# Phase-Change Inks

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*Phase-change, or hot melt, inks are solid at ambient temperature and liquid at the moment of printing. Such inks contain no volatile solvent to be trapped in ink film or to produce Volatile Organic Compounds (VOC). The phase-change inks found application in non-impact printing technology by either thermal transfer or "solid ink" digital printing. The environmental and health problems caused by inks containing volatile organic compounds, such as toluene, call for new solutions in the rotogravure printing industry. Because of their low VOC content, phase-change inks might be a reasonable solution for gravure printing.*

## PHASE-CHANGE INKS FOR INK-JET PRINTING

Ink jet is the fastest growing printing process with a rate of growth of over 20% per annum being reported.[1] Industrial application of ink jet is found in marking and coding packaging for the food, beverage, dairy, and pharmaceutical industries. It is used for printing postal bar codes for the handling of mail.[2] Edible grades of ink are applied in printing eggshells, citrus fruit skins, cookies, and confectionery. Ink jet is used to personalize mass mailings for advertising and promotions. A large and growing consumer market for ink jet was established in packaging, publication, and specialty areas. Actually, it is used anywhere that a small piece of information needs to be added—after conventional impact printing. Ink-jet printers have established their fastest growth in wide format digital color printing, outdoor graphics, banners, signs, and/or posters. Their use in small office and home office applications is well established.[2]

Two different principles of ink jet are used: drop on demand (DOD) and continuous ink jet (CIJ).[3] In continuous ink jet, a high voltage is applied to an electrically responsible crystal that is in contact with ink. A stream of uniformly sized and spaced droplets is generated with applied pressure pulses at a suitable frequency. Droplets are directed to a moving surface, and a line of dots is created. Droplets are charged with varying degrees of voltage as they leave the nozzle. They pass between oppositely charged plates, deflected to a degree proportional to the charge carried. Creation of droplets is a continuous process; some droplets are not destined to be printed—no voltage is applied to these droplets, and therefore these are not deflected. They are collected to be trapped, filtered, and returned to the ink reservoir—in line with the printing operation.[1-4] For some continuous ink jets, the unprinted drops are deflected, but the process is similar.

Drop on demand is a simpler system; no electrostatic charge is generated in the droplet and deflection and recovery are not necessary. An ink droplet is generated when it is needed for printing. DOD ink formulations are simpler than CIJ—the ink must be designed for the particular device used. DOD is capable of producing excellent print quality on suitable, usually absorbent, substrates. DOD is often used in proofing and office printing applications.[1-4]

The most important component of ink-jet printing technology is probably the ink. Ink chemistry and formulations not only dictate the quality of the printed image, but they also determine the drop ejection characteristics and the reliability of the printing system.[5] Ink-jet printing uses liquid inks with very low viscosity. Low viscosity is important for the transport of ink through the nozzle, for drop formation, and for drop integrity. Fluidity is achieved by the use of low molecular weight resins, very low solids content, utilization of dyes instead of pigments, and the use of viscosity modifiers. Ideal systems maintain a constant viscosity regardless of the shear rate. The best systems do not become more or less fluid upon leaving the reservoir. The viscosity, surface tension, and conductivity are the main characteristics for ink-jet inks. Conductivity,

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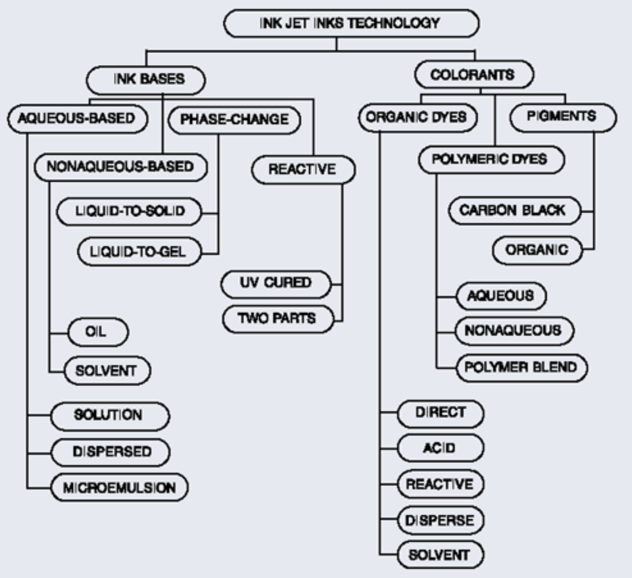

*Figure 1—Ink-jet ink map.*[5]

which is very important for continuous ink jet, is not an issue for DOD technology. Therefore, inks for CIJ are more demanding than the DOD inks. Many different types of inks have been developed and used in ink-jet applications (*Figure* 1).

Aqueous- or water-based inks are often used in home and small office ink-jet printers. Water-based ink-jet inks have a viscosity range from 2 to 8 cP.[4] Solvent-based inks are often used in industrial marking applications on non-porous substrates.[6] Pigmented ink-jet inks, both solvent and aqueous, are used for outdoor advertising, because they have better image permanence.[7] A specific group of nonaqueous inks are oil-based ink-jet inks. UV (ultraviolet) curable inks are highly resistant to solvents, and have excellent lightfastness.[7-9] They cure rapidly when exposed to radiant energy from the UV band of the spectrum. As heat is not required to crosslink the printed UV ink, color variations, which can occur with heat sensitive pigments, are minimized.

Phase-change inks are solid at room temperature.[2-4,6,10] The ink is melted into a reservoir where it is kept in a fluid state by a heating element. The hot, liquid ink is pumped through a nozzle using thermal drop on demand technology. The ink is jetted out from the printing head as a molten liquid at elevated temperature. Upon hitting a recording surface, the molten ink drop solidifies immediately, thus preventing the ink from spreading or penetrating the printed media. The quick solidification ensures that the image quality is good on a wide variety of recording media. The solidified ink drops are fused on top of the paper to increase ink adhesion and prevent light scattering owing to the lens effect of the hemisphere shaped ink dot (*Figure* 2). Colored waxes are brought into contact with the substrate and a thermal head. The thermal head is digitally addressed and the arrays of pixels must heat up and cool down at a frequency of 33-36 kHz to give acceptable printing speed.[10]

The fact that the ink dries by solidification prevents the ink from migrating into the pores of the substrate, which allows the ink to create better density in the solid areas with a thinner ink film. These inks also have the potential for higher gloss, due to the lack of migration into the substrate,[11] enhanced color saturation,[4,10] and reduced dot gain.[4]

## COMPONENTS OF PHASE-CHANGE INKS

The possible components of digital hot melt inks are found in *Table* 1. Chemically, hot melt inks are composed of resins of different chemical composition, waxes, colorants, and tackifiers, for improved adhesion to the substrate, and different additives such as viscosity modifiers, conductivity additives, antioxidants, creasing agents, biocides, and corrosion inhibitors (*Table* 1). We will briefly discuss the function of these components; the details are given in the references in *Table* 1.

The hot melt inks consist of a semicrystalline vehicle composed of resins, waxes, and optionally, low molecular weight components like higher fatty acids or higher alcohols. Stearic acid and/or lauric acid and their hydroxylated derivatives can be selected as higher fatty acids and stearyl alcohol and/or 12-hydroxystearic acids can be chosen as higher alcohols. These vehicles, when solidified, form large spherulitic structures. Control of the spherulite size during solidification is very critical for the image quality and durability. Large spherulites lead to hazy and brittle prints. The spherulite size should be in the same order as the wavelength of the visible light. Vehicles must give homogeneous dispersion of pigments or dyes, good flow properties, sharp melt/solidification properties, ink transparency, negligible sublimation of material, competitive cost, good edge definition and dot size, and abrasion resistant images on thermoplastic materials. Vehicles that could be commercially viable include solid waxed base carriers. Melt onset starts around 60°C and melting point maximum is at six to eight degrees more. A very sharp melting point can be achieved, which, if desired, can be manipulated within a small temperature range. Since they are totally solvent free, such vehicles have an advantage over existing conventional ink bases. Hot melt vehicles have good heat stability and do not sublime. The wax-like nature of the vehicle is especially suitable for dyes with a highly oleophilic character.

The resin compound of the vehicle may be urethane resin, urethane/urea resin, polyamide, acrylic, ethylene vinyl acetate resin, linear and branched polyester resin, polyethylene resin, or oxidized polyethylene resin, among many others. The resins ensure the adhesion of ink to the printed substrate. They also control the viscosity of ink at the time of melting, and impart transparency to the ink by inhibiting the crystallization of wax. If the resin content is less than 5% by weight, the melt viscosity will not be high enough to eject ink in ink-jet recording systems and neither the transparency of ink nor the adhesion to printing substrate can be ensured. If the content of the resin in the ink composition is more than 50% by weight, the ink composition may have an excessively high melt viscosity so that it becomes difficult to eject ink at the operating temperature of printer heads used in ink-jet recording. Consequently, the ink may soak poorly into the paper, may be rubbed off the substrate and good print quality cannot be maintained.[25] Structurally, the resins used can be homopolymers, or heteropolymers, linear or crosslinked, hybrid polymers, and/or reversibly crosslinked polymers.

It is possible to formulate a hot melt ink that has a good print quality, has superior transparency, adhesion and heat resistance, and can form sharp colors most suited for the hot melt ink-jet recording.[10] Polymers used in phase-change or hot melt inks generally have melting points in the range of about 60° to 140°C. The polymer should be thermally stable in a molten state, so that gaseous products are not generated or deposited on the printer device.[29] Two or more polymers can be combined to bring special properties from each one. To be able to combine otherwise noncompatible polymers, these are chemically reacted to form hybrid polymers[12,13] to achieve specific printer, substrate, or end-use requirements. This allows the unique property enhancing attributes of two incompatible polymers to be exploited in the same ink composition.[14] Hybrid polymers can be used as a sole polymer of the ink formulation or in a combination with other polymers, including other hybrid polymers. Reversibly crosslinked polymers are also used in phase-change ink formulations. They are prepared by chemically attaching a crosslinker to a polymer that possesses one or more types of functional groups capable of reacting reversibly with the crosslinker. A reversibly crosslinked polymer allows a significant amount of polymer to be used to bind the colorant to the substrate without degrading the quality of the printed image. It can be used as the sole polymer of the ink formulation or in combination with other polymers. The amount of crosslinking agent present in the ink compositions is between 0.2 to 10%, based on the weight of the polymer.[34]

Terpene resins are used in phase-change inks because of their good compatibility with many other vehicles. They prevent the waxes from crystallizing, and therefore impart transparency to the ink composition. The addition of the terpene resin does not damage the fundamental performance of an ink, such as sharpness of color and good print quality. If the terpene resin in the ink composition is less than 0.5% by weight in the composition, the ink composition tends to discolor in a heated molten state. If it is more than 15% by weight in the composition, the ink composition has poor transparency and a higher melt viscosity. Usually, the terpene resin in the ink composition ranges between 3 to 8% by weight.[25]

Polyamide resins are obtained by condensation polymerization of an amine and an organic acid. They provide good ink adhesion, control the viscosity of the ink composition, inhibit the crystallization of waxes, impart transparency to the ink composition, and promote steric hindrance of pigments. The polyamide resins for hot melt ink formulation usually have an average molecular weight from 600 to 400,000 and are present in the ink composition in an amount between 5 and 60%. If the amide resin in the composition is less than 5% by weight, the ink composition cannot ensure the sufficient melt viscosity required and the ink may have no transparency. If it is more than 60% by weight, the ink composition may have a high enough melt viscosity to make it difficult to perform good ink ejection at operation temperature of ink-jet printer heads used in ink-jet recording.[56]

The urethane resins and mixed urethane/urea resins are very pure, being free of salts and other insoluble contaminants, which makes the inks easy to filter and provides for high reliability in ink-jet printing devices. The urethane resins and mixed urethane/urea resins can be tailored to give certain physical properties that optimize the performance of the inks in ink-jet printing devices and on the output substrate. These desirable ink properties include melting point, viscosity, transparency, and dynamic mechanical properties. The urethane resins and mixed urethane/urea resins can be used in certain combinations with polyethylene waxes and monoamide ingredients to give ink compositions that display an improved yield stress versus temperature curve. This enables ink droplets to be spread and fused at elevated temperatures during the fusing and transfer steps in an indirect printing process. Urethane resins also reduce the coefficient of friction of hot melt inks.[17]

Waxes are another very important component of phase-change inks. They can be used alone or as a mixture of two or more waxes, and should be contained in the ink composition in an amount ranging from 5 to 95% by weight as the total weight of the wax component. If the wax component is less than 5% by weight, properties of other additives may dominate and hence the ink composition may have a higher or indeterminate melting point, which will tend to make the ink composition not melt sharply at ink-jetting temperature. If the wax is more than 95% by weight, the ink composition may have an insufficient melt viscosity, so that it may adhere to the printing substrate with difficulty.[26] Waxes are usually selected from the family of petroleum waxes, synthetic hydrocarbon waxes, higher fatty acids, higher alcohols, and their derivatives, modified waxes with a primary or secondary hydroxyl group, grafted with allyl alcohol or alkoxylated.[15] Natural plant and animal waxes can also be used.[15] Petroleum wax consists of paraffin wax and microcrystalline wax. The most important synthetic hydrocarbon waxes are a polyethylene wax and a Fisher-Tropsch wax. The main representatives of plant waxes are candelilla wax and carnauba wax. The most important animal waxes used in phase-change inks are beeswax and lanolin.

Bisamide modified wax brings an increase in clearness and adhesive properties of the ink composition. Thus, when images are actually printed using the hot melt ink composition containing the bisamide wax, sharp images with a good print quality can be achieved on usual print-

*Figure 2—Left: Phase-change ink drops on the surface of a bond paper. Right: Phase-change ink drops after being fused by cold pressure rollers.[5]*

ing paper and transparencies. The hot melt ink composition may not obtain sufficient clarity and adhesive properties if the bisamide wax is too small a fraction of the total wax content. On the other hand, the melting point of the hot melt ink composition may become difficult to control if too much bisamide wax is used. Bisamide wax is usually present in hot melt ink formulation in an amount of 10 to 50% by weight.[27]

Maleic anhydride modified wax, as the wax component, brings about improvement in the wettability of the ink composition and improvement in the print quality. Improvements in clarity of the hot melt ink composition

**Table 1—Components of Hot Melt Inks for Digital Printing Devices**

| Components | Function | Conc. % | Literature source |
|---|---|---|---|
| **Resin/polymer** | Imparts Adhesion | 5 – 60 | |
| Urethane resin, urethane/urea resin | | | 17 - 22 |
| Acrylic resin | | | 23, 24 |
| Polyamide resin | | | 21, 25, 26 - 29 |
| Polyethylene resin, oxidized polyethylene | | | 30, 31 |
| Terpene resin, terpene phenol resin, rosin resin | | | 25, 29, 32 |
| Polyester resin, branched polyester | | | 23, 33 |
| Ethylene vinyl acetate resin | | | 30 |
| Reversibly-crosslinked polymer | | | 34 |
| Epoxy resin | | | 23 |
| Isocyanate-derived resin | | | 17, 20, 21 |
| **Wax** | Ink vehicle | 5 – 60 | |
| Amide wax, diamide wax | | | 27, 29 |
| Petroleum wax, paraffin wax, polyethylene wax | | | 17, 18, 19, 29 - 31, 34 - 36 |
| Polyethylene oxide wax | | | 29 |
| Colored urethane wax | | | 21 |
| Fisher-Tropsch wax | | | 34 |
| Montan ester wax | | | 28 |
| Alcoholic wax, ketone wax | | | 26, 28, 29, 36, 37 |
| Maleic anhydride modified wax | | | 27 |
| Isocyanate-derived wax | | | 21 |
| Carnauba wax, candelilla wax, beeswax | | | 30, 34 |
| **Plasticizer** | Provides flexibility | 1 – 15 | 38 |
| **Viscosity modifier** | Lowers viscosity | 5 – 20 | 39-41 |
| **Antioxidant** | Prevents oxidation | 1 – 10 | 17, 29, 34, 38, 39, 41 - 45 |
| **Light-fastness antioxidant** | Protects ink | | 41, 46 - 51 |
| **Low-molecular compound** | Ink vehicle | 5 – 60 | |
| Liquid cyclic vehicle | | | 46 |
| Triblock copolymer vehicle | | | 55 |
| Water | | | 52 |
| Nonpolymeric ester compound | | | 42 |
| Thermoplastic vehicle | | | 53 |
| Ketone | | | 39 |
| Saturated fatty acid, unsaturated fatty acid | | | 32, 34 |
| **Alcohol compound** | Ink vehicle | 0.5 - 49 | |
| Cyclic alcohol | | | 21, 30, 38, 44, 47, 49 - 51 |
| Aromatic alcohol | | | 18, 24, 49 |
| Higher alcohol-tetracosyl, hexacosyl, octacosyl | | | 28, 34 |
| Monohydric aliphatic/aromatic alcohol | | | 17, 18, 24, 48, 49 |
| Amino alcohol | | | 49 |
| **Thiourea/Carbamate compounds** | Creasing agent | 1 – 98 | 38, 43, 44, 46, 47, 51, 54 |
| **Light-fastness UV absorber** | Protects ink from UV degradation | 1 – 10 | 39, 42, 48, 49 |
| **Light-fastness compound** | Electromagnetic radiation | 10 – 0.5 | 38, 40, 41, 43 - 47, 50, 51, 54 |
| **Conductivity enhancing agent** | Enhance conductivity | > 5 | 34, 39, 40 |
| **Biocide- Prevent ink from microbial growth** | | 0.01 – 5 | 24, 35, 52, 54 |
| **Pigment** | Adds color to ink | 0.1 – 20 | 23, 24, 28, 30, 34, 38, 41 - 48, 50, 51, 53, 54, 55 |
| **Dye** | Adds color to ink | 0.1 – 20 | 18, 20, 21, 25-36, 38, 42 - 45, 46, 48, 49, 52, 54 |

itself and in print quality may not be expected if too little maleic anhydride modified wax is used. At high concentrations of maleic anhydride modified wax, the hot melt ink composition may become fragile. Therefore, the maleic anhydride modified wax ranges from 5 to 60% by weight.[27]

**Table 2—Phase-Change Ink Composition for Drop On Demand Ink-Jet System[27]**

| Component | Function | Concentration (wt %) |
|---|---|---|
| Stearic acid amide wax | Ink vehicle | 48 |
| Methylenebisstearic acid amide wax | Ink vehicle | 15 |
| $\alpha$-Olefin maleic anhydride copolymer resin | Impart adhesion | 15 |
| Amide resin | Impart adhesion | 20 |
| Neopen Yellow 075 | Colorant | 2 |

Ketone modified wax also improves the transparency of the ink composition and the adhesion of ink to the recording medium. Ketone waxes have a melting point between 50° and 150°C. The ketone wax can be used in an amount between 20 and 50% by weight in the hot melt ink composition, where the proportion of the ketone wax held in the wax component can be large, and hence the ink composition has a lower melt viscosity than the case when other waxes are selected. If the ketone wax is less than 20% by weight, the action to lower the melt viscosity cannot be effective, and it will be difficult to impart the thermal resistance. If it is more than 50% by weight, the melt viscosity may be lowered too much. Low viscosity ink may have decreased adhesion to printing substrates. The ketone wax may bleed to the surface to make it impossible to maintain a good print quality.[26]

Isocyanate-derived waxes provide the clear vehicle for the colored inks. They are generally transparent solids having melting points between 20° and 150°C, viscosities in the range between 10 and 5000 cP at 150°C, and a glass transition temperature ($T_g$) between –30° and 100°C. Isocyanate-derived waxes are formed in the reaction of a fatty isocyanate with a suitable nucleophile, or in the reaction of a fatty nucleophile with a fatty isocyanate.[21] The uncolored isocyanate-derived waxes from these reactions are generally opaque waxy solids, having sharp melting points between 50° and 130°C, and viscosities between 1 and 25 cP at 140°C. The higher $T_g$ or the melting point of wax, the higher is its viscosity. They are used in certain combinations with other phase-change ink carrier materials to give ink compositions that display an improved yield stress versus temperature curve. This enables ink droplets to be spread and fused at elevated temperatures at a lower pressure during the fusing and transfer steps.[21] Isocyanate-derived waxes also exhibit excellent gloss properties.

Carnauba wax is a natural plant wax, widely used in phase-change ink formulations. It consists of aliphatic and aromatic esters of long-chain alcohols and acids, with smaller amounts of free fatty acids, alcohols, and resins. Carnauba wax contains mainly fatty esters (80-85%), free alcohols (10-15%), acids (3-6%), and hydrocarbons (1-3%). As a peculiarity, carnauba wax contains esterified fatty dialcohols (about 20%), hydroxylated fatty acids (about 6%), and cinnamic acid (about 10%). Carnauba wax is very hard and has one of the higher melting points (82-88°C) for the natural waxes of an acid number of 8, and a saponification number of 80. The hardness and high melting point, when combined with its ability to disperse pigments such as carbon black, increases the use of carnauba wax in thermal printing inks.

Coloring agents that are incorporated into the ink composition include pigments and dyes. Any dye or pigment or combination of one or more dyes or pigments may be used as long as the colorant can be dispersed in the phase-change ink composition and is compatible with the other components of the ink. Colorant may be selected from pigments, dyes, metals, and metal oxides. They must be thermally stable. Thus, there should not be deposition of dye or aggregation of pigment from the ink composition that can be caused by thermal changes when the printer is operated. Dyes or pigments, or a combination of one or more dyes or pigments, can be implemented as long as the colorant can be dispersed in the ink composition.[16]

No particular limitation is imposed on the type or the amount of pigment used. A large range of pigments, organic and inorganic, may be used either alone or in combination. Pigments used in ink-jet inks typically are in the dispersed state and are kept from agglomerating and settling out of the carrier medium by placing acidic or basic functional groups on the surface of the pigments, attaching a polymer onto the surface of the pigments, or adding a surfactant to the ink.[34] Pigments tend to be more lightfast than dyes,[57,58] which is an important factor in connection with the storage of printed images. Pigments also tend to be more heat-stable than dyes and this is especially important when the ink is applied at an elevated temperature of around 80° to 150°C. Pigments are less likely than dyes to bleed or sublime and they may be either opaque or transparent, whereas dyes are transparent and have little covering power. Dyes have usually been preferred for formulation of hot melt inks, particularly for ink-jet inks, since they are completely dissolved in the medium and cannot settle whereas pigments, being suspended and dispersed, may settle to the bottom of a reservoir or agglomerate to block ink-jet ink nozzles.[53] Dyes for formulation of phase-change inks can be water soluble or water insoluble such as basic, acid, and direct dyes.[34] The dyes can be reactive. These contain groups capable of forming covalent bonds with the substrate. The amount of dye present in the ink compositions is about 2 to 10 wt%. Fine particles of metal or metal oxides can be included as colorants for the hot melt ink compositions. Metal and metal oxides are normally used in the preparation of mag-

**Table 3—Phase-Change Ink Composition for Drop On Demand Ink-Jet System[29]**

| Component | Function | Concentration (wt %) |
|---|---|---|
| Amide resin | Impart adhesion | 12 |
| Terpene resin | Impart adhesion | 5 |
| Ketone wax | Vehicle | 50 |
| Monoamide wax | Vehicle | 30 |
| C.I. Solvent Yellow 162 | Colorant | 1.5 |
| Irganox 1010 | Antioxidant | 1.5 |

**Table 4—Phase-Change Ink Composition for Acoustic Ink-Jet Printing Process[59]**

| Component | Function | Concentration (wt %) |
|---|---|---|
| 4-(Hexadecylamino) benzylamine resin | Impart adhesion | 40 |
| p-Methoxyaniline | Viscosity modifier | 20 |
| 4,4′-Methylene-bis (2,6 dimethylaniline) and phosphinic acid (50:50 mixture) | Conductivity enhancing agent | 30 |
| Neozapon Black X51 | | |
| Tetrakis(2,4-di-tert-butyl phenyl)-4,4′- | Colorant | 5 |
| biphenyldiphosphonite | Antioxidant | 5 |

**Table 5—Phase-Change Ink Composition for Acoustic Ink-Jet Printing Process[50]**

| Component | Function | Concentration (wt %) |
|---|---|---|
| 1-Allyl-3-(2-hydroxyethyl)-2-thiourea | Ink Vehicle | 65 |
| 1-Eicosanol | Crease agent | 20 |
| 2-Dodecyl-N-(2,2,6,6-tetra methyl-4-piperidinyl) succinimide | UV absorber | 5 |
| Tetra sodium-N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate | Antioxidant | 5 |
| Sudan Blue 670 | Colorant | 5 |

netic ink-jet inks. The chemical nature of the metals and metal oxides might be silica, aluminum, titanium, and finely milled copper.[34]

Various chemical additives may be added to the ink composition. Nitrogen-modified acrylate polymers are used in phase-change inks as dispersion-stabilizing agents with many types of pigment and almost all ink vehicles. In order to be effective, a concentration of the nitrogen-modified acrylate polymer should range from 3 to 10% by weight.[53]

Plasticizers make ink softer, more flexible, and more adherent to the substrate. Plasticizers help to enhance gloss, improve adhesion to problematic surfaces, protect against becoming too brittle at too low temperatures, and prevent blocking and discoloration at higher temperatures. Plasticizers used in hot melt inks are phosphates, epoxy compounds, polyesters, sulfonamides, polyglycol derivatives, phthalates, and citrates. Plasticizers are used to control the spherulite size and printed image hardness.

Lightfastness is the ability of an image to retain color in a certain type of light. The primary degradation mechanism is oxidation. All printed images lose color, or density of color, when exposed to various sources of light. Lightfastness compounds stabilize the ink composition during the exposure to the electromagnetic radiation of UV and/or near visible light. Lightfastness of a printed image depends on the choice of the colorant in the ink and the immediate environment of the ink particles; a combination of these factors determines the resulting lightfastness of a print.[57,58] The size of the image forming ink dot and the medium have an influence on its lightfastness. The smaller the ink dot, the more surface area relative to its mass it has exposed, thus it can react more with other substances. Chemically, lightfastness additives can have structures such as 1,1–(1,2–ethane diyl) bis(3,3,5,5–tetramethyl piperazinone); or 6–ethoxy–1,2–dihydro–2,2,4–trimethyl quinoline, etc.[43,44]

UV absorbers primarily protect generated images from UV degradation. UV absorber is present in the ink ranging from 1% and below 10% by weight of the ink. UV absorbers include substances such as 2,4'–dibromoacetophenone, or 4'–morpholinoacetophenone.[42]

Phase-change ink compositions are in a molten state during printing. To prevent thermally induced oxidation from occurring in this state, antioxidants are added to the ink formulation. The amount of antioxidants used is usually 0.1 to 1.0% by weight of the ink composition.[25] They protect the images and the ink components from oxidation during heating.[42] They also prevent the ink from skinning over and react with free radicals formed during autooxidation. They are also incorporated into an ink in order to delay the initiation of oxidative polymerization drying. Antioxidant is present in the ink below 10% by weight of the ink.

Biocides are sometimes used to prevent microbiological growth in inks. The biocide protects hot melt inks from color and odor change, destabilization phenomena, pH, and viscosity change. The change of color and odor from fungi and algae, with adhesion loss and cracking, are avoided with the use of a biocide having strong fungicidal and algaecidal effects. To prevent the growth of microorganisms, a biocide may be added in the range of about 0.01 to 5%, based on the weight of the ink composition.[34] Biocides are used for the preservation of manufactured inks inhibiting microbial deterioration to ensure their shelf life. Suitable biocides include sorbic acid, vinylidene–bis–thiocyanate, bis(trichloromethyl)sulfone, and zinc pyridinethione, etc.[34]

One or more corrosion inhibitors may be added to inhibit the corrosion of the metal that comes in contact with the phase-change ink. Suitable corrosion inhibitors, present in the range of about 0.1 to 5% (based on the weight of the ink composition), include ammonium dithionyl naphthalene sulfonate, methyl-1-adamantane sulfonate, octadecyl–4–chlorobenzene sulfonate, and many others.[39]

Thiourea compounds, such as 1–allyl–2–thiourea; or 1–allyl–3–(2–hydroxyethyl)–2–thiourea can be used as crease agents, with a melting point ranging between 25° to 100°C and an acoustic-loss value between 5 to 40 dB/mm. Carbamate compounds also function as a crease agent, with a melting point of less than 100°C and an acoustic-loss value between 5 to 40 dB/mm.[51]

## FORMULATIONS OF PHASE-CHANGE INKS

*Tables* 2–5 illustrate example formulations for phase-change inks.[27,29,50,59] *Tables* 2 and 3 give relatively simple formulations of inks used for drop on demand system (or pressure pulse system), in which vibratory pressure of a piezoelectric device is utilized to eject ink. Black ink (*Table* 4) exhibited an acoustic loss value of 67 decibels per millimeter, a viscosity of 8.8 cp at 150°C, and a conductivity of 6.8 log(picomho/cm) at 150°C. Another example formulation of conductive ink, which has the power of transmitting electrical signals generated by electric field assisted acoustic ink-jet printing processes, is given in *Table* 5. It is assumed that all these formulations can be used for piezoelectric, as well as acoustic ink-jet printers.

## PHASE-CHANGE INKS FOR ROTOGRAVURE

In the history of rotogravure printing, water-based inks preceded solvent-based inks, but they were abandoned because of slow drying rates.[60-64] Since the beginning of the 1960s, toluene has been used as a solvent in most rotogravure publication printing plants. Toluene has been implicated as a cause of lung cancer,[65] genotoxicity,[66,67] and neurotoxicity.[68] For all of these health-hazard problems, water-based inks are coming into use again. The use of water-based inks for packaging and product gravure increased from 26% in 1993 to 50% in 1997.[64] There have been some technical problems related to the application of water-based inks to the high press speed, such as relatively slow drying rates, issues such as printability on a variety of substrates, and their cost/performance ratio. However, aqueous formulations also have serious environmental disadvantages, as they cause greater water pollution and consume more energy.[69] UV curable gravure inks are not a reality so far.[70]

Phase-change inks have not yet been accepted in the rotogravure industry. There are a number of reasons: phase-change inks do not have appropriate rheological properties and print quality, and they cost more than conventional gravure inks. Obviously, not enough effort has been made to formulate optimum performance hot melt inks for rotogravure. Research is currently being done in an attempt to create a new generation of phase-change inks, which do not have any sort of dangerous effluent or carcinogenic properties.[11, 71-74] The chemical composition of hot melt inks for rotogravure is similar to that of hot melt inks for digital printing. A requirement is that they have a viscosity of about 15 cP at printing temperature, which is the running viscosity at a rotogravure press. Hot melt inks have advantages over conventional inks because they do not contain volatile organic compounds.[11,73] Viscosity control is easy, carried out just by controlling the hot melt ink temperature.[4] Consistent print density can be achieved due to freedom from the viscosity fluctuations when solvent is introduced to adjust viscosity. Print has fewer missing dots due to absence of solvent evaporation between doctoring and ink transfer from the cells.[4] The use of hot melt ink will also represent a further benefit: the solvent handling element of gravure printing plant can be eliminated, which represents no explosion hazards, improved working environment, and eliminated transportation of hazardous solvents. It was calculated that an overall energy saving of about a factor of 15, compared with a solvent-based system, can be achieved.[4]

The rotogravure press design has to be slightly modified when using hot melt ink. The gravure cylinder (image carrier) and doctor blade as well as ink reservoir should be heated. There is no need for a drying system. Therefore, the paper web can be shortened, thus reducing white paper waste, the make-ready printed waste, and press running waste. It also saves money on the drying system operation and maintenance. Eventually, the chilling mechanism for the ink solidification process may be installed. Overall, these changes mean that the space requirement for the gravure press is substantially reduced.

## SUMMARY

Phase-change inks are well established in nonimpact printing, especially in drop on demand ink-jet printing. Many different resins, waxes, colorants, and additives are used for the formulation of phase-change inks. There is a need to more intensely research the possibilities of implementing this type of ink in the rotogravure, mainly because of the environmental concerns.

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