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HOT MELT INKS FOR ROTOGRAVURE - FORMULATION, PRINTABILITY
AND RHEOLOGY

by

Hrishikesh Shreeram Bhide

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Science
Department of Paper Engineering, Chemical Engineering, and Imaging

Western Michigan University
Kalamazoo, Michigan
December 2003

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Hrishikesh Shreeram Bhide

HOT MELT INKS FOR ROTOGRAVURE – FORMULATION, PRINTABILITY AND RHEOLOGY

Hrishikesh Shreeram Bhide, M.S.

Western Michigan University, 2003

A new generation of “Hot melt inks for Rotogravure” was formulated. They melt during heating and reach printable viscosity between 75°C and 130°C, depending on formulation. After printing onto substrate, they solidify. Selections of the best formulations were done based on ink rheology, and print analysis. The formulated inks were also printed on the Moser sheet-fed proofing press. The rheological data indicated that hot melt inks (without viscosity modifier) have viscosity in the range of 10^0 - 10^1 Poise at 95°C. After printed on a laboratory gravure K-Proofer, the inks showed good reflective density (0.90 - Yellow, 1.30 - Magenta, and 1.35 - Cyan) and rub resistance properties (95-98% - yellow; 70-85% - magenta, and 80-85% - cyan). The gloss properties (4.0-4.4 % - yellow, 3.1-3.3 % - magenta, and 2.6-3.5 % - cyan) were quite low.

Hot melt ink (with viscosity modifiers) had viscosity in the range of 10^{-2} - 10^{-1} Poise at 95°C. Inks showed promising reflective density (0.90 - yellow, 1.30 - magenta, and 1.35 - cyan), and rub resistance properties (96.5-98.5 % - Yellow; 93.5-95 % - magenta, and 93.5-95.5 % - cyan). The gloss values (5.5-6.2 % - yellow, 5-5.1 % - magenta, and 5.1-5.9 % - cyan) were higher compared to hot melt ink (without viscosity modifier). The viscosity modifier had a positive influence on rheological properties.

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CHAPTER I

INTRODUCTION

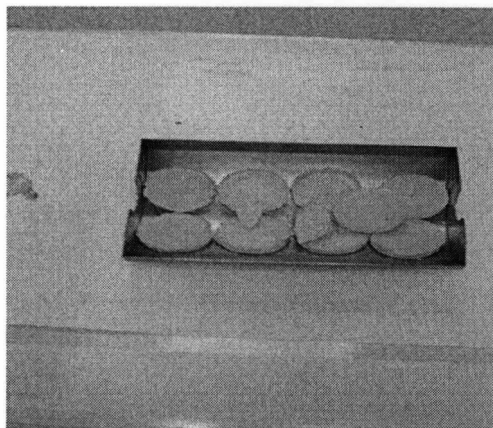


Figure 1: Hot Melt Inks for Rotogravure

A new generation of phase change, or hot melt ink were formulated. Such inks are solid at room temperature and liquid at the moment of printing. Inks were formulated based on (a) ethyl vinyl acetate chemistry and (b) polyurethane chemistry. Inks were printed using a K-Proofer for screening printability studies. Selection of the best formulations was done based on (a) ink rheology, (b) reflective density, (c) specular gloss, and (d) rub resistance. Screened inks having the best properties were printed on the Moser sheet-fed proofing press. The rheology of the best formulations were studied and compared to conventional rotogravure inks. Based on rheological measurements, additional changes on ink formulations were done. Earlier the work was done on the “Hot Melt Ink for Rotogravure”, but the rheology of the ink was the problem. Therefore, the work were carried out in order to lower the viscosity of the hot melt ink to bring it to the desired viscosity by selecting environmental friendly

polymers and pigments. Thus, the rheology of the ink was adjusted by (a) manipulating the melt temperature, (b) polymer type, and by (c) controlling the amount of additives.

CHAPTER II

COMPONENTS OF HOT MELT INKS

Chemically, hot melt inks and ink jet inks are composed of (a) thermoplastic polymers, (b) waxes, (c) colorants, (d) tackifiers, for improved adhesion to the substrate, and different additives such as (a) viscosity modifiers, (b) conductivity additives, (c) antioxidants, (d) creasing agents, (e) biocides, and (f) corrosion inhibitors (Table 1). They have same properties, such as (a) solid at room temperatures and (b) liquid during printing. Their components perform the same functions that are given in Table 1.

Table 1: Components of Hot Melt Inks Used in Digital Printing

Components	Function	Conc.%	Literature source
Resin/Polymers	Imparts	5 – 60	
Urethane , Urethane/Urea resin	Adhesion		[4], [5], [6], [9], [10], 31
Acrylic resin			[32], [33]
Polyamide resin			[9], [33], 34], [35], [36], [38]
Polyethylene, Oxidized polyethylene			[1], [39]
Terpene, Terpene phenol resin,			[8], [34], [38]
Polyester, Branched polyester			[32], [40]
Ethylene Vinyl Acetate resin			[39]
Epoxy resin			[32]
Isocyanate-derived resin			[6], [9], [31]
Wax	Ink vehicle	5 – 60	
Amide wax, Diamide wax			[36], [38]
Petroleum wax, Paraffin wax,			[1], [4], [31], [38], [39], [41]
Polyethylene wax			[42],
Polyethylene oxide wax			[38],

Table 1 - Continued

Colored urethane wax			[9],
Fisher-Tropsch wax			[41],
Montan ester wax			[37]
Alcoholic wax, Ketone wax			[35], [37], [38], [42], [43]
Isocyanate-derived wax			[9],
Carnauba, Candela, Bees Wax			[39], [41]
Viscosity modifier	Lowers viscosity	5 – 20	[7], [19], [44], [45]
Antioxidant	Prevents oxidation	1 – 10	[31], [38], [41], [46], [44], [45], [47], [48], [49], [50]
Lightfastness antioxidant	Protects ink from thermal degradation	1 - 5	[15], [16], [17], [45], [51], [52], [53]
Low-molecular compound	Ink vehicle	5 – 60	
Liquid cyclic vehicle			[17],
Triblock copolymer vehicle			[54],
Water			[55],
Non polymeric ester compound			[41],
Thermoplastic vehicle			[56],
Ketone			[44],
Saturated fatty acid, Unsaturated fatty acid			[8], 41]
Alcohol compound	Ink vehicle	0.5 - 49	
Cyclic alcohol			[9], [15], [39], [46], [49], [52]
Aromatic alcohol			[16], [53]
Higher alcohol-Tetracosyl, Hexacosyl,			[4], [15], [33]
Octacosyl			[37], [41]
Monohydric aliphatic/aromatic alcohol			[4], [15], [31], [33]
Amino alcohol			[15],
Thiourea /	Creasing agent	1 – 98	[46], [48], [49], [51], [52],
Carbamate compounds			[53], [57]
Lightfastness UV absorber	Protects ink from	1 – 10	[15], [17], [28], [41]

Table 1 - Continued

	UV degradation		
Lightfastness compound	Electromagnetic radiation	10 – 0.5	[7], [16], [45], [46], [48], [49], [50], [51], [52], [53]
Conductivity Enhancing agent	Corrosion inhibitors	> 5	[41], [44]
Biocide	Prevent ink from microbial growth	0.01 – 5	[3], [41], [55], [57]
Pigments	Adds color to ink	0.1 – 20	[16], [17], [32], [33], [37], [39], [41], [45], [46], [48], [49], [50], [51], [52], [53], [56], [57]
Dyes	Adds color to ink	0.1 – 20	[1], [6], [8], [9], [15], [17], [31], [34], [35], [36], [37], [38], [39], [41], [42], [46], [48], [50], [51], [55], [57], [58]
Metals and metal oxides	Adds color	0.1-20	[41], [50]

The resin compound of a hot melt ink may be (a) urethane resin, (b) urethane/urea resin, (c) polyamide, acrylic, (d) ethylene vinyl acetate resin, (e) linear or branched polyester resin, (f) polyethylene resin, (g) oxidized polyethylene resin, or 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 of the ink by inhibiting the crystallization of wax. Structurally, the resins used can be (a) homopolymers, (b) heteropolymers, (c) linear, (d) crosslinked, (e) hybrid polymers, or (f) reversibly crosslinked polymers. If the resin content is less than 5% by weight, the melt viscosity will not be high enough to eject ink in an 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, which becomes difficult to eject ink at the operating temperature of printer heads used in ink-jet recording. Consequently, the ink may soak poorly into paper, may be rubbed off the substrate and good print quality cannot be maintained [1]. Normally resin percentage should be in the range of 30-40% for hot melt inks for rotogravure.

Hot-melt ink should have a (a) good print quality, (b) superior transparency, (c) adhesion and (d) heat resistance, and can form sharp colors most suited for the hot-melt ink-jet recording [2]. Polymers used in phase change or hot melt inks generally have melting points in the range of about 60°C 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 [3]. Two or more polymers can be combined to bring special properties of each one. To be able to combine otherwise non-compatible polymers, these are chemically reacted to form hybrid polymers [4][5] 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 [6]. Hybrid polymers can be used as a sole polymer of the ink formulation or in a combination with other polymers, including other hybrid polymers. Reversible 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 of types of functional groups capable of reacting reversibly with the crosslinker. Reversible crosslinked polymers allow 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 and 10% based on the weight of the polymer [7].

Waxes are another very important component of phase change inks. They can be used alone or in the form of 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 insufficient melt viscosity, so that it may not adhere well to the printing substrate [8]. Waxes are usually selected from the family of petroleum waxes, synthetic hydrocarbon waxes, higher fatty acids, higher alcohols, and their derivatives, modified waxes with primary or secondary hydroxyl group, grafted with alcohol. Natural plant and animal waxes can be also used [9]. The most important synthetic hydrocarbon waxes are polyethylene waxes. The main representatives of plant waxes are (a) candella wax and (b) carnauba wax. The most important animal waxes used in phase change inks are (a) beeswax and (b) lanolin.

Coloring agents that are incorporated into the ink composition include (a) pigments and (b) dyes. Any dye, 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. The colorant

may be selected from (a) pigments, (b) dyes, (c) metals, and (d) 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 combination of one or more dyes or pigments, can be implemented as long as the colorant can be dispersed in the ink composition [10].

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 [7]. Pigments tend to be more lightfast than dyes [11][12], 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°C to 150°C. Pigments are less likely than dyes to bleed or sublime and they may be either (a) opaque or (b) 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 [14]. Dyes for formulation of phase change inks can be water soluble or water-insoluble such as (a) basic, (b) acid, and (c) direct dyes. The dyes can be reactive. 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 magnetic ink jet inks. The chemical nature of the metals and metal oxides might be (a) silica, (b) aluminum, (c) titanium, and (d) finely milled copper [7].

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 [14].

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 [11] [12]. The size of ink dot has an influence on its lightfastness. Chemically, lightfastness additives can have structures such as (a) 1,1-(1,2-ethane) bis(3,3,5,5-tetramethyl piperazinone); or (b) 6-ethoxy-1,2-dihydro-2,2,4-trimethyl quinoline and many others [15] [16].

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 (a) 2,4'-dibromoacetophenone, or

(b) 4'-morpholinoacetophenone [17].

Hot melt 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 [1]. They protect the images and the ink components from oxidation during heating [17]. They also prevent the ink from skinning over and react with free radicals formed during auto-oxidation. They are also incorporated into ink in order to delay the initiation of oxidative polymerization drying. Antioxidant is present in the ink below 10 percent by weight of the ink.

Biocides are sometimes used to prevent microbiological growth in inks. The biocide protects hot melt inks from (a) color and odor change, (b) destabilization phenomena, (c) pH and (d) viscosity change. The change of color and odor from fungi and algae, with adhesion loss and cracking are avoided with the use of biocide having strong fungicidal and algacidal 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. Biocides are used for the preservation of manufactured inks inhibiting microbial deterioration to ensure their shelf life. Suitable biocides include (a) sorbic acid, (b) vinylidene- bis-thiocyanate, (c) bis(trichloromethyl)sulfone, (d) zinc pyridinethione, etc [7].

One or more corrosion inhibitors may be added to inhibit the corrosion of the metal that is exposed to 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 (a) ammonium dithionyl naphthalene sulfonate, (b) methyl-1-adamantane sulfonate, (c) octadecyl-4-chlorobenzene sulfonate, and many others [18].

Thiourea compounds, such as (a) 1-allyl-2-thiourea; or (b) 1-allyl-3-(2-hydroxyethyl)-2-thiourea can be used as crease agents, with a melting point ranging between 25°C to 100°C and an acoustic-loss values between 5 to 40 dB/mm. Carbamate compounds also functions as a crease agent, with a melting point of less than 100°C and an acoustic-loss value between 5 and 40 dB/mm [19].

Digital Hot Melt Inks

Table 2: Digital Hot Melt Ink Composition [20]

Component	Function	Concentration, %
Solid wax mixture	Ink vehicle	40 to 70
Viscosity modifier	Lowers viscosity	5 to 20
Tackifier	Imparts adhesion	1 to 15
Plasticizer	Provides flexibility	1 to 15
Dye or pigment	Provides color	1 to 10
Antioxidant	Heat stability	0.05 to 2

Phase-change ink is solid at room temperature. The ink is jetted out from the print head as a molten liquid. 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 image quality is good on a wide variety of recording media. The solidified ink drops are fused on top of paper to

increase ink adhesion and prevent light scattering owing to the lens effect of the hemisphere shaped ink dot.

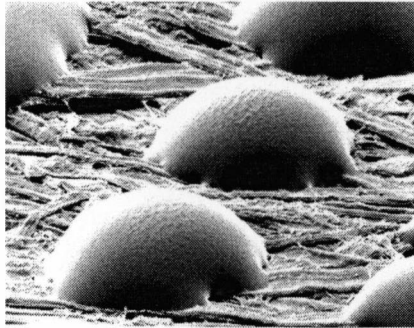


Figure 2: Hot Melt Ink Drops on the Surface of a Bond Paper [20]

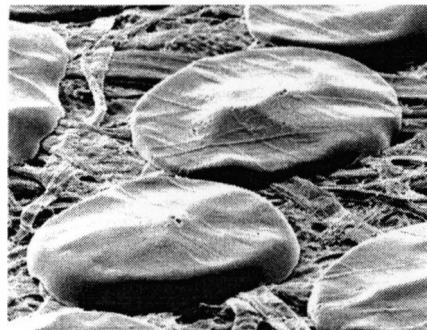


Figure 3: Hot Melt Ink Drops After Fuse by Cold Pressure Rollers [20]



Figure 4: Fused Hot Melt Ink Drop on a Paper After Offset Drum Transfer Process [20]

Rotogravure Printing Process

Gravure printing is capable of producing high quality images on a wide range of substrates. This is made possible because the gravure cylinder can be manufactured in such a way that the ink film thickness can vary from cell to cell. This is an advantage because in other types of printing the ink thickness stays the same and cannot be changed on press. This is also a downfall for rotogravure printing. The process of engraving a cylinder is quite expensive and time consuming. The image carrier is an engraved cylinder that carries the image in recessed cells. The cylinder is engraved in one of three ways. Chemical etching allows the operator to control the width and depth of each cell independently. Electromechanical engraving uses a diamond stylus to literally dig out the cells on the cylinder. This does not allow the operator to control the width and depth of the cell independently. This process is more repeatable than chemical etching. Laser engraving uses a laser to engrave the image directly to the cylinder surface [11]. This process saves time and this translates into cost reduction. The gravure press is mechanically simple. A typical rotogravure press has a very simple inking system. The engraved cylinder spins in a bath of ink. Pumps are used to maintain the correct level of ink in the ink pan where the cylinder is located. A doctor blade wipes the ink from the non-image area of the cylinder. This leaves the ink in the engraved cells for printing. The printing nip utilizes high pressures between the plate cylinder and the impression roller to create contact between the ink and paper. The use of electrostatic assist (ESA) allows for ink transfer that is more consistent. ESA is a process where an electrical field is applied to the gravure cylinder and impression roller, which then excites the ink in the cell. The

electrical excitement of the ink in the cell causes the ink to form a meniscus that rises slightly above the level of the cylinder engraving. This excitement helps the ink to transfer in an almost perfect fashion. These advances have all helped gravure achieve print quality that exceeds all other processes in terms of image clarity and color strength [21].

Rotogravure Inks

Rotogravure inks are split into three market segments. Publication gravure printing includes products like high volume, high quality magazines (National Geographic). Packaging gravure prints products like (a) cereal boxes, (b) cigarette packaging and other products that require high quality and long runs. Product gravure includes printing of various materials such as (a) wallpapers and (b) vinyl floorings. The short ink train requires the ink to be liquid and must be capable of drying quickly after transfer to the substrate. There are two different types of gravure ink. There is (a) solvent-based ink and (b) water-based ink. Solvent inks are made using organic liquids such as (a) toluene, (b) xylene, (c) hexane, and other (d) organic solvents, which have the potential of causing cancer. Water-based inks are made using chemistries that combine water and either glycols or alcohols [11]. However, these inks need to have a higher pigment concentration, due to the slower wetting of the surface. The packaging gravure market utilizes almost 50% water based inks [22].

CHAPTER III

ROTOGRAVURE INK COMPONENTS

Ink components not only dictate the quality of the printed image, but they also determine the viscosity and ink transfer characteristics and thus the reliability of the printing system.

Pigments

The pigments used in gravure inks can be classified in one of two ways. Organic pigments are those that can be derived from carbon-based materials. Inorganic pigments are those that contain no organic carbon atoms. There are also metallic pigments, which are finely ground powders made from (a) copper, (b) zinc, (c) bronze, and (d) aluminum. Dyes can also be used in gravure inks, but most are highly transparent and do not have good lightfastness, which limits their use. Once the ink is finished and ready for the press, it needs to be constantly agitated in order to prevent the pigment from settling out of its fine dispersion. Lack of agitation is one source of sedimentation. Rapid addition of solvent in order to adjust viscosity is also another potential cause of sedimentation [11].

The most widely used cyan pigment for process printing ink is phthalocyanine blue. This pigment is resistant to chemicals and solvents. It also has excellent lightfastness. This pigment is well suited to gravure ink because it does not bleed in the presence of harsh solvents [23]. The chemical structure of this pigment is shown in Figure 5.

Most yellow pigments are -azo pigments, and the most widely used yellows are diarylide yellow. These pigments display excellent transparency and excellent color strength. These pigments are easily ground, which allows for fine dispersion and small particle size. The small particle size imparts good flow properties to this pigment and improves print gloss [24]. The chemical structure for a typical process color yellow pigment is shown in Figure 6.

The most widely used magenta pigments for process work are Lithol Rubine. These pigments are classified by their $-N=N-$ bond. This pigment is well suited to rotogravure ink. The chemical structure for a Lithol Rubine magenta pigment is shown in Figure 7.

Another magenta that could potentially be used for formulation of hot melt ink is a quinacridone magenta pigment. Quinacridone is a quite expensive pigment, but is suitable for hot melt inks, because of its thermal stability. The chemical structure is shown in Figure 8.

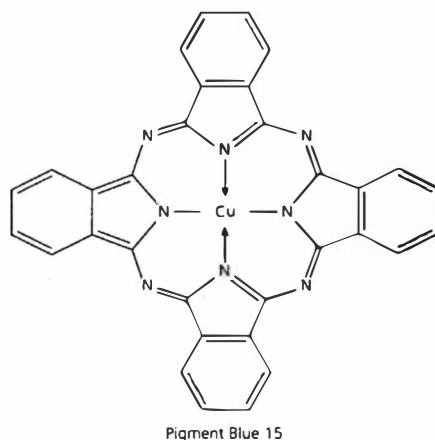


Figure 5: Phthalocyanine Blue Pigment 15

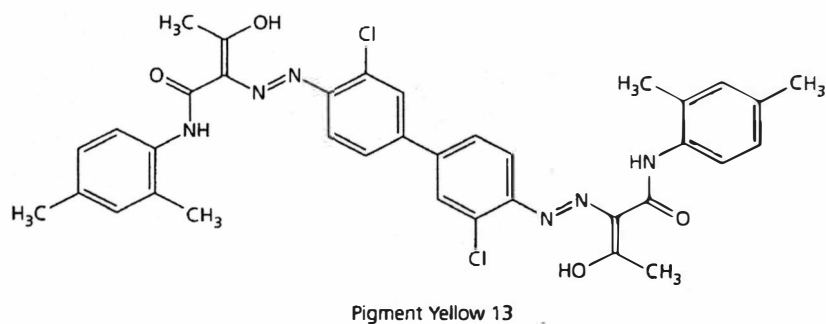


Figure 6: Pigment Yellow 13

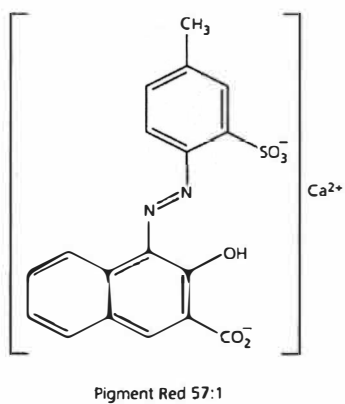


Figure 7: Pigment Red 57

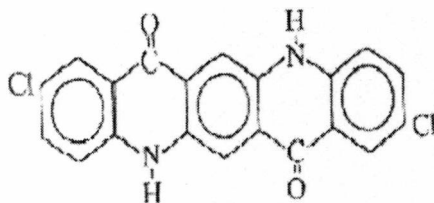


Figure 8: Quinacridone Magenta Pigment

Resins

Traditional rotogravure inks also contain resins, and polymers or vehicles. Resin acts as the binder, which holds the pigment on the substrate. Resins can be classified as (a) film formers, or (b) non-film formers. Film forming resins can be plasticized in order to form a flexible film on the substrate. These types of resins are essentially the adhesive component in the ink. Film forming resins act as the binding agent and they give the ink film chemical resistance and durability. Film forming resins that have the ability to form films without plasticizing additives are named internally plasticized. Polyamide and vinyl resins both display this property. Nitrocellulose and acrylic resins are very brittle and will not plasticize unless additives are used to make the resin more flexible [11]. These types of resins display excellent scratch and rub resistance. They are highly heat resistant and can withstand the temperature associated with heat-sealing. Nitrocellulose is compatible with (a) rosin derivatives, (b) alkyd resins, and (c) shellacs [22]. Non-film formers cannot form the flexible film required for gravure printing, even with the addition of plasticizers. These resins are used in gravure ink to increase gloss. They are also used to improve adhesion to stocks that require better adhesion properties. Maleic resin is the predominant type of non-film forming resin. Non-film forming resins lower the heat resistance of ink and can lower the curing temperature of ink [11]. Rosin is a naturally occurring substance that is obtained from pine trees. Wood rosin is obtained by crushing tree stumps and extracting the rosin and rosin oil with petroleum solvent. Gum rosin is extracted by tapping live trees and forcing the rosin out of the tree. Gum rosin has a higher melting point than wood rosin. Rosin is used in virtually all inks. It

is the most widely used resin in publication gravure inks; this is due the fact that rosin is inexpensive, but still yields excellent adhesion.

Synthetic polymers also make up a large group of resins that can be used in rotogravure inks. Acrylic polymers have excellent clarity and chemical inertness. They also have excellent lightfastness properties as well. Acrylic resins are versatile enough to co-polymerize with several other types of synthetic polymers. Acrylics can cross-link and form copolymers with epoxies, amines, urea and melamine resins to achieve different molecular weights and softening points [22]. The proper choice of resin system is based on the purpose of use, the cost, and the solvent system used.

Ethyl Vinyl Acetate Copolymer Chemistry

Mixing PE polymers along with vinyl acetate to form the copolymer produces ethyl Vinyl Acetate (EVA). This copolymer can yield excellent adhesion properties. It is currently used in hot melt adhesives in the folding carton industry. These polymers have excellent flexibility and adhesion and yield good clarity and gloss. These copolymers can operate over a wide range of temperatures. They also have excellent (a) impact resistance, (b) elasticity, and (c) environmental stress cracking. These polymers can have melting points in the range 66 – 140°C and higher, depending on the amount of vinyl acetate present. The density of this copolymer is typically below one g/cm³, ranging from 0.936 to 0.953 g/cm³.

Polyurethane Chemistry

Polyurethane may be suitable for formulation of hot melt inks. Polyurethanes occur as several different types of materials. They can exist as homo- or copolymers, and the copolymer category can be split up into (a) random, (b) alternating, (c) segmented, (d) block or (e) graft types. The polymer chains themselves can be (a) branched, (b) linear, or (c) networked as well, which allows for many different possibilities when choosing polyurethane. The molecular weight of polyurethane can have a drastic effect on the rheological properties of the polymer system. (Figure 9) shows that the molecular weight does not affect the hardness value of the polyurethane. The molecular design of the polyurethane determines the structure of the system [12].

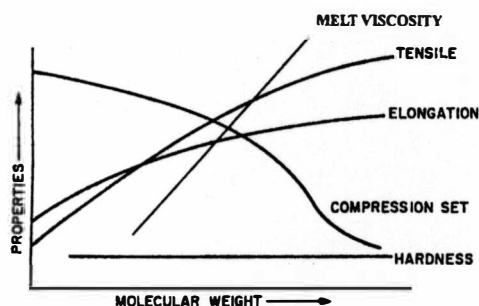


Figure 9: Properties of Polyurethane Polymer Matrices

This makes polyurethanes good choices for printing applications, because they do not need so many additives in order to plasticize the film. Polyurethanes do have the potential to degrade when exposed to heat for long periods. A higher molecular weight raises the critical temperature at which the polymer system breaks down, thereby allowing the polymer to be more heat stable. Linear polymer chains are also more temperature and moisture dependent [12].

Solvents

Solvents are liquids, which are capable of dissolving other materials without significantly changing any physical properties. Solvents do not undergo any chemical state changes, which allows them to dissolve the ink resin and then after transfer to the substrate they can evaporate from the ink in order to form the ink film [11]. Solvents are classified into one of three categories. Active solvents dissolve resin by themselves. Latent solvents require the addition of an active solvent in order to dissolve resin particles. Diluents are non-solubilizers of resin. These solvents cannot be used to dissolve resin, but instead are used as viscosity modifiers. Most of the solvents used cause air pollution if they are released into the environment. Solvent recovery systems are used in order to prevent the solvent from escaping into the environment. Water-based inks provide an alternative to organic solvents.

Additives

Waxes are an example of an additive that is used to give the ink film some scuff resistance. Paraffin wax is one example of a wax that could be used in ink. Wax is also classified by oil content into three grades; (a) fully refined, (b) semi-refined and (c) scale. These waxes consist of straight chain, *n*-alkanes with carbon backbones of length $C_{18} - C_{50}$ [15]. Paraffin wax is obtained as a by-product of petroleum refining. Microcrystalline waxes are also obtained from petroleum distillation, but are softer than paraffin waxes and have higher melting points. These waxes are composed of (a) normal, (b) branched, and (c) cyclic alkanes with carbon backbones, which range in length from $C_{23} - C_{85}$.

Modifiers are used in addition to waxes to impart specific characteristics to the final ink film. The use of modifiers with paraffin wax increases the ink film's (a) durability, (b) adhesion, (c) scuff-resistance, (d) plasticity, and (e) water resistance. Modifiers also help to increase the resistance of the ink film to extreme temperature changes. Modifiers can be made up of synthetic polymers such as a graft polymer of polyethylene and maleic anhydride with low functionality [12].

CHAPTER IV

PROBLEM STATEMENT

Gravure inks are made by (a) blending pigments, (b) solvents, (c) resins (or binders), and other (d) additives. Vehicles transfer the pigment mixture to a surface in a thin uniform film. When ink is deposited on a substrate, the vehicle solvent should evaporate completely [26]. Gravure ink frequently uses materials containing (a) VOC (Volatile Organic Compound) and some may contain (b) HAP (Hazardous Air Pollutant). Small printing facilities may not have an environmental impact by themselves. However, when combined with other sources of pollution, they can affect overall environmental quality. Toluene is one of the frequently used vehicle solvents by ink manufacturers, which is a VOC, which causes, (a) smog, (b) air toxins, (c) ozone formation and (d) global warming [27] [28]. VOC's can be highly flammable, can result in toxic and narcotic effects when inhaled and can contribute to the formation of tropospheric ozone and smog thus resulting in differences in weather patterns [29]. Due to ozone exposure, there are increased hospital admissions and emergency rooms for respiratory problems. It can also lead to (a) respiratory infection, (b) irreversible changes in lung structure and (c) lung inflammation and can (d) aggravate preexisting respiratory diseases, such as asthma. Current technology is able to trap and recover up to 93% of the solvent being used, but the rest is being emitted into our environment.

A better way to reduce pollution is to prevent it in the first place. Pollution prevention includes using raw materials more efficiently, replacing toxic materials

with non-toxic ones [27]. Using hot melt inks could possibly be the solution. These inks do not need a drying system. Therefore, the paper web can be shortened, thus saving (a) white paper waste and (b) reducing the make-ready printed waste and (c) press running waste. It also saves money on the drying system operation and maintenance. The use of HMI will eliminate the creation of VOC. The aim of this work is to formulate (a) hot melt inks for rotogravure, (b) optimize their properties, and (c) test their printability properties on different substrates.

CHAPTER V

EXPERIMENTAL

Materials Used in Hot Melt Inks

Pigment chips

- (a) AAMX Yellow (Yellow)
- (b) Polyethylene Red (Magenta)
- (c) Phthalo Blue – Green shade (Cyan)

These pigment chips are pre-dispersed pigment preparation in resin system of EVA. The pigment powders are pre-dispersed by drum tumbling or mixing in twin shell ribbon or high-speed blenders. Dispersion aids help reduce viscosity to improve mixing [30].

Polymers

EVAC copolymer 2528 – Melting Point 85°C - Its an ethylene vinyl acetate copolymer (EVAC) with high co-monomer content, designed for high speed coating, It offers high clarity, low sealing temperature, and good adhesion to papers. It is also stabilized with antioxidant.

Escorez 1580 (Petroleum Hydrocarbon Resin) – Melting Point 77°C - It is a unique low softening point, aliphatic resin with a narrow molecular weight distribution. It is designed to tackify a variety of polymers. It also contains oxidation inhibitor, which provides protection of the polymer during the storage.

Wax

Carnauba Wax (Plant Wax) - Carnauba Wax is obtained from the leaves of a palm tree known, as Copernicia Cerifera. It is compatible with most animal, vegetable and mineral waxes and a large variety of natural and synthetic resins. It also increases water repellency and adhesive properties of the ink.

Low Molecular Compounds

Ocatdecanol 59°C

Hexadecanol 59°C

They are used as an alcohol compound, which lowers the viscosity of the inks and helps in solidification of the ink as it has the property of shear thickening with increasing stress and temperature.

Viscosity Modifiers

Hydrocarbon esters have been used as the viscosity modifiers in the formulation of the gravure inks. They helps in decreasing the viscosity of the inks also increases runnability and flow to the ink.

Hot Melt Ink Formulations

Hot melt inks for Rotogravure has the property to remain solid at ambient temperature and melt during heating and reach printable viscosity between 75°C and 130°C, depending on their formulation. After printing onto substrate, they solidify.

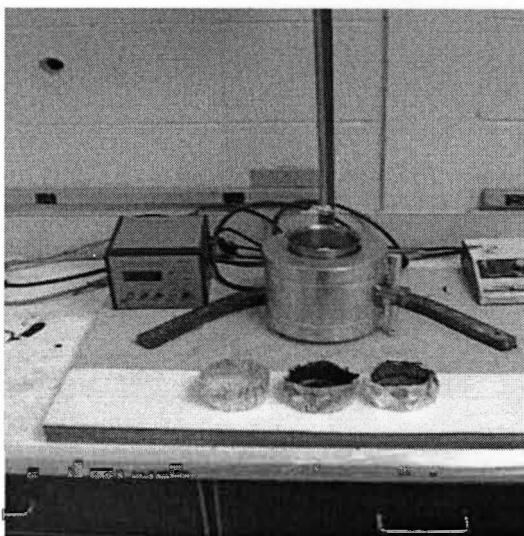


Figure 10: Blending of HMI

Two types of inks were formulated (a) Formulation A, (b) Formulation B. Hot melt ink blending was carried out using a “Lignin High Speed Mixer” fitted with a W50 chamber and cam blades. Mixing time was 20-25 min; mixing torque was reported after the first minute of mixing after stabilization of the torque response. The mixing temperature was varied from 75-105°C. All composite samples were compression molded into plates of 3 mm thickness for further blending and testing.

Formulation A

In this formulation, 24 parts by weight of the above-described polymer and 10 parts by weight of pigment was melted in the 2 parts by weight of Carnauba Wax and 64 parts by weight of Octadecanol in “Lignin High Speed Mixer” at temperature from 70°C to 115°C and homogenized with a three-blade mixer for approximately 20-25 minutes to ensure thorough dispersion of the polymer and other components.

Formulation B

In this formulation, 24 parts by weight of the above-described polymer and 10 parts by weight of pigment was melted in the 2 parts by weight of Carnauba Wax, 63.8 parts by weight of Hexadecanol and 0.2 parts by weight of “Oil” (polyalphaolefin) in “Lignin High Speed Mixer” at temperature from 60°C to 115°C and homogenized with a three-blade mixer for approximately 20-25 minutes to ensure thorough dispersion of the polymer and other components.

Drawdowns on K-Proofer

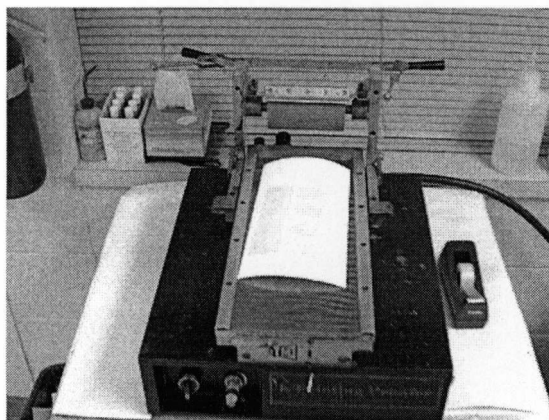


Figure 11: Gravure K-Proofer

The drawdowns were performed using a heated laboratory K-Printing Proofer (Figure 11). In this process, ink is transferred from an electromechanically engraved printing plate directly onto the substrate, which is attached to the rubber covered impression roller. Doctor blade and roller adjustments are made via micrometers allowing repeatable settings before drawdowns. The printing plate: a Double 8 Wedge

Plate (150 lines/inch), Dot area: 100- 60%. K-Proofer is pneumatically driven, using supply air pressure 80 PSI at 250 ft/min.

K-Printing Proofer Draw Down Steps

- 1) Mount the substrate on the rubber impression roller with the help of adhesive tape.
- 2) Adjust the doctor blade angle at 45°.
- 3) Heat the engraved plate and doctor blade with heating coils to 100 - 150° C.
- 4) After heating the plate to the desired temperature, heated ink is poured on the engraved plate, just ahead of the doctor blade.
- 5) Now take a draw down, as the doctor blade moves forward, the ink over the engraved plate is metered off, thus ink fills the tiny cells of the plate.
- 6) As the doctor blade moves ahead simultaneously an impression roller with loaded substrate is brought in contact with the plate. At the point of contact, ink is drawn out of the cells onto the substrate by capillary action.
- 7) Unload the paper and load another substrate.
- 8) The drawdowns were made with the LWC, SCA, and SBS substrates.

Moser Retrofit

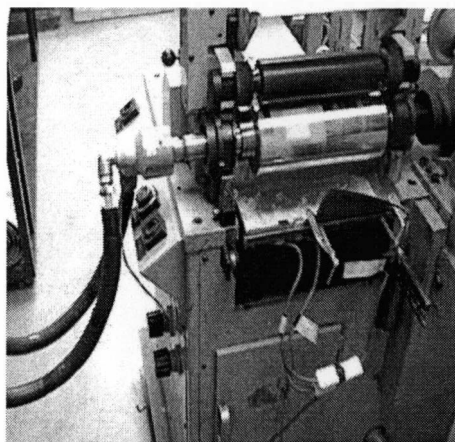


Figure 12: Moser Sheet-fed Gravure Proofing Machine

The Moser proofing press (Figure 12) was equipped with a hollow engraved cylinder, which has a rotary union that allows heated media to be circulated through the image carrier. The ink pan had been fitted with a silicone rubber-heating pad, which is capable of heating up to 200°C. The heating pad was adhered to the ink pan by means of an adhesive backing on the heating mat itself. The rotary union circulates Mobiltherm 603 (heat transfer) oil through the cylinder with the use of a heated oil-circulating bath.

Gravure printing cylinder was heated to a temperature in the range of 75-105°C, by a thermal oil circulator and the hot-melt ink was placed into the machine's ink trough, which was heated to a temperature of 75-105°C, by heating pads, and the ink was melted.

Three types of substrate LWC (Light Weight Coated), SCA (Super Calendered A-Grade) and SBS (Solid Bleached Sulfate Board) were hand-fed through the press and prints were obtained.

Rheology

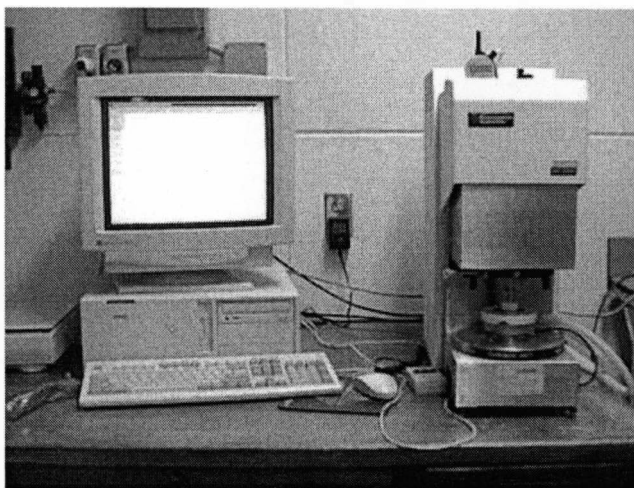


Figure 13: DSR 5000 Dynamic Stress Rheometer

For rheological measurements, Rheometric Scientific 5000 (Figure 13) was employed for steady stress sweep test. In this test a range of stress levels (75-105°C), each at constant amplitude was carried out. Successive measurements were taken at each stress level. Stress amplitude can be incremented or decremented, with stress increments scaled either logarithmically or linearly. The logarithmic stress sweep generates stresses that are logarithmically incremented, resulting in equally spaced data points when plotted as a function of logarithmically scaled stress. Stress amplitudes were selected by specifying the initial and final stress and the number of data points to measure between each decade of stress. The test can be used to characterize samples that display extreme non-linearity (filled thermoplastics and thermoplastic blends).

Parallel plate geometry was used in the rheology testing. While there was a suggestion of using cone and plate geometry. But by using the cone and plate

geometry, it was difficult to maintain a gap of 0.05mm between a cone and a plate. So parallel plate was more flexible to use as compared to the cone and plate.

The most successful formulations were tested to quantify the rheological properties of the ink. A steady stress sweep test was performed on the DSR 5000 stress rheometer. A 25 mm parallel plate in conjunction with a peltier plate heating system was used as the system to achieve the necessary temperatures for the inks to be heated and liquefied and for the tests to be performed. The following conditions will be set on the rheometer in order to complete the testing:

Steady Stress Sweep

Geometry Type = Parallel Plates

Diameter = 25.0 [mm]

Initial Stress = 3019 dynes/cm²

Final Stress = 1.58e+10⁵ dynes/cm²

Maximum time per data point = 15 sec

Temperature = 85⁰C, 90⁰C, 95⁰C, 100⁰C, 105⁰C, 110⁰C and 115⁰C respectively

Delay = 180 sec (to equilibrate sample)

Printability Analysis

An “X-Rite 408 Reflection Densitometer” (Figure 14) was calibrated according to manufacturer recommendations and used for reflection density measurements.

Reflective Density

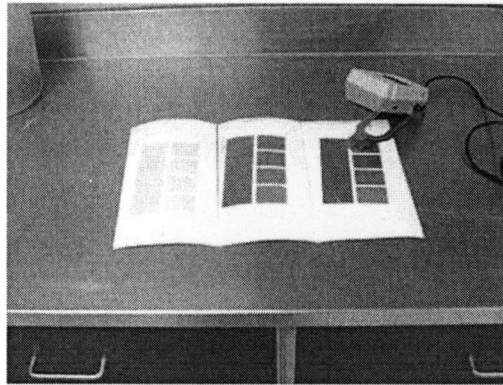


Figure 14: X-Rite 408 Reflection Densitometer

The density range describes the difference between the maximum and minimum density in an image. A recommended reflective density values for the rotogravure printing are 0.90 for Yellow, 1.30 for Magenta, and 1.35 for Cyan for LWC, SCA and SBS.

A reflection densitometer measures the amount of light that is reflected from an image. The incident light is projected at an angle of 45° , while the light sensitive densitometer head is located at 90° . Ink film thickness directly affects the reflective density of the printed ink.

Hot melt ink has a tendency to settle quickly on the surface of a substrate, causing thicker ink film. While the solvent base gravure inks penetrates more into the substrate as compared to the hot melt inks. Thus thicker the ink film, higher the density and vice versa.

The substrate SCA is more porous and less smooth than LWC and SBS. When hot melt inks are printed on the surface of the SCA, it gets absorbed more as

compared to LWC and SBS. Thus reflective density is less on SCA than LWC and more on SBS.

Specular Gloss

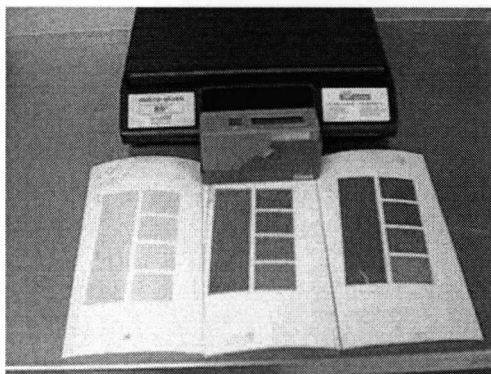


Figure 15: Specular Gloss Meter

A Gardner gloss meter (Figure 15) with 60° angle of specular reflection was used. Gloss is a visual impression that is caused when a surface is evaluated. A smooth and highly polished paper will be shinier, or have higher gloss. Measuring gloss can help insure that the HMI's formulated are being produced at the highest level of quality.

This apparatus measured the percentage of perfect reflectance of the ink film and the substrate. The gloss was measured in both the machine and cross-machine directions on both the solid printed and unprinted regions. The paper gloss was subtracted from the printed gloss, to obtain the delta gloss.

Rub Resistance

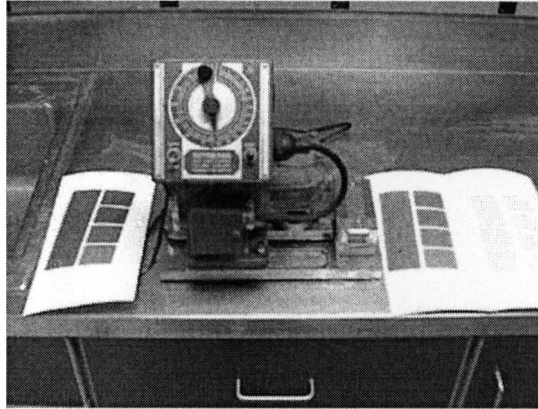


Figure 16: Sutherland Rub Resistance Tester

The significance of the ink rub resistance test (Figure 16) is to differentiate between strong and weak ink films as well as their adhesion to substrate resistance to rubbing and scuffing. Sutherland rub resistance tester is a motor driven device for moving a weighted test specimen over a printed or unprinted sample through an arc of $8.5^\circ \pm 0.5^\circ$ for a predetermined number of strokes.

The stroke comprises one to-and-fro motion of the test weight. Test speeds can be selected from fixed speeds of 42 and 85 cycles a minute.

First, the density of a solid patch was determined. That solid patch of print was attached to a one-kilogram block. Then, an unprinted sample of the exact same substrate was be secured below the one-kilogram weight. The two samples were rubbed together for fifty strokes, and then the density was taken again. The rub resistance values were calculated as follows.

$$D_{\text{solid}} - D_{\text{rubbed}} / D_{\text{solid}} \times 100\%$$

CHAPTER VI

RESULTS AND DISCUSSION

Formulation A - Without Addition of Rheology Modifier

#	Ingredients	Parts	Mixing Temp (°C)	Melting Point (°C)
1	1-Octadecanol, 95%	64	70	70
2	Carnauba Wax	2	85	85
3	Polymer: EVA 2528 (Ethylene Vinyl Acetate)	24	90	76
4	Pigment Dispersion	10	100	95

Table 3: HMI Without Addition of Rheology Modifier (Formulation A)

These inks are based on “Ethylene Vinyl Acetate Co-polymer” chemistry, solid at ambient temperature and liquid at the moment of printing by application of heat in the range of 85-130°C. They are environmental friendly, as they do not contain volatile organic compounds and hazardous air pollutants.

Formulation B - With Addition of Rheology Modifier

#	Ingredients	Parts	Mixing Temp (°C)	Melting Point (°C)
1	1-Hexadecanol, 95%	63.8	70	60
2	Carnauba/Polyethylene Wax Alloy	2	85	85
3	Polymer: Escorez 1580 (Hydrocarbon Resin)	24	90	76
4	Pigment Dispersion	10	100	95
5	Rheology Modifier (Polyalphaolefins)	0.2	80	n/a

Table 4: HMI With Addition of Rheology Modifier (Formulation B)

These inks are based on “Hydrocarbon Resin” chemistry, solid at ambient temperature and liquid at the moment of printing by application of heat in the range of 75-130°C. They are environmental friendly, as they do not contain volatile organic compounds and hazardous air pollutants. Special oil (polyalphaolefins) has been added into this formulation as a viscosity modifier.

Viscosity v. Stress of HMI Ingredients (Formulation A)

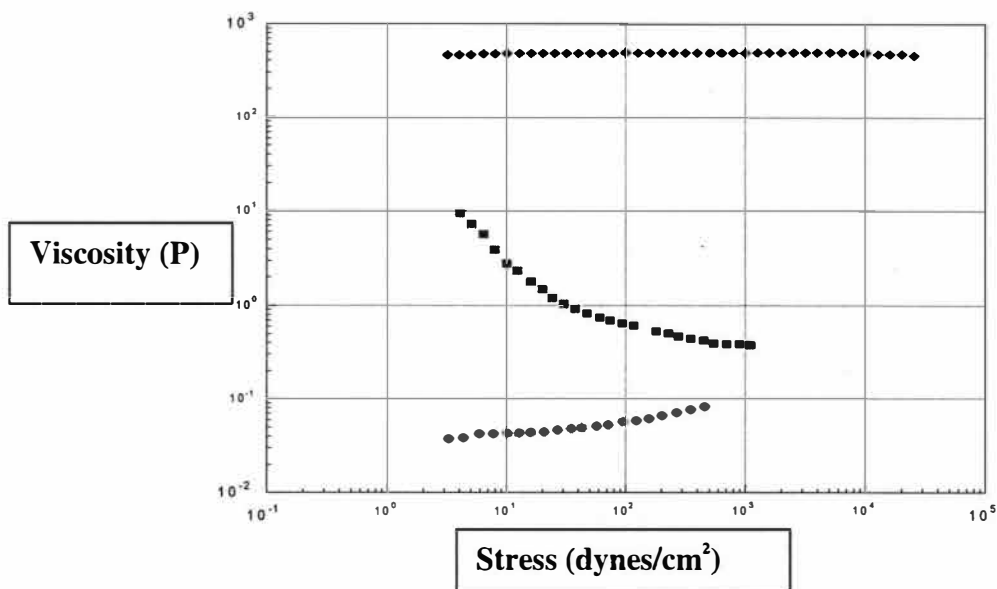


Figure 17: Viscosity v. Stress of Hot Melt Ink Ingredients (Formulation A)

(■ Polymer 2528, ■ Carnauba Wax, ● 1-Octadecanol)

The rheological data of the base ingredients used in the formulation “A” were measured at 95°C and is shown above in (Figure 27). The data shows that viscosity of the polymer does not change as the stress changes. Thus the measurement shows that the polymer MVA 2528 has high viscosity in the range of 10^2 - 10^3 poise, and its viscosity is not decreasing with the increasing stress force.

The viscosity of the carnauba wax started decreasing in the first 10 dynes of stress steps between 10^0 - 10^1 at 10 [dynes/cm²], and decreased to below 1 poise at around 50 [dynes/cm²]. The viscosity data of carnauba wax seem very promising with a viscosity in the range from 10^{-1} - 10^0 poise. It was decided that this wax could be used for HMI ink formulation, along with the EVA polymer.

The rheological data for (1-Octadecanol, 95%) show low viscosity in the range of 10^{-2} to 10^{-1} . The viscosity of the alcohol compound started increasing in the first 10 dynes of stress steps, thus showing shear thickening with the increasing stress, which helps in maintaining the quick solidification of ink. Octadecanol reacts with other components and tends to crystallize, causing shear thickening behavior. It was used in HMI formulation because it showed and maintained very low viscosity for HMI.

Viscosity v. Stress of HMI Ingredients (Formulation B)

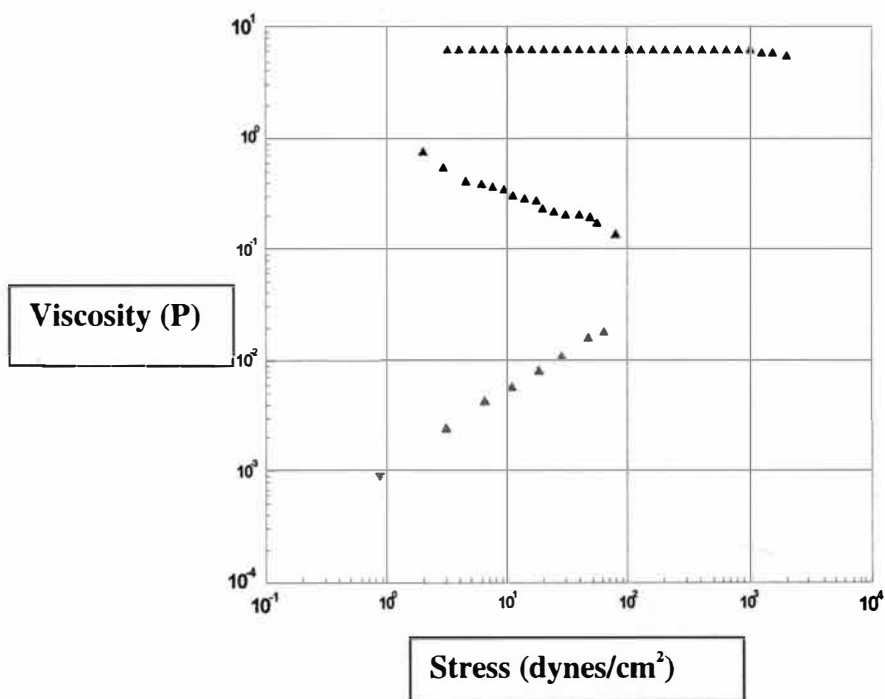


Figure 18: Viscosity v. Stress of Hot Melt Ink Ingredients (Formulation B)

(▲ Resin , ■ Carnauba/ Polyethylene Wax, ▲ 1-Hexadecanol)

The rheological data of the base ingredients used in the composition were measured at 95°C with a steady stress sweep test. The data (Figure 18) show that viscosity of the polymer does not change with the increasing stress. Thus the polymer has a viscosity in the range of 10^1 - 10^2 Poise.

The viscosity of the carnauba/polyethylene wax alloy started decreasing in the first 10 dynes of stress steps, with viscosity between 10^0 - 10^{-1} Poise, and it decreased to below 10^{-1} Poise at around 100 [dynes/cm²].

The (1-Hexadecanol, 95%) showed a low viscosity in the range of 10^{-3} to 10^{-2} . As its viscosity started increasing in the first 10 dynes of stress steps, thus showing shear thickening with the increasing stress, which will help to solidify the ink more quickly at ambient temperature.

Rheology of Hot Melt Ink (Formulation A)

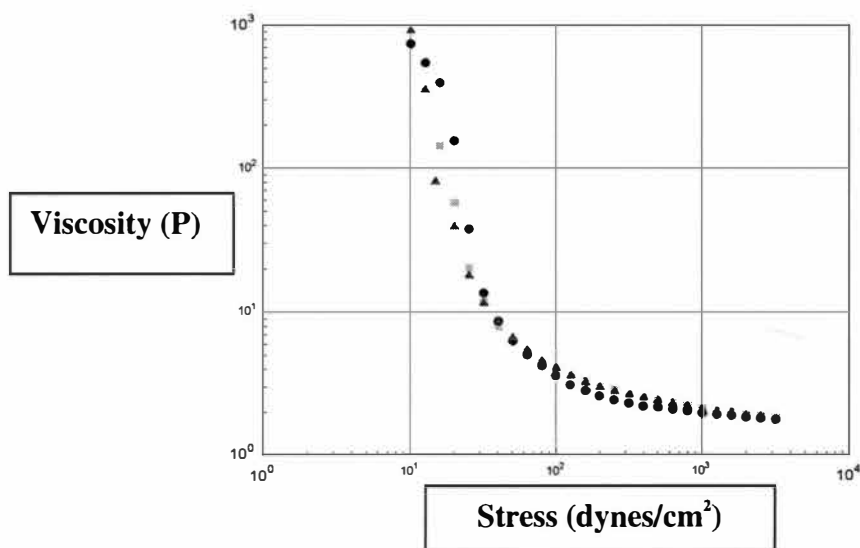


Figure 19: Viscosity v. Stress of Hot Melt Ink Formulation (Formulation A)

(\triangle Yellow , \blacktriangle Magenta , \blacktriangle Cyan)

The rheology of finished inks was measured at 105°C. The viscosity began to decrease with increasing stress, but the viscosities associated with the values were in the order of between 10^0 - 10^1 poise, while the correct printing viscosity for the gravure printing is in the range of 10^{-1} poise. This suggest that the inks have too high of viscosity. The cause might be attributed to the degree of polymerization of EVA, 24% polymer by weight in the dispersion and shear thickening of (1-Octadecanol, 95%) at increasing stress. The laboratory data indicate that the hot melt ink had a tendency to decrease in viscosity with temperature increasing above 105°C. However, it was not possible to verify that on the Stress rheometer, due to manufacturer's recommendation of temperature range of use.

Rheology of Hot Melt Ink (Formulation B)

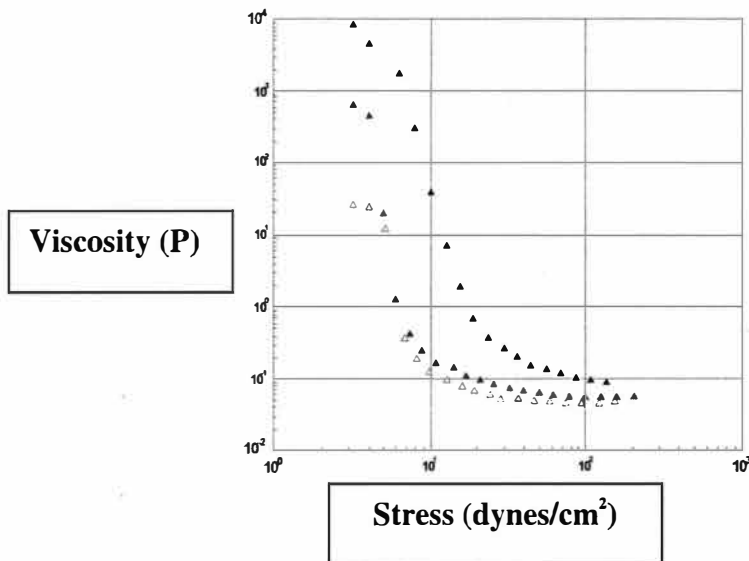


Figure 20: Viscosity v. Stress of Hot Melt Ink Formulation (Formulation B)

(\triangle Yellow , \blacktriangle Magenta , \blacktriangle Cyan)

The rheology of finished inks at 105°C is shown in Figure 20. The viscosity began to decrease with increasing stress and temperature, and dropped in the order of between 10^{-2} - 10^{-1} poise for yellow, magenta and cyan. This suggests that the ink has a required viscosity for trapping of inks at respected temperatures; the cause is attributed to the high degree of polymerization of EVA, shear thickening of (1-Hexadecanol, 95%), and addition of viscosity modifier. The data indicate that the ink had a tendency to decrease in viscosity with increasing temperature.

It was important to reduce viscosity of “Hot Melt Ink for Rotogravure”, because the ink formulated prior had high viscosity. Therefore, the work was carried out in order to lower the viscosity of the hot melt ink to bring it to the desired viscosity by selecting environmentally friendly polymers, rheology modifiers or alcoholic compounds.

Modification of Properties Due to Rheology Modifiers

Improve runnability of ink on the press.

Becomes more thermally stable at high temperatures.

Ink does not fume.

Comparison of Viscosity v. Stress of Hot Melt Ink Formulation Using Cyan Ink With/ Without Addition of Rheology Modifier

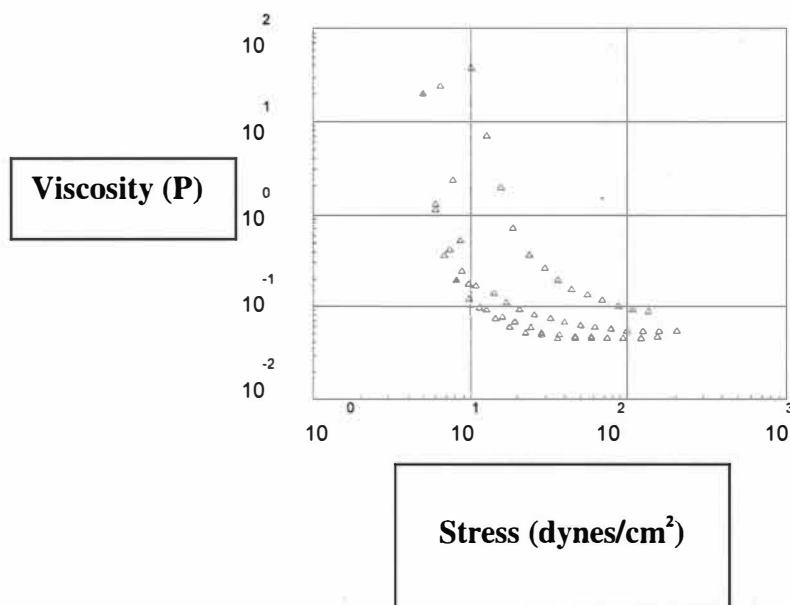


Figure 21: Comparison of Viscosity v. Stress of Hot Melt Ink Formulation Using Cyan Ink With /Without Addition of Rheology Modifier

- ▲ Cyan Ink @95°C without rheology modifier
- ▲ Cyan Ink @95°C Using rheology modifier I
- ▲ Cyan Ink @95°C Using rheology modifier II
- ▲ Cyan Ink @95°C Using rheology modifier III

The (Figure 21) shows that, the ink viscosity is in the range of 10^0 - 10^1 poise for Cyan (Without Rheology Modifier) @ 95°C and 10^{-1} - 10^{-2} poise for Cyan (With Rheology Modifier).

Printability Analysis

Reflective Density (Formulation A)

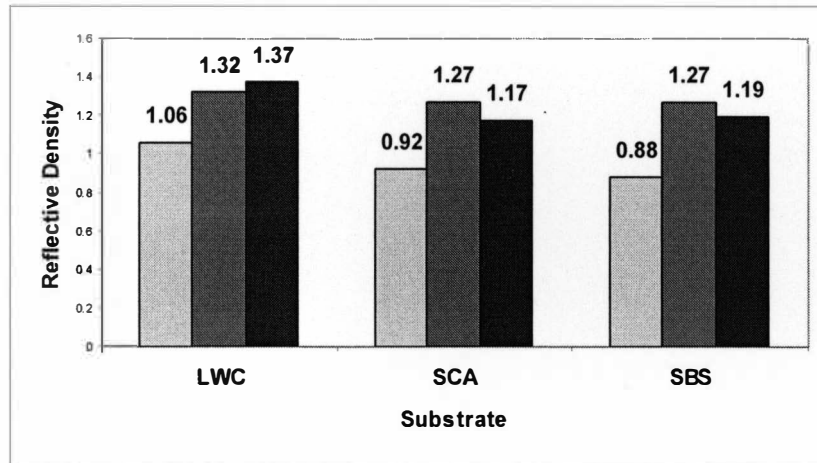


Figure 22: The Reflective Density of Hot Melt Ink on Different Paper Substrates

Yellow Ink,
 Magenta Ink,
 Cyan Ink

Figure 22 shows the reflective density for hot melt ink is very similar for all the different substrates, the density of yellow, and magenta is excellent on all the substrates, while the density of cyan is good on LWC and slightly lower on SCA and SBS. The density values reached at LWC are matching the target densities [0.90 for yellow, 1.30 for magenta, and 1.35 for cyan] recommended for publication gravure for all the substrates.

Reflective Density (Formulation B)

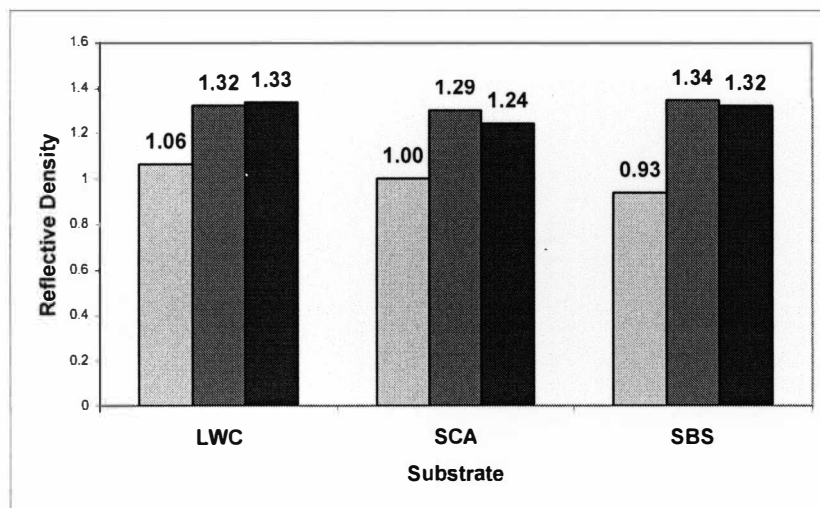


Figure 23: The Reflective Density of Hot Melt Ink on Different Paper Substrates

■ Yellow Ink, ■ Magenta Ink, ■ Cyan Ink

Figure 23 shows the reflective density for hot melt ink is very similar for all the different substrates; the density of yellow, and magenta is good on all the substrates. The density values for LWC (.93-1.06), SCA (1.29-1.34) and SBS (1.24-1.33) are matching the target densities [0.90 for Yellow, 1.30 for Magenta, and 1.35 for Cyan] recommended for publication gravure.

Specular Delta Gloss (Formulation A)

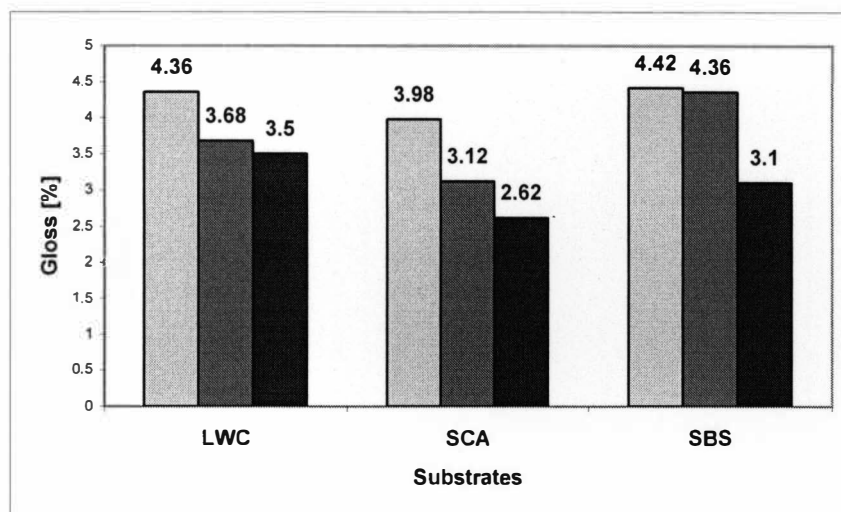


Figure. 24: The Delta Gloss of Hot Melt Ink on Different Substrates

Yellow Ink,
 Magenta Ink,
 Cyan Ink

Theoretically, hot melt ink formulations should have excellent gloss properties due to very good ink holdout on the surface of the printing substrate. Current hot melt ink formulations have gloss values highest at yellow ink, than at magenta and lowest at cyan ink, having values in range of 4.4 to 3.1 %. SBS board showed overall highest specular gloss on magenta and yellow ink (Fig.24.). The delta gloss was between 3.98-4.42 % for Yellow, 3.12-4.36 % for Magenta, and 2.6-3.5 % for Cyan lower on LWC, and SCA, than on SBS board.

Specular Delta Gloss (Formulation B)

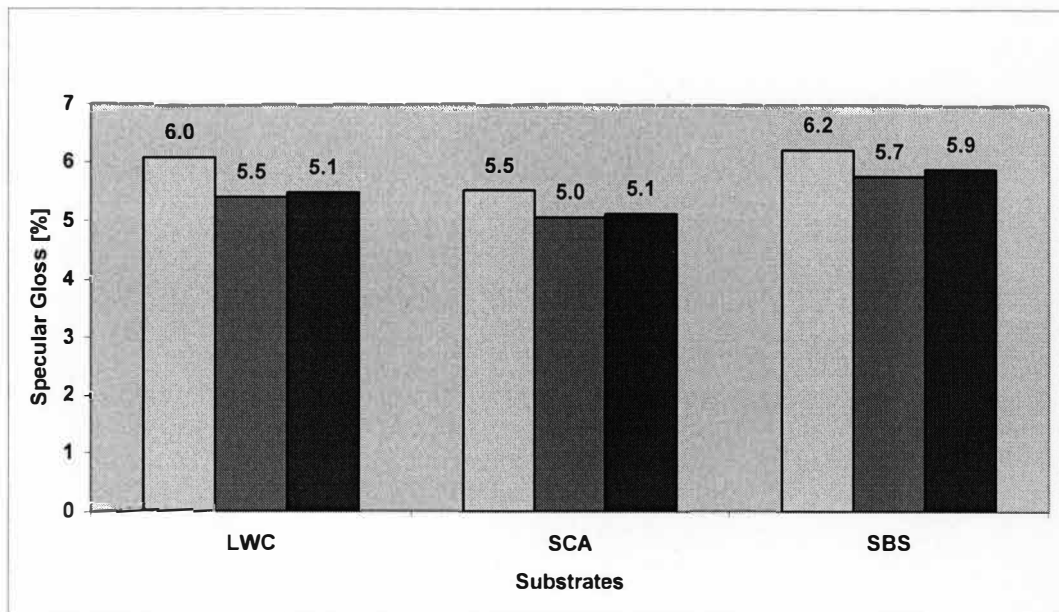


Figure 25: The Gloss of Hot Melt Ink (Formulation B) on Different Substrates

Yellow Ink,
 Magenta Ink,
 Cyan Ink

Current hot melt ink formulations had gloss values highest at yellow ink, than at magenta and lowest at cyan ink, having values in range of 5.5 to 6.2 %. SBS board showed overall highest specular gloss. The gloss values are between (5.5-6.2 % for Yellow, 5.0-5.7 % for Magenta, and 5.1-5.9 % for Cyan) which are lower on LWC, and SCA, than on SBS board. The gloss values were bit higher on all substrates as compared to the formulation “A”.

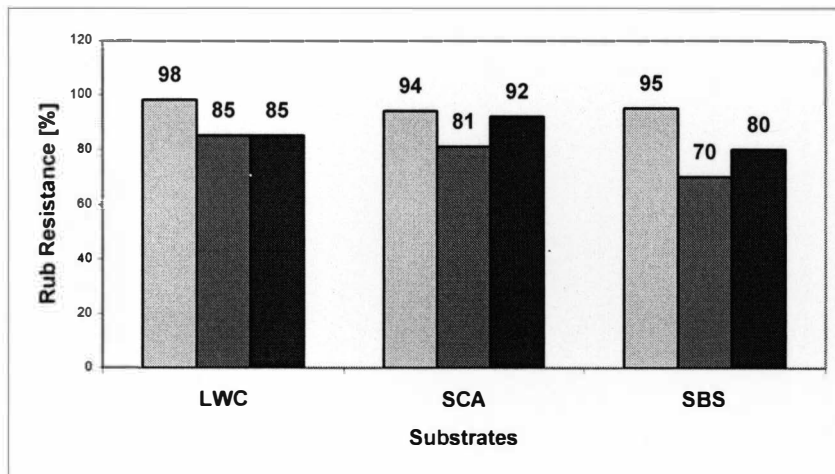
Rub Resistance (Formulation A)

Figure 26: The Rub Resistance of (Formulation B) Hot Melt Ink on Different Substrates

■ Yellow Ink, ■ Magenta Ink, ■ Cyan Ink

Rub resistance of hot melt ink is illustrated on Figure.26. LWC, SCA and SBS showed poor rub resistance [i.e. between 95-98% for yellow; 70-85% for magenta, and 80-85% for cyan]. The LWC and SCA sample lost more ink. The worst rub resistance was observed on magenta ink. The data indicate that the inks formulated have good end-use properties.

Rub Resistance (Formulation B)

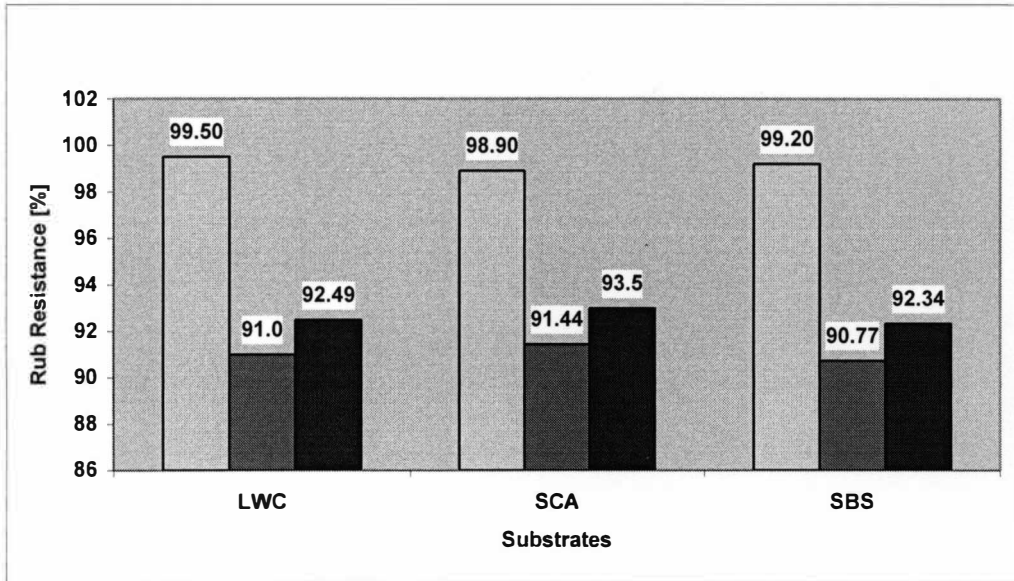


Figure 27: The Rub Resistance of Hot Melt Ink on Different Substrates

YELLOW INK,
 MAGENTA INK,
 CYAN INK

Rub resistance of hot melt ink is illustrated in (Fig.27). LWC, SCA and SBS showed poor rub resistance [i.e. between (90.77-91.44 %) for Magenta, and (92.34-95.5 %) for Cyan]. The substrates LWC, SCA and SBS lost more magenta and cyan ink, indicating less amount of ink adhesion. While all the three substrates showed excellent rub resistance i.e. in the range of (98.90-99.90 %) for yellow indicating high amount of ink adhesion.

CHAPTER VII

CONCLUSION AND RECOMMENDATIONS

The aim of this work was to formulate, analyze, and print hot melt ink formulations. The rheological data indicated that present hot melt inks have required viscosity (10^2 - 10^1 Poise) for yellow, magenta and cyan at 105°C for rotogravure printing. However, their viscosity rapidly decreased with increasing temperature and stress. After printed at laboratory gravure K-Proofer, the inks showed excellent reflective density, matching the target densities [0.90 for Yellow, 1.30 for Magenta, and 1.35 for Cyan] recommended for publication gravure. Rub resistance property for yellow (98.90-99.90 %) is excellent. The gloss properties were quite low on magenta (5.0-5.7 %) and cyan (5.1-5.9 %).

The oils (polyalphaolefins) cannot serve as major component of hot melt inks, as it ruins the solidification property of the ink at ambient temperature. However, they can be used in the ink formulation in the amounts around 0.2% wt as viscosity modifiers, as they decrease inks viscosity. Mottle was more profound on cyan (print density unevenness) (data not shown). Viscosity modifiers and carnauba/polyethylene wax showed good printability, they had positive influence on ink rheological properties, thermal stability, and ink runnability.

The next research should focus on increasing the specular gloss for all the three inks, increase in rub resistance for magenta and cyan inks and eliminate the mottling problem. It is recommended to print the inks at high temperatures. These inks are worthy of the time and effort because of their overwhelming environmental

benefits. They have the potential to change the gravure industry, and raise the environmental standards of today's inks.

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