to lift from the substrate surface during polyester removal and the fine lines wash away. Since the polyester is a smooth amorphous film there are no mechanical interlocking forces involved. Generally attempts to decrease adhesion to polyester result in decreased adhesion to the substrates. A blend of compounds can be chosen to balance the adhesion to

polyester and the substrate. For example, two different types of monomers can be chosen; one to increase adhesion to the substrate and another to decrease the adhesion to the polyester.

Optical Density of the Film

Since the active ingredients in the film are sensitive to the near UV region and the polyester film cuts off light below 320 nm optical density in the region 320-400 nm is considered here. Photoinitiators, colorants and adhesion promoters absorb light in this region. The optical density of the film is proportional to the concentration of the light absorbing species at that wave length. At a given optical density the light absorption fraction decreases exponentially with film thickness. Suppose the optical density of a 1.0 mil thick film is 2.0 at 366 nm. The top 0.1 mil of film absorbs 36.9% of the incident light and the bottom 0.1 mil of film absorbs 0.6%. Since the light absorption fraction is different, the extent of polymerization decreases with depth of film. The cross link density at the interface is small and the film is washed away during development. Severe undercut is often observed. This problem can be solved by decreasing the optical density of the film. When the optical density of the film is 0.5, the top 0.1 mil absorbs 10.8% of the light and the bottom 0.1 mil absorbs 3.9%. Light absorption fraction can be brought closer at low optical densities. But low optical densities require low concentrations of the active ingredients which limits speed.

Resolution depends on the type of substrate. Optically opaque substrates absorb the excess light. Smooth surfaces reflect more light. The polished silicon wafer surface is mirror like and reflects the near UV light. On mirror-like surfaces the light absorption fraction of the film on the top and the bottom can be made almost equal. For example when the optical density of a 1.0 mil is 0.5, the top 0.1 mil absorbs 10.9% light and the bottom 0.1 mil absorbs 3.9%. 31.6% light is reflected. Now the bottom 0.1 mil film absorbs 3.2% of the reflected light and the top 0.1 mil 1.2% of the reflected light. Total light absorbed by the top layer is 12.1% and the total light absorbed by the bottom layer is 7.1%. Similar light absorption fraction results in straight side walls and better resolution. Resolution on mirror-like silicon wafer is always better than that of glass epoxy plastic.

Light absorption fraction varies with wave length. It is low at low optical density and high at high optical density. Strong absorption in the UV region with a sharp drop in absorbency near 400 nm is preferred for photoinitiators. Semiconductor particles with a band gap of 3.0 eV show sharp absorbency drop near 400 nm. But there were other concerns associated with these particles and the particles scatter light. One way to have an almost constant light absorption fraction in the region is to add an inert window dye which absorbs in the region where the photoinitiators do not absorb. Some yellow dyes have an absorption maximum around 430 nm with a broad tail in the near UV region. An yellow dye can be selected to match the photoinitiator absorption spectrum.

Side Wall Geometry

Optimum UV exposure and optimum development conditions are required for straight side wall geometry. Two similar compositions containing a difunctional monomer and a trifunctional monomer are compared in the figure. Trifunctional containing film shows a rectangular side wall geometry whereas the side wall of difunctional containing film is swollen in the middle. This swelling can be eliminated by selecting a more reactive photoinitiator system.

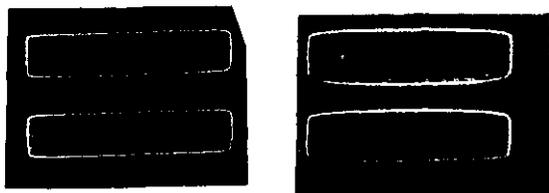


Figure 2. Side wall Geometry of Difunctional and Trifunctional based Ink Jet Barrier films

Chemical Composition

All the ingredients in the film composition affect resolution. A hydrophobic polymer is the main ingredient in the Ink Jet Barrier film. Low Tg polymers provide the required resiliency to withstand the pressure fluctuations during the operation of the pen. But brittle films show excellent resolution which is attributed to the development characteristics. Brittle films are partially crystalline, detach from the neighboring groups and develop cleanly. High resolution with low Tg polymers can be achieved by mixing two or more polymers.

Monomers have to be selected to increase the compatibility with the main polymer. Multifunctional monomers give higher photospeed and good resolution and also improve ink resistance, but tend to give brittle films.

The photoinitiator system plays a major role in determining the resolution of the film. Ketone type photoinitiators generate high energy radicals during UV exposure. These high energy radicals can also abstract hydrogen atoms from the polymer chain and spread the line width. Low energy radicals generally react with the monomers and do not abstract hydrogen atom from polymers. Such photoinitiators generally improve resolution. Selection of photoinitiators depends on the monomer system and the other colorants.

Process

Resolution is a function of chemistry and process. Collimated light source is a pre-requisite for good resolution¹⁰. Uncollimated light gets scattered at the film substrate interface leading to polymerization in the unexposed areas. Exposure without the polyester sheet reduces light scattering at the polyester film interface and also decreases the distance between the phototool and the film¹¹. But removal of the polyester sheet exposes the film to aerial oxygen and decreases photospeed and resolution. Also stickiness to phototool is a concern.

Several non-chlorinated solvents are available for development. It has been found that a blend of solvents is better than a single solvent. The best choice is a blend of a good solvent and non-solvent for the photopolymer film. The ratio of the solvent blend has to be optimized for the specific film. The effect of development temperature on resolution for an aqueous developable solder mask film is shown in the table. Optimum development is observed at 40°C.

Table VI. Resolution vs. Development Temperatures(°C)

Development Temperature	Time to Clear (sec)	Resolution Lines/mm
24	78	10.1
29	58	11.3
40	35	12.7
52	16	10.1

High temperature makes the developer solution more aggressive and decreases resolution. Flammable solvents have an advantage here. We can select solvent blends with freezing point below room temperature. Low developer solution temperature reduces the vapor pressure as well as improves resolution.

Two types of developers are commercially available: conveyorized and spin spray. High pressure spin spray developers have been used to demonstrate improved resolution.

Thickness Control

Ink Jet barrier film separates the substrate and the top plate. Thickness of the Ink Jet Barrier film determines the amount of ink available for ejection. Thicker films result in larger gap which allows faster refilling. Faster refilling allows faster firing rate. But also larger ink volume in the chamber results in larger drop size. Film thickness has to be selected for a specific drop size and a firing rate.

The critical property here is the tight thickness control. The Barrier film thickness has to be same between orifices in an array of pen nozzles for constant drop size from all the nozzles. Also Ink Jet Barrier film thickness has to be constant within a pen for constant drop volume from each orifice. Identical thickness is required for all the pens for consistent quality. Very tight tolerance of Barrier film thickness within a roll, roll-to-roll, and lot-to-lot is required. State-of-the-art coating facility is used to coat the Ink Jet Barrier film. A high Cpk has been demonstrated between several rolls and lots.

Conclusions

Dry photopolymer film of controlled thickness is a suitable material for Ink Jet Print Head. Narrow ink channels can be resolved using the Ink Jet Barrier film. Chemical composition of the film as well as the process conditions affect resolution. Solvent developable films

show improved ink resistance compared to aqueous developable films. Higher adhesion to the substrate improve resolution. Adhesion to the substrate varies depending on the surface structure and morphology. Chemical composition of the film has to be optimized for the substrate, top plate, ink chemistry and process conditions combination.

Acknowledgment

The author would like to thank Ray Work III, Martin Hill, Dennis Cox and Butch Brion for the encouragement and support.

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