
High Ink Resistance Barrier Films for Ink Jet Printers

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Abstract

Ink Jet Barrier Film is a photoresist sandwiched between a polyester and a polyolefin. The 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. Developed film on a substrate can be laminated on to a top plate at elevated temperatures. Aggressive co-solvents and surfactants are used in ink jet inks to provide fast dry time and print quality. These ingredients in the ink diffuse into the film during storage and use. The swollen film delaminates from the substrate and/or top plate. Delamination of the barrier film is accelerated under the pen firing conditions. Chemical approaches to solve these problems will be discussed.

Introduction

Industrial and office printing applications of ink jet printers are growing rapidly¹. New printers and inks are introduced by several suppliers almost on an annual basis. One of the components that controls print quality is the print head. Different print head designs are used. Canon print heads are side shooters and HP print heads are top shooters^{2,3}. Piezoelectric materials are used to generate the force to expel the ink drop in some devices⁴. A super heated ink is used to generate the force to expel the ink in thermal bubble jet print heads. In all cases ink jet print heads are made of a three layer structure; substrate, spacer and the top plate. The substrate and the top plate are separated by the spacer. Different pen designs, manufacturing and process conditions, require different types of materials for substrates and top plates. The spacer acts as an ink conduit. Ink from the reservoir flows to the firing chambers through the channels in the spacer. The amount of ink present in the firing chamber is determined by the thickness of the spacer layer. Thicker spacer films maintain a larger amount of ink in the firing chamber. Also these spacer films act as thermal and electrical insulators between the ink chambers. The main function of the spacer, the barrier film, is to keep the substrate

and the top plate positioned at a fixed distance during storage and operation of the pen.

The substrate and the top plate are made of different materials. Mechanical and chemical properties of the substrate and the top plate are different. Parts of these layers are exposed to ink during storage and operation. Ink chamber temperature in the print head might reach 100°C during firing and cool down rapidly during collapse of the bubble. Nucleation and bubble growth pressure is in the range of 15 MPa⁵. The substrate, barrier film and the top plate are exposed to millions of temperature and pressure shocks during the life time of the pen. The substrate, barrier film and the top plate respond differently to temperature and pressure fluctuations. The three layers should stick together at elevated temperature and pressure conditions in the ink during millions of temperature and pressure shocks.

Ink jet inks often contain aggressive co-solvents and surfactants⁶⁻⁸. These co-solvents and surfactants are used to provide faster wetting and dry time. These inks tend to attack the barrier film during storage and operation. Also the adhesion between the substrate and the barrier film and between the barrier film and the top plate degrades during temperature cycling leading to separation of these three layers. The quality of the pen determines the type of ink that can be used which determines the print quality. The life time of a pen is limited to mechanical stability of these three layers under the storage and operating conditions. We will discuss the chemical and mechanical approaches to increase the stability and life time of the pens.

Photoimageable Ink Jet Barrier Films

Any film of known thickness can be used as an ink jet barrier film. A variety of engineering polymers are commercially available which are chemically resistant to aggressive inks. But most of these engineering polymers, such as polyether ether ketone (PEEK), do not adhere to the substrate or the top plate. It is possible to use a thin layer of adhesive on either side of the engineering polymers and laminate the substrate and the top plate. But these adhesives introduce two more interfaces which tend to fail during storage and operation. Also the engineering polymers and the thermoplastics are not photoactive. Other methods of patterning can be used to make the ink chambers in the engineering polymers.

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Photoimageable polymer films are made of polymers, monomers, photoinitiators, and other additives. These films instantly adhere to the substrate and the top plate. Photoresolution of these films is excellent. Aspect ratios of 5 - 8 have been observed under laboratory conditions. It is possible to laminate and process a large substrate which reduces the processing costs significantly compared to laser drilling.

The versatility of this approach is attributed to the formulation latitude. The film can be designed to adhere under manufacturing conditions specifically to the substrate and the top plate of choice. Chemical resistance of the film can be designed to resist the specific ink.

Ink jet barrier films are pre-coated, defect free, high quality dry photopolymer films of controlled thickness sandwiched between a polyester base sheet and a polyolefin cover sheet⁹. The polyolefin cover sheet 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 to remove the unexposed part of the film. The top plate is attached and then film is thermally cured. Alternatively, it is possible to coat a photoimageable solution directly on the substrate using a photoresist spin coater. The film is dried in the oven to remove the solvent and then processed like the dry film.

Stability of Ink Jet Print Heads

The ink jet print head substrate is a silicon wafer or glass. These materials do not absorb ink ingredients and are stable during storage and operation. The top plate is made of glass, ceramics, plastics or metals. The plastics tend to absorb the ink ingredients and lead to bulk and interfacial failure. The preferred ink jet barrier layer is a photopolymer film. Depending on the ink and film composition the cured ink jet barrier film might absorb the ink ingredients leading to bulk and interfacial failure. The failure of the ink jet print head can be classified into two groups; bulk failure and the interfacial failure. Bulk failure is swelling and deformation of the barrier film or the top plate caused by the ink. Interfacial failure is caused by poor adhesion of the ink jet barrier film to the substrate and/or the top plate. Some interfaces have good adhesion in the beginning but tend to fail after ink soak test. This is attributed to the diffusion of ink ingredients into the bulk film and the interphase.

Stress Generated During Fabrication

During manufacturing of the ink jet print head is exposed to temperature and pressure treatments. These treatments result in stress in the three layer structure. When a photopolymer film is laminated on to copper or aluminum foils and cured at 300° F, the two layer structure tends to curl. The amount of curl is related to the mechanical and chemical properties of the film. When a non-aqueous developable permanent additive type photopolymer film was laminated and cured on an 6" × 6" Aluminum foil the stress was so severe the two layer structure curled in to a roll. For a photopolymer film the diameter of the roll was found to be proportional to the thickness of the aluminum foil. A photopolymer film that

was developed for ink jet printer head applications which has different mechanical and adhesion properties was laminated and cured under the same conditions. Rolling of the film or even curling of the film was not observed. The cured photopolymer film on aluminum foil stays flat. Apparently this film results in less stress. It was possible to relate the mechanical and adhesive properties of the film to the amount of curling. Also the cure temperature plays a major role in determining the stress at the interface. Higher cure temperature increases the Tg of the cured film. High Tg materials generally show good ink resistance; but high temperature cure results in more curling of the two layer material indicating the higher residual stress at the interface. It is possible to design the ink jet barrier film so that the residual stress at a specific interface is minimal.

Stress in the three layer structure is more severe than the two layer structure described above. Generally the substrate and the top plate are rigid materials and the warping/curling of the material is not seen. Unless all three layers are made of the same material residual stress is always present.

During storage and operation the print head is exposed to temperature and pressure shocks which result in additional stress. The three layers eventually fall apart and the pen becomes unusable. It is important to reduce stress during storage and operation.

Diffusion Coefficient of Water in the Barrier Film

A major component of ink jet ink is water. Even in the absence of other aggressive ingredients such as cosolvents and surfactants, water diffuse into the ink jet barrier film and the plastic top layer. Low diffusion constant and low weight gain are preferred. Increasing the cross link density of the barrier film decreases the water diffusion. Diffusion of water into a film can be determined gravimetrically by determining the weight gain as a function of time¹⁰. A known weight of a polymer film was immersed in solvent at 80°C¹¹. The film was removed after a set time, wiped clean of any water drops and then weighed again. The weight gain reaches an equilibrium limiting value in about two hours. The amount of water absorbed under equilibrium conditions is dependent on the chemical nature of the film. Water absorption by three families of polymer films is compared in the Table.

Polyester is inert to water under ambient conditions. However, it tends to swell in N-Methyl Pyrrolidone (NMP) solution. The amount of swelling increases exponentially with the amount of NMP present. In neat NMP these films swell readily and become soft. Extended periods of soaking dissolves the polyester film completely. Percent weight gain after three hours soak in water or aqueous NMP solution is same for 92 gauge Mylar and 200 gauge Mylar which shows the diffusion process is not surface area limited. Even the thick polyester films reach an equilibrium condition in three hours at 80°C. Filled polyester films show about 50% decrease in weight gain. Polyethylene is inert to water as well as NMP. Polypropylene is inert to water but tend to swell in NMP solutions. Dytex[®] is a Nylon[®] film and it swells in

water as well as NMP solutions. These results indicate that hydrophobic nature of the film is important to maintain a low diffusion constant and weight gain. Hydrophilic films such as Nylon® absorb water.

Table I. Swelling of Polyester and Polyimide Films in Solvents. Weight Gain After Three Hours Soak at 80°C

Film	Water	NMP		
	100%	10%	50%	100%
Mylar® 92D	0.77	1.07	1.78	soft
Mylar® 92A	0.94	1.09	3	soft
Mylar® 300A	0.67	1.41	1.33	soft
Mylar® 200D	0.37	2.12	2.89	soft
Polyethylene Clear	0.24	0.25	0.48	
Polyethylene 1 sided matte	0.6	0.01	0.29	
Polyethylene 2 sided matte	0.25	0.32	0.31	
Polypropylene Clear	0.12	0.36	1.21	
Polypropylene 1 sided matte	0.26	0.06	1.13	
Dytek®	4.4	18.7	32.56	soft
75R	2.13			0.07
200E	2.94			0.10
200H	2.88			23.69
200LJ	0.72			75.19
200KJ	0.05			53.76
200EKJ	0.05			17.38
160HKJ	0.81			30.01
200HLJ	3.85			23.07
200KN	4.05			22.69

Polyimide films are made by reacting dianhydrides and diamines. Polyimide films are oriented and the packing density depends on the structure of the polyimide. Aromatic dianhydride-aromatic diamine systems pack well and the diffusion of water is low. However, the diffusion coefficient and the equilibrium weight gain are highly dependent on the type of monomers used. Neat polyimides and polyimide coated on polyimides were used for the test. Some polyimides absorb water but are resistant to NMP. Some polyimides are resistant to water but absorb copious amount of NMP. Solvent absorption of polyimides is a function of monomer used and process conditions. By coating a hydrophobic barrier layer on a polyimide, diffusion of water can be decreased.

Water absorption by the film leads to two defects; dimension of the film changes, and the interfacial properties of the film also changes. Change in thickness of the film after swelling was determined to be small (<0.5 micron) when the solvent absorption is less than 10%. Films that absorb >10% solvent become soft and the thickness could not be determined accurately. Changes in interfacial properties leads to delamination of the barrier film and/or the substrate leading to failure of the pen.

Unlike the polymer films discussed above which are typically made of a single polymer, photopolymer films are made of several ingredients; polymers, monomers, photoinitiator system, colorants, coating aids, adhesion promoter, etc. Diffusion coefficient for water was deter-

mined to be 1E-10 cm²/sec. Aqueous developable photopolymer films have diffusion constants about an order of magnitude higher than non-aqueous developable photopolymer films. Weight gained by two non-aqueous developable (A & B) and one aqueous developable film (C) is compared in the following table.

Table II. Swelling of Photopolymer Films. Weight Gain After Three Hour Soak in Solvents

Film	10% NMP	Water
A	8.74	0.52
B	2.97	0.67
C	7.7	7.74

Aqueous developable film absorbs large amount of water as it was designed to disperse in aqueous alkaline solution. Among non-aqueous developable films, film A absorbs more in 10% NMP solution. The major chemical difference between these two films is monomer. Film B contains higher functional monomer which results in increased cross linking. In neat water, film A performs better than film B because the monomer used in film A is more hydrophobic than the monomer used in film B. Process conditions also play a major role in determining the stability of these films. For example, UV cure increases the cross-link density at the surface more than in the bulk film when compared to thermal bake. Bake time, temperature and the ramp time determine the kinetics of polymerization and affect cross link density. Process conditions should be selected to suit the material characteristics of the print head.

Effect of Ink on Bulk Film

Chemical resistance of the barrier film can be classified into two groups; bulk chemical resistance and interfacial chemical resistance. Since there are two interfaces, interfacial chemical resistance from both interfaces should be considered. Bulk chemical resistance of a polymer film can be easily determined. Soak the cured photopolymer film in the ink at operating temperature for several weeks and examine the film for any bulk defects such as bubbles, voids and softness in the film. The bulk film failure is a function of two factors; chemical nature of film and chemical nature of ink. Chemical nature of film and the ink can be individually characterized and the interactions between the ink ingredients and film ingredients can be predicted. Three films laminated on to a silicon substrate were cured at 300°C until the thermal polymerization reaction is complete and then soaked in ink vehicles. These ink vehicles were chosen for convenience. The ink vehicles are colorless and the barrier films are dark green in color. It is easier to see the bulk and surface defects. Dark colored inks tend to mask the defects. It is assumed here that the effect of colorants is negligible. This is true for pigment based inks. Pigments alone do not affect the film properties. Dyes in dye based inks can diffuse into the film and affect the end use properties. Percent increase in height of three different films is shown in the Table. All three of these films were blank exposed and cured at 300°C for 60 min.

Table III. Thickness Change(%) in Photopolymer Films After Ink Soak

Films	Ink X	Ink Y	Ink Z
A	2.95	3.89	1.1
B	0.86	3.52	2.02
C	delam.	delam.	delam.
Alcohols	yes	yes	yes
Pyrrolidone	---	yes	---
pH	>7	>7	<7

Aqueous developable film delaminates in both acidic and basic inks. The delamination is attributed to chemical interaction of the film with the acidic or basic inks. Non-aqueous developable films show an increase in film thickness after soaking in pyrrolidone based inks. Film A performs better in acidic inks and film B performs better in basic inks. Swelling of film B in 10% NMP is significantly less. However, in the presence of surfactants and stabilizers both films perform similarly. Film B is the best choice for ink X and film A is the best choice for ink Y.

Ink diffusion in some ink jet barrier films can be seen when dye based inks are used. The dye diffuses into the film during storage and operation and the gradient of color in the barrier film can be easily observed.

It is obvious that the ink properties affect the bulk and interfacial properties of the ink jet barrier film. No single film works best for all the commercially available inks. It is possible to change the film composition and/or the process conditions to improve the performance of the print head.

Some engineering polymers are chemically inert and stand up to aggressive inks at elevated temperatures. But these materials are difficult to process. Most of the engineering polymers are not available as films and do not stick to the substrate or top plate.

Instant Adhesion and Cross-Hatch Adhesion

Photopolymer films have low viscosity and stick to the substrate when laminated at elevated temperatures. Instant adhesion as shown in the Table is the force required to peel the film from the substrate.

Table IV. Instant and Cross-Hatch Adhesion of Photopolymer Films

Substrate	Film B Adhesion	X-Hatch	Film A Adhesion	X-Hatch
Glass	1000	poor	253	mod
Epoxy	930	excellent	>167	excellent
Copper	889	mod	>227	good
Gold	799	poor	300	poor
Silicon	1395	mod	>300	mod
Kapton®	681	excellent	135	excellent
Aluminum	753	poor	308	good
Polypropylene	8	---	37	---

Instant adhesion of photopolymer films relates to photoresolution. Narrow lines and channels can be resolved when the instant adhesion of the photopolymer film is high. Chemical composition of the film and the

process conditions also affect resolution. Good adhesion of the photopolymer film to the substrate is a pre-requisite to resolve narrow dams. Film B was designed to adhere to metals and some plastic. However, adhesion to polyethylene was poor. Instant adhesion of the film B to the substrate could not be determined for several substrates because the film starts to peel off from the polyester. Adhesion of the film to substrate is higher than the adhesion to polyester.

Cross-hatch adhesion is the adhesion of the cured photopolymer film to the substrate. Cured photopolymer film on the substrate is scribed several times with knife in the X and Y directions. These lines are about 1 mm apart. A pressure sensitive tape was rubbed on the cross-hatch area and peeled off with a steady force. The cross-hatch area was examined at 10X and the lifting of the film at the interface was recorded. Excellent cross-hatch adhesion refers to no lifting and poor refers to brittle film which delaminated completely. Some interfaces show high instant adhesion but poor cross-hatch adhesion. Generally brittle films show poor cross-hatch adhesion. Surface preparation and chemical composition of the film play a major role in determining the interfacial adhesion. Both instant adhesion and cross-hatch adhesion can be improved by corona treating the surface of the substrate before lamination.

Cross-hatch adhesion of the photopolymer film B is excellent after thermal bake. However, cross-hatch adhesion drops after soaking the material in ink vehicle at 80°C for 5 hours. Film B showed excellent cross-hatch adhesion even after soaking in the ink vehicle at 80° C for several days.

Cross-hatch adhesion is determined for the two layer interface. Ink jet printer pen head is a three layer material and there is stress generated in the material during fabrication. Excellent cross-hatch adhesion of the two layer interface does not reflect the integrity of the pen head made of the same materials. But poor cross-hatch adhesion is an indication that the pen will fall apart.

Improved adhesion of the film to the substrate and the top plate can be achieved in two ways; chemical adhesion and mechanical adhesion^{12,13}. Mechanical adhesion is achieved by roughening the surface of the substrate and the top plate. Low Tg materials can be chosen which flow and fill the roughened surface during high temperature lamination. Chemical adhesion can be achieved in several ways. Polymers and monomers can be chosen which selectively adhere to the substrate and the top plate. But, generally such systems increase the adhesion to the base sheet and cover sheet of the dry film which introduces handling problems during processing. Alternatively, a small amount of adhesion promoter can be added to the film formulation which diffuses to the interface during the process and chemically interacts with the surface. The adhesion promoters can be chosen based on the type of surface involved. The adhesion promoters can be added to the film composition or the adhesion promoter can be coated on the substrate before laminating the dry film. The advantage of the later process is the versatility. Adhesion promoters that are

not compatible with the bulk film composition can be chosen. Also different adhesion promoters can be coated on the substrate and the top plate.

Summary

Aggressive cosolvents and surfactants are used in inks to provide fast dry time and print quality. Ink components diffuse into the barrier film and the top plate leading to interfacial and bulk failure.

Photopolymer films (pre-coated dry films or spun-on films) are good ink jet barrier materials. Type of substrate, top plate, process conditions and chemical composition of the ink determine the type of photo-imageable ink jet barrier film required. No single barrier film works well with all the materials and process conditions. Interfacial and bulk properties of the photopolymer film can be modulated to meet the performance requirements of the pen.

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