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Hot Melt Inks for Rotogravure-Formulation, Print Ability and Rheology

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HOT MELT INKS FOR ROTOGRAVURE – FORMULATION, PRINTABILITY AND RHEOLOGY

by

James Atkinson

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
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Western Michigan University
Kalamazoo, Michigan
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James Atkinson

HOT MELT INKS FOR ROTOGRAVURE – FORMULATION, PRINTABILITY AND RHEOLOGY

James Atkinson, M.S.

Western Michigan University, 2001

A new generation of phase change, or hot melt ink will be formulated. This ink was solid at ambient temperature and liquid at the moment of printing. Inks will be formulated on the basis of polyethylene and Ethyl Vinylacetate chemistry. Inks were printed using a Meyer rod for screening printability study. Selection of the best formulations will be done on the basis of reflective density, specular gloss, mottle, and rub resistance. Screened inks having best properties were printed on the Moser laboratory sheetfed proofing press. More detailed printability analysis was done after Moser printing, including dot structure analysis, tone gradation, and mottling. The rheology of the best formulations was studied and compared to conventional rotogravure inks. Based on rheological measurements, additional changes on ink formulations were made.

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CHAPTER 1

INTRODUCTION

Rotogravure printing is accomplished by using an engraved cylinder, which rotates in a bath of ink. The excess ink is wiped off the cylinder by a doctor blade. The simplicity of gravure printing allows for the use of ink systems that dry very quickly. The solvents that are used need to be highly volatile. Currently, the presses being used require large dryers. This creates a long paper path, which creates waste at the beginning of the run when the press is webbed up. If the web breaks, then more paper must be used to fix the break. The majority of the cost of a printing job is the cost for the paper. If the path of the web can be shortened, then rotogravure printing can become more economical. The press can be more efficient in terms of startup waste and with web break waste. However, rotogravure is losing market share because of the expense that is involved with rotogravure (i.e. cylinders, paper, inks, etc.). In order to compete, production costs must decrease. Using hot melt inks could possibly be the solution. These inks do not need a drying system. Therefore, the paper web can be shortened. This could potentially represent huge savings in white paper waste. It could also reduce the makeready printed waste and press running waste. This suggestion does not even mention the money saved on the drying system operation and maintenance. The use of hot melt ink will eliminate the creation of volatile organic compounds (VOC's). VOC's are produced by the use of solvent-based ink systems during printing. Current technology is able to trap and recover up to 93% of the solvent being used, but the rest is being emitted into the air.

1.1 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 making a cylinder is very expensive and labor intensive. The structure, length, and quality requirements are changing. These all represent a disadvantage for rotogravure printing, and rotogravure is becoming less competitive due to these changes. 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 [9]. 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 more consistent transfer. ESA is a process where an electrical field is applied to the 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 raises 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 [5].

1.2 Traditional Inks for Rotogravure

Rotogravure inks are split into two market segments. Publication gravure printing includes products like high volume, high quality magazines (National Geographic). Packaging gravure prints products like cereal boxes, cigarette packaging and other products that require high quality and long runs. The short ink train requires the ink to be very liquid and must be capable of drying quickly after transfer to the substrate. There are two different types of gravure ink. There is solvent-based ink and water-based ink. Solvent inks are made using organic liquids such as toluene, xylene, hexane, and other organic solvents, which have the potential of causing cancer. Water-based inks are made using chemistries that combine water and either glycols or alcohols [9]. 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 [8]. Printers that print gift wrap use 100% water based inks for that process [8]

1.3 Ink Components

1.3.1 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 copper, zinc, bronze, and aluminum [9]. 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 [9]. Lack of agitation is one source of sedimentation. Rapid addition of solvent in order to adjust viscosity is also another potential cause of sedimentation [9].

The most widely used blue pigment for process cyan ink is Phtalocyanine 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 [6]. The chemical structure of this pigment is shown in Figure 1.

Most yellow pigments are -azo pigments, and the most widely used yellows are Diarylide yellow. These pigments display excellent transparency and excellent color strength [7]. 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 as well [7]. The chemical structure for a typical process color yellow pigment is shown in Figure 2.

The most widely used magenta pigments for process work are Lithol rubines. These pigments are classified by their –N=N- bond. This pigment is well suited to rotogravure ink. The chemical structure for a lithol rubine red pigment is shown in Figure 3.

Another red that could potentially be used for an ink is a quinacridone magenta pigment that is made by Sun Chemical. The chemical structure is shown in Figure 4.

Carbon black is the most widely used black pigment. It is nearly unaffected by light, solvent, heat, and acid [7]. Carbon black has varying particle sizes, oil absorption properties, volatiles contents, and pH. Carbon black, therefore, comes in several different forms. Furnace black is the most important of the black pigments. This pigment is made by burning atomized mineral oil in bricklined furnaces with controlled air supplies [7].

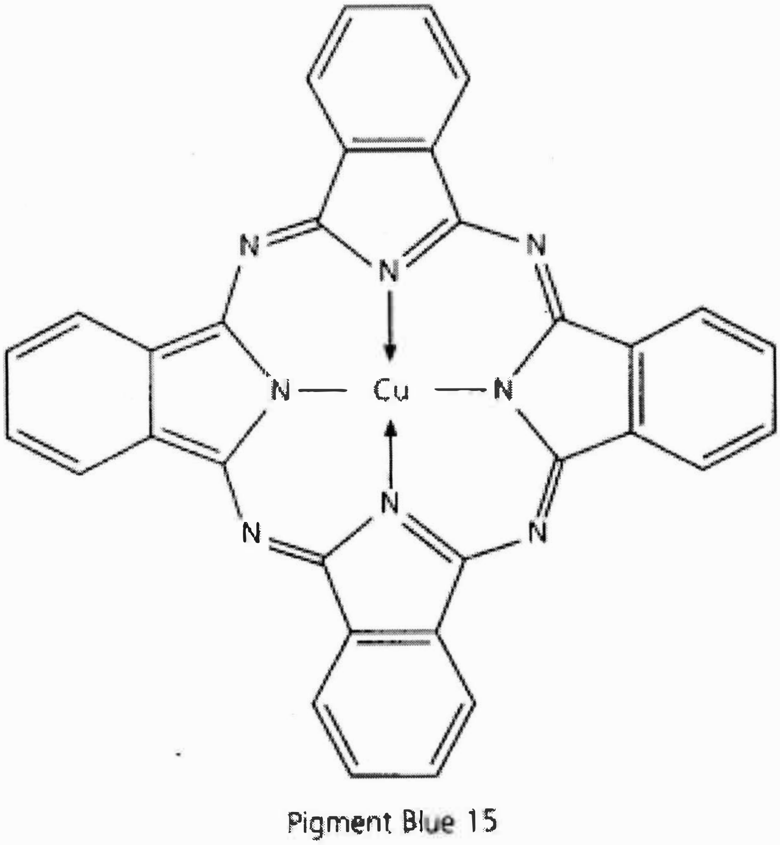


Figure 1: Pthalocyanine Blue Pigment 15

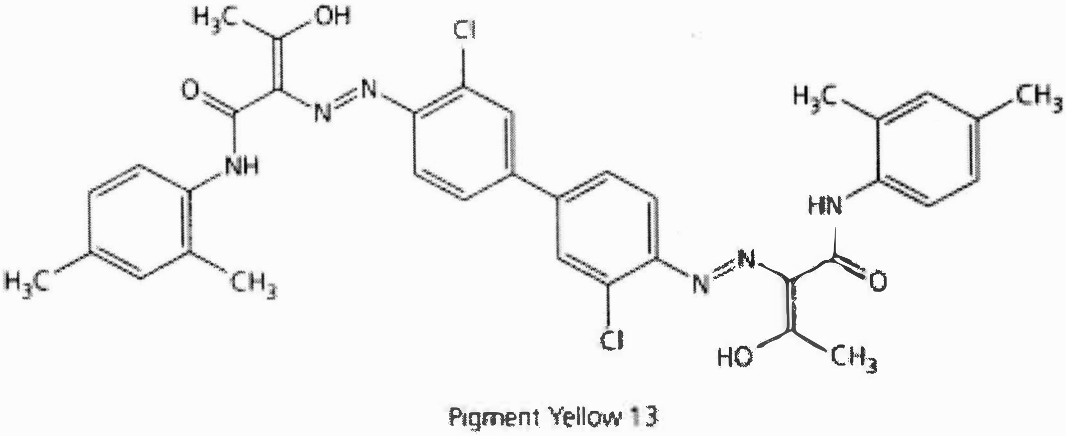
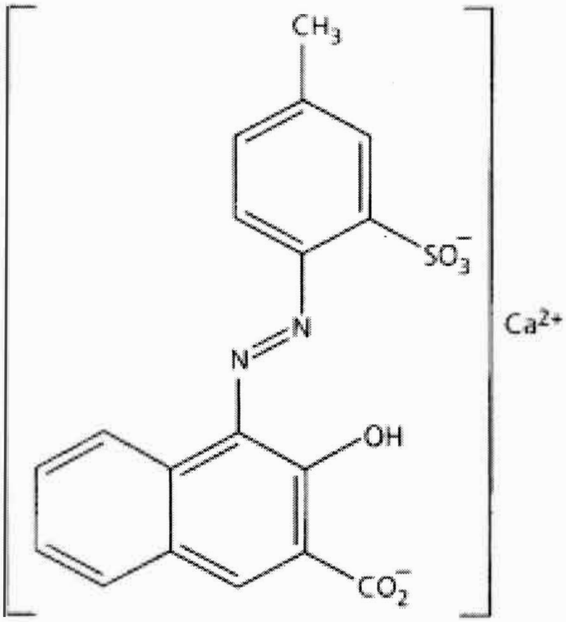


Figure 2: Pigment Yellow 13



Pigment Red 57:1

Figure 3: Pigment Red 57

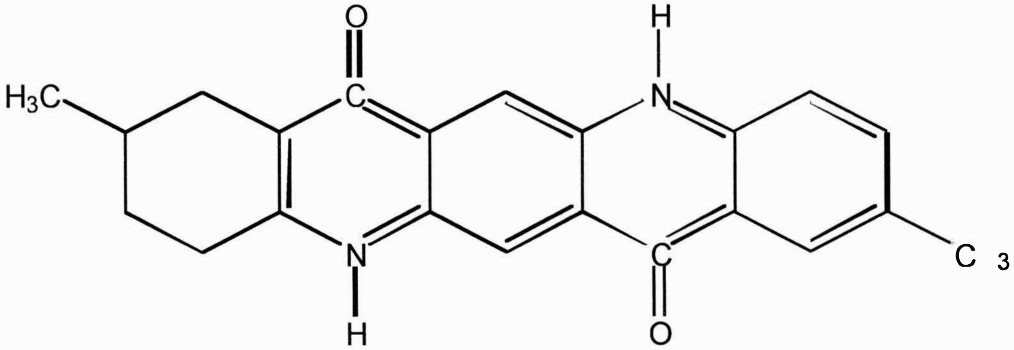


Figure 4: Quinacridone Magenta Pigment

The oil is burned, then the furnace is cooled and bag filtered to obtain the pigment particles. This pigment has a lower volatile count than most of the other black pigments. Channel black is obtained by burning natural gas, while limiting the air supply to the fire. This pigment has high gloss and color strength, but is rarely used and is not manufactured in the United States [7]. Lampblack is made by burning unsaturated residues of creosote oil, a by-product of distillation of coal tar [7]. This pigment has a dull finish, and therefore is not desirable for use in ink [7]. The particle size influences the flow properties of ink as well. If the particle size is small, then the flow properties will be enhanced. If large particles are present, then the rheology of the ink will be more viscous, therefore reducing the ability of the ink to flow freely throughout the inking system on the press. The particle size of a pigment has a pronounced effect on the color strength and opacity of the finished ink. As the particle size increases, the color strength decreases. This is illustrated further by the graph below. The graph shows that the opacity first increases, peaks at approximately 0.4 microns, then decreases from that point on as the particle size increases. The color strength of the pigment will decrease as the particle size increases because of the fact that a smaller number of larger pigment particles do not absorb the light wavelengths as efficiently as a larger number of smaller particles [23]. The opacity phenomenon occurs because if the particle size is smaller than the wavelength of the light, then the light cannot be scattered. In this case, the light passes around the particle and is transmitted through the ink film, therefore decreasing opacity [23]. The inks used for process printing require high color strength at low opacity. These properties are needed because the process colors are overlapped when printing full color images. The ink film needs to be transparent for process color printing in order that light can pass through all three of the ink films in order to transmit the correct color back to the eye, which creates the effect of color on the printed image. Figure 5 illustrates the effect of particle size on color strength and opacity. When the pigment is mixed into the dispersion, the vehicle surrounds the pigment particle and it is attracted to the polar surface of the pigment and is adsorbed onto the surface [23]. This concept is illustrated in Figure 6.

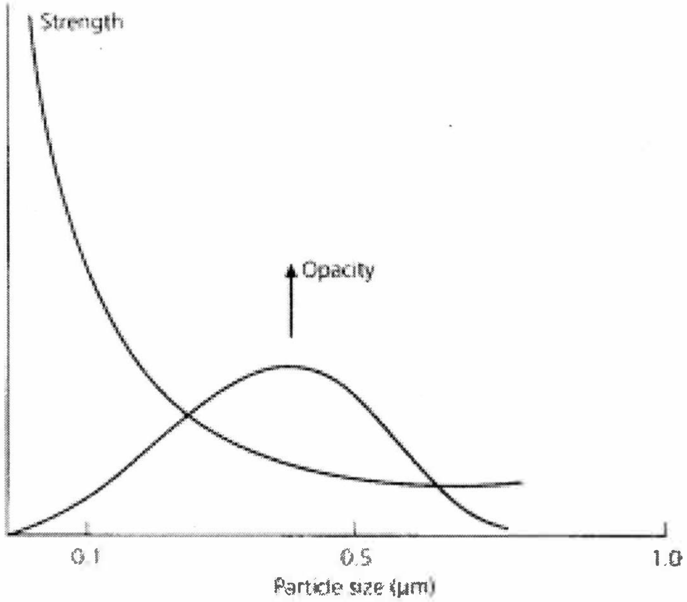


Figure 5:Color Strength and Opacity vs. Particle Size

The resin usually used to perform this operation is abietic acid. The structure of abietic acid is shown in Figure 7. The carboxyl group on the molecule is the end that adsorbs onto the pigment structure. The nonpolar terpenoid hydrocarbon tail is able to associate itself with low polarity media [23].

In gravure inks, the polar pigment molecules do not necessarily disperse well in polar solvents [23]. In this case, the pigments are subjected to high shear in order to disperse them into the resin system. A two-roll mill is used in order liquefy the resin, and also to break up the pigment floccules for dispersion into the molten resin [23]. After dispersion, the mixture is cooled and solidified [23]. The solid mass is then broken into pieces of dispersed pigment.

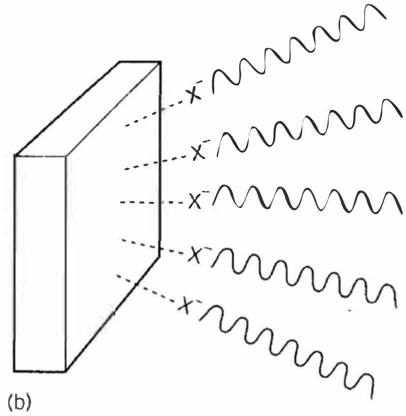


Figure 6: Adsorption

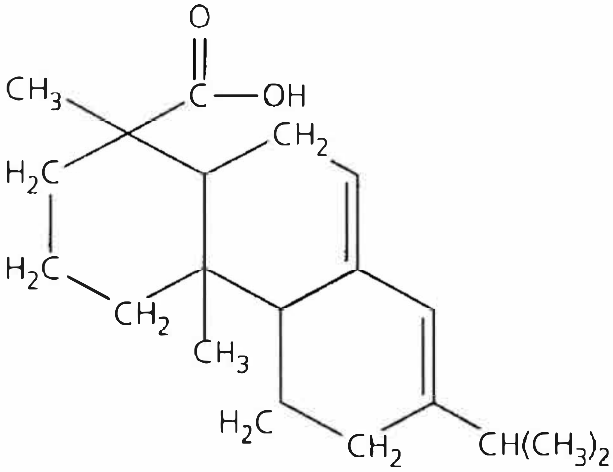


Figure 7: Chemical Structure of Abietic Acid

1.3.2 Resins

Traditional rotogravure inks also contain resins, or vehicles. Resin acts as the binder, which holds the pigment on the substrate. Resins can be classified as film formers, or 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 [9]. Nitrocellulose and acrylic resins are very brittle and will not plasticize unless additives are used to make the resin more flexible [9]. These types of resins display excellent scratch and rub resistance. They are highly heat resistant and can withstand the temperature associated with heat sealing [8]. Nitrocellulose is compatible with rosin derivatives, alkyd resins, and shellacs [8]. 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. These resins are also used to improve adhesion to stocks that require better adhesion properties [9]. Maleic resin is the predominant type of non-film forming resin. Non-film forming resins lower the heat resistance of an ink and can lower the curing temperature of an ink [9]. 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 [8]. 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 [8]. 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 [8].

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 [8]. 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 [8]. The proper choice of resin system is based on the purpose of use, the cost, and the solvent system used.

1.3.3 Solvents

Solvents are liquids, which are capable of dissolving other materials without significantly changing any physical properties [9]. 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 [9]. 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. However, solvent recovery is an expensive process, and not all printers can afford to implement these tactics in order to prevent air pollution. Water-based inks provide an alternative to organic solvents.

1.3.4 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. Paraffin wax is classified by melting points into three grades 52-57°C, 60-63°C, and 66-68°C [15]. Wax is also classified by oil content into three grades; fully refined, semi-refined and scale [15]. These waxes consist of straight chain, *n*-alkanes with carbon backbones of length $C_{18} - C_{50}$ [15]. This 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 normal, branched, and cyclic alkanes with carbon backbones, which range in length from C_{23} – C_{85} [15].

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 durability, adhesion, scuff-resistance, plasticity, and 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 [15].

1.4 New Trends in Rotogravure Inks

Research is currently being done to attempt to create inks that do not have any sort of dangerous effluent or carcinogenic properties. Hot melt inks operate on the premise that when heated, the components "melt" and become a homogenous liquid. These inks consist of a crystalline substance that is solid at room temperature, but can be heated and melted to gravure printing viscosity [10]. Examples of this component include cetyl alcohol, stearyl alcohol, and 12-hydroxy-stearic acid [10]. This component group acts in the same manner as the solvent in traditional gravure ink. If the first component can also act as a lubricant in a fine dispersion, it will allow the dried ink film to be resistant to damage from operations that scuff the surface of the ink film. The second component is an amorphus substance, which is also solid at room temperature. Examples of this component include materials such as polyacrylates that are rich in hydroxyl groups [10]. This component must be soluble in the first component in order to accomplish the goal, which is to have a substance that is solid at room temperature, but when heated, turns to a homogeneous liquid with a suitable printing viscosity. The second component acts as the bonding agent in the ink. This is similar to the action of the resin in conventional gravure ink. These two components along with waxes and amides for increased dye solubilizing power and dyes for color, create an ink that, when heated, is suitable for gravure printing [10]. The dye must be soluble in the first component in order to impart color to the ink [10]. If pigments are used, then there must be a third component group, which will influence the flow and adhesion properties to best suit the printing application being used. These inks have advantages over conventional inks because they do not contain volatile organic compounds (VOC's) [10]. However, this is not the only advantage to hot melt inks. 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 [10]. These inks also have the potential to have higher gloss due to the lack of migration into the substrate [10]. Hot melt inks must not dry too fast or else there is a potential to create a screening effect if the ink is not allowed adequate spreading time before drying on the substrate. Hot melt inks require stringent temperature control as well. If the temperature exceeds the melting point by too much, the components will begin to decompose. This results in a very offensive odor and the smoke emitted can cloud up a room quickly. These inks require the printing cylinder to be preheated as well [11]. If the cylinder is not preheated, the ink solidifies on the cylinder, requiring downtime and cleaning. Hot melt inks have not yet been accepted in industry because the inks cost more than conventional gravure inks. The cost issue has also been the aspect that holds water-based gravure to a small percentage of the market. Press speed is also an issue to which hot melt inks are being held up from industry use. If the speed can be increased to commercial speeds, then there is no reason why hot melt inks cannot be practical for use in industry. The design of the press must also be altered in order to print using hot melt inks. The printing cylinder must be heated in some manner that the ink will not solidify on the cylinder [11]. This might be accomplished using a cylinder that is heated with silicone oil from the inside. Infrared heaters can also be used to heat the cylinder from the outside [11]. The press must be fitted with a cooling roll after the nip which acts as the chilling mechanism for the solidification process necessary for hot melt inks. The ink must also have a heating apparatus that will keep the ink in the liquid state so that it can be delivered to the printing cylinder correctly [11]. If hot melt inks are used, the need for a dryer system is totally alleviated. These modifications are relatively inexpensive when compared to the cost of a dryer system. The blowers, heaters, and solvent recovery mechanisms are much more expensive than a heated plate cylinder and a cooling roller. This makes these inks very desirable for printers who do not currently own any gravure printing equipment.

1.4.1 Polyurethane Chemistry

Polyurethanes may be suitable for hot melt inks. Polyurethanes exist in nature as several different types of materials. They can exist as homo- or copolymers, and the copolymer category can be split up into random, alternating, segmented, block or graft types [22]. The polymer chains themselves can be branched, linear, or networked as well, which allows for many different possibilities when choosing a polyurethane. When speaking about polyurethanes on a mechanical level, they are thought of non-ideal solids [22]. The molecular weight of polyurethane can have a drastic effect on the rheological properties of the polymer syst on certain p The graph shows that the molecular weight does not affect the hardness value of the polyurethane. These materials can have a large variety of physical characteristics. The molecular design of the polyurethane determines the structure of the system, whether the polymer is soft and elastic or hard and rigid [22].

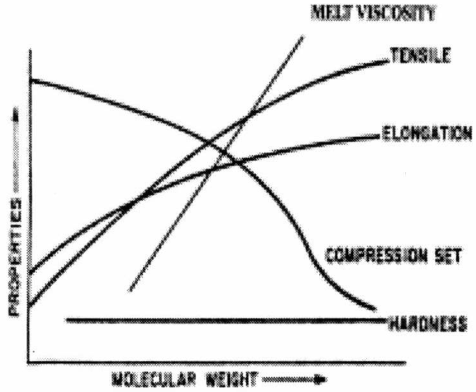


Figure 8: Properties of Polyurethane Polymer Matrices

This makes polyurethanes good choices for printing applications, because it does not need so many additives in order to make it plasticize the film. Polyurethanes do have the potential to degrade when exposed to heat for long periods. This can be overcome by using a polyurethane that has higher molecular weight [22]. 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 [22]

1.4.2 Polyethylene Chemistry

Polyethylene (PE) wax is manufactured from Ethylene, which is made by cracking petroleum naptha. The ethylene is then polymerized to produce various waxes with different melting points. The PE can also polymerized to yield varying density and hardness as well. The molecular weight of PE can range from 500 – 3000 g/mole. PE's that are oxidized have a much better affinity for the formation of emulsions, but non-oxidized PE's are not good emulsion formers [7]. High-density PE's have tightly packed, crystalline structures. These polymers are used in products like paints, coatings, and polishes. They have a melting point range from 85^{0}C to 141^{0}C. These polymers do not seem to be viable for use in inks due to the tightly packed structure. Low-density PE's are tougher and form better crystalline regions. The densities of these polymers generally have density ranges from 0.90 – 0.94 g/ml. These polymers can have melting points which range from 30^{0}C to 141^{0}C, and are used to improve abrasion resistance, mar resistance, lubricity, anti-blocking and slip of the polymer solution it is added to [7]. It seems that some amount of low-density PE should be used in an ink if the ink film is to have some rub resistance.

1.4.3 Ethyl Vinylacetate Copolymer Chemistry

Ethyl Vinylacetate(EVA) is produced by mixing PE polymers along with vinyl acetate to form the copolymer. This copolymer can yield excellent adhesion properties. It is currently used in hot melt adhesives in the folding carton industry. According to BP's website, these polymers have excellent flexibility and adhesion. These polymers also yield good clarity and gloss. These copolymers can operate over a wide range of temperatures. They also have excellent impact resistance, elasticity, and environmental stress cracking. These polymers can have melting points ranging 66 - 140^{0}C and higher, depending on the amount of vinyl acetate present. The density of this copolymer is typically below one g/cm^3, ranging from 0.936 to 0.953 g/cm^3.

1.4.4 Rheology of Polymer Melt Solution

Every material has a certain resistance to flow. This resistance when overcome by an externally applied force will enable the material to move from its parent location towards/away from the direction of the force depending upon the type of force. The study of deformation of flow is termed as 'rheology'. It is important to understand the rheological properties of flow to predict their behavior when subjected to various operations like pumping, metering, mixing etc.

The resistance to flow is termed as ‘viscosity’. The force per unit area, required to produce motion is defined as the *shear stress*. The shear stress is proportional to the velocity gradient dv/dx (also known as *shear rate*). The constant of proportionality is called the viscosity. Thus,

$$\tau = [\mu]/(dv/dx)$$

So, the viscosity of the material is obtained by applying a known shear stress to a material and measuring the velocity gradient. The viscosity of ink can be significantly affected by shear rate and shear rate can vary greatly during the coating process. Thus, to avoid runnability issues, the viscosity of a polymer solution should be measured over an appropriate shear range to enable the dipersions’ response to the shear rates generated by the printing process to be correctly predicted. Depending on the behavior of viscosity for a material with respect to the applied shear, it can be classified as:

1. Newtonian Liquid: A single value of viscosity applied at all times regardless of the rate of shear. E.g. water
2. Non-newtonian liquids: Liquids are not free flowing. The viscosity depends on the rate of shear at which the viscosity is measured.
3. Elastic materials: The solids within the system are characterized by the property of elasticity.
4. Viscoelastic: These materials exhibit elastic, as well as viscous behavior.
5. Plastic flow: The system requires an initial stress to break the bonds within it to start flowing.

6. Pseudoplastic flow: This occurs when the particle dispersion contains long chain polymers, such as carboxymethylated cellulose, PVOH, etc, gradually causing the flow to increase.

7. Dilatant flow: Dilatant flow describes an increase in viscosity under conditions of medium to high shear.

There are several factors that affect the flow properties of a fluid. Some of them are high solids, particle size, particle size distribution and shape, and electrostatic interactions. Temperature also has an effect on the flow properties. A change in molecular weight will affect the flow properties. When a material is subjected to shear and stress it will eventually yield and the bonds that are creating viscosity will break down and the material flows. Yield refers to slippage between pairs of neighboring particles. This concept assumes that there is no relative movement between some of the other pairs that are locally arranged around the pairs that are slipping. This tells us that the slippage is not evenly distributed throughout the sample, but the slippage is localized to specific planes. Yield can even occur in solid materials even if they are glassine, or disordered solids. These polymers display a higher yield stress at decreasing temperatures. In a simple model, successive layers of a material move in relation to a stationery reference layer.

The equation that represents the relative distance traveled (dx), in radians, of two successive layers is the shear strain (γ), is equal to the following:

$\gamma = \tan \alpha = d/dx$, where α = the angle through which the amount of displacement is measured, perpendicular to the surface of the two layers rotating in relation to each other. These planes move parallel to each other and in simple shear strain events there is no movement perpendicular to the shear plane. This flow is assumed to be non-turbulent and that the displacement of successive layers is proportional to that layer's distance from the reference layer. The displacement of the layers of the material is represented by the following formula:

$$\dot{\gamma} = d\gamma/dt$$

The stresses that are applied parallel to the plane of a body of material are referred to as the shear stress. If the material is to remain at rest, the opposite face of the material must exert an equal and opposite force. If the material also has two other faces that have equal and opposite forces, the system will be able to prevent angular acceleration within the material. The resistance to flow is usually provided by the internal bonds of the material. If and when the flow is laminar (non-turbulent) the following equation:

$\gamma = d\gamma/dt \; (d \, / \, dl) = v \, / \, l$, where v = the velocity of the layer being sheared and l = the distance of the layer being measured from the reference layer

This equation says that if the flow is laminar that the layer will travel the distance within a certain time at a specific velocity.

$$dl = v * dt$$

CHAPTER 2

EXPERIMENTAL

2.1 Materials

Pigment chips - supplied by Sun Chemical

Magenta – Quinacridone PE Flush Red 122 L280013

Yellow – AAMX Yellow 13 L751349D28707

Pthalo Blue Green Shade

Polymers - Supplied by Slovnaft

EVAC copolymer A (Elvax 210) - 85^0C – melt index 400

EVAC copolymer AA (Elvax 210)- 85^0C – melt index 2500

EVAC copolymer B (Elvax 220)- 105^0C

EVAC copolymer C (Evatane 28-40) - 120^0C

EVAC copolymer D (Evatauc 28 -40) - 124^0C

PE – Bralen VA 20 - 60 - 82^0C softening point (T_g)

PE - Bralen SA 20 - 71 - 82^0C T_g

PE - Bralen SA 200-22 - 115^0C T_g

Additives - supplied by the Michelman Europe group

Slip agent – Structol - supplied by Michelman

Carnauba Wax – to lower viscosity and melting point – Michelman Europe

Substrates - supplied by the Printing Pilot Plant

Light weight coated paper – 33 lb/ream

Solid Bleached Sulfate board - C1S paperboard

Super-calendered A grade

2.2 Methods

2.2.1 Hot Melt Ink Formulations

1. Characterization of composites based on pigments and polymer matrix

(Samples were prepared in November 2000)

Composite preparation: Melt blending was carried using a Brabender Plasticorder fitted with aW50 chamber and cam blades. Mixing time was 10 min, mixing torque data were reported after the first minute of mixing after stabilization of the torque response. Mixing temperature was varied from 120–190°C. All composite samples were compression molded into plates of 3mm thickness for further testing.

Table 1:

Characterization of Composites Based on 20 wt. % of Pigment Yellow 13 and Ethylene Vinyl Acetate Copolymers Matrix

Composite number	Polymer matrix Type	Mixing temperature	Melt flow rate (g/10 minutes)	Melting point (°C)
1	Elvax 210	100	365-440	85
2	Elvax 220	120	134-180	105
3	Evatauc 28-40	140	27-29	125

Table 2:

Characterization of Composites Based on 20 wt. % of Pigment Red 122 and Low Density Polyethylene

Composite number	Polymer matrix Type	Mixing temperature	Melt flow rate (g/10 minutes)	Melting point (°C)
4	LDPE Bralen VA-20-60	130	20	115
5	LDPE Bralen 200	130	200	115
6	LDPE Bralen 70-21	130	70	155

Table 3:

Characterization of composites based on 20 wt. % of Pigment blue15:3 and Polypropylene

Composite number	Polymer matrix Type	Mixing temperature	Melt flow rate (g/10 minutes)	Melting point (°C)
7	PP Tatren ME 311	190	5	165

2. The polymer matrix was melted in with Carnauba wax under heat and mixed with a three-blade mixer for approximately twenty minutes to ensure thorough dispersion of the polymer matrix into the wax. The samples were poured into an aluminum container so that the inks could be handled easily and transported to the rheometer lab in an efficient manner. The polymer matrices were mixed in the following proportions to yield the respective 33%, 25%, and 20% concentrations of polymer matrix:

a. 5g of yellow polymer matrix and 10g of Carnauba wax, yielding a 33% mixture

b. 5g of yellow polymer matrix and 15g of Carnauba wax yielding a 25% mixture

c. 5g of yellow polymer matrix and 20g of Carnauba wax, yielding a 20% mixture,

d. The figures all represent the samples as the concentration percentages.

The inks will be formulated predominantly on the basis of Polyethylene(PE) and Ethyl Vinylacetate (EVA) chemistry. Low density PE was used in the formulations to formulate inks that are suitable for printing. Carnauba wax will be used to lower the viscosity of the ink. A 33.3%, a 25%, and 20% dispersion of EVA and PE (the polymers) and the Carnauba wax.

2.2.2 Printing

Drawdowns

The drawdowns were done using a Meyer rod #3. This should allow for a film thickness of .003 inches. Preliminary printability analysis to determine if the inks are ready for further testing. The preliminary test will be a density check to determine if the ink film is thin enough upon drawdown. If the density reading is above 2.0, then more work will need to be done in order to get an ink film, which is thin enough to attain a density near SWOP standard for each color of ink.

Moser Retrofit

The Moser proofing press is now equipped with a hollow cylinder which has a rotary union that allows for heated media to be circulated through the cylinder. The ink pan has been fitted with a silicone rubber heating that is capable of heating up to 450°F. The heating pad can be adhered to the ink pan by means of an adhesive backing on the heating mat itself. The rotary union will circulate Mobiltherm 603 (heat transfer) oil through the cylinder with the use of a heated circulating bath. The press retrofit was purchased from Wortco Inc., who engineered the cylinder and rotary union. Tegatron was the company that manufactured the cylinder and engraving. This allowed for accurate temperature control on press, whereas the preliminary set of inks was run using a system that did not allow the operators to control the temperature of the entire ink pan, due to the lack of intimate contact between the heating elements and the ink pan. The silicone mat was adhered to the ink pan, so good contact lead to accurate temperature control. This attempt has a much better chance for success due to the factors described above.

2.3 Analytical

2.3.1 Rheology

1. The most successful formulations were tested to quantify the rheological properties of the ink. The testing utilized a stress rheometer, which can be used to test the elasticity and shear properties of the ink at printing temperature. The rheology test initially attempted to determine if the inks had a low enough viscosity for gravure printing. If the inks are determined to have adequate viscosity, then a press test is viable and should be undertaken at a viscosity of 15 cP. Rheology readings will determine if the ink is viable for printing in terms of viscosity vs. shear rate at specific temperatures.
2. A steady stress sweep test was performed on the DSR 5000 stress rheometer. A 25 mm parallel plate in conjuction 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 were set on the rheometer in order to complete the testing:

Steady Stress Sweep:

Sweep Mode: Logarithmic

Initial Stress = 0.1 dynes/cm^2

Final Stress = 10000 dynes/cm^2

Points per decade = 10

Maximum time per data point: 10 sec

Temperature: 85^{0}C, 90^{0}C, 95^{0}C, 100^{0}C, 105^{0}C, and 110^{0}C respectively

Delay = 180 sec (to equillibrate sample)

Steady Stress Sweep test: In this test a range of stress levels, each at constant amplitude were 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 are 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).

Recommendations for improving the formulation were made. Continued rheometer tests to check the viscosity vs. shear rate characteristics of the ink.

2.3.2 Printability Testing

The inks were tested using a sampling of substrates that are used in publication gravure. The substrates to be tested include an LWC grade, a supercalendered grade, and a C1S board grade. These substrates were printed and then tested for printability. Density, Gloss, rub resistance, and mottle was measured in order to quantify the printability.

Density

These measurements were taken using a reflection densitometer. 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°.

Gloss

The specular gloss was measured using the Gardener 60° gloss meter. This apparatus measures the percentage of perfect reflectance of the ink film and the substrate. The gloss is measured in both the machine and cross-machine directions on both the solid printed and unprinted regions. Then the paper gloss was subtracted from the printed gloss, and the delta gloss was the difference.

Rub Resistance

This test was accomplished using the Sutherland Rub Tester. First, the density of a solid patch must be determined. That solid patch of print was attached to a one-kilogram block. Then, an unprinted sample of the exact same substrate was secured below the one-kilogram weight. The two samples are rubbed together for fifty strokes, and then the density was taken again. The rub resistance value was calculated as follows.

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

Mottle

Tobias and Associates manufacture the Tobias mottle tester. This machine measures the variation in either gloss or density across the width of the sample, while the variation in several rows down the sample was measured as well. A sample was attached to the rotating drum and then the scan begins. The scanning head moves to the scan start and begins to scan the density around the drum. The sample is rotated back around to the starting point while the scanning head moves across the sample to the next row to be measured. This occurs until at least 2000 data points have been taken. The numbers are indexed and averaged, then output on the screen for printing. The densitometer that this machine is equipped with is ten times more sensitive than that of a hand held densitometer. The parameters for the scans done on the mottle tester were as follows;

Number of readings to average per data point – 13
Space between data points in mm – 40
Number of data points per scan – 115
Length of scan in mm – 46
Digital filter window width in mm – 10
Filter pass – high
Width of sample – 1/3 of drum
Scans per sample – 20

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Hot Melt Ink (HMI) Formulations

The mixing operations were carried out in the ink lab using a hot plate, a three-blade mixer, and a stainless steel beaker. The stainless steel prevents any foreign contamination of the inks from the heat breaking down the mixing container.

Table 4:

Characterization of Composites Based on 20 wt. % of Pigment Yellow 13 And Ethylene Vinyl Acetate Copolymers matrix

Composite number	Polymer matrix Type	Mixing temperature	Melt flow rate (g/10 minutes)	Melting point (°C)
1	Elvax 210	100	365-440	85
2	Elvax 220	120	134-180	105
3	Evatane 28-40	140	27-29	125

The carnauba wax was mixed with the polymer matrix at the following concentrations:

a. 5g of yellow polymer matrix and 10g of Carnauba wax, yielding a 33% mixture

b. 5g of yellow polymer matrix and 15g of Carnauba wax yielding a 25% mixture

c. 5g of yellow polymer matrix and 20g of Carnauba wax, yielding a 20% mixture,

The figures all represent the samples as the concentration percentages

The PE samples were mixed as shown

Table 5:

Characterization of Composites Based on 20 wt. % of Pigment Red 122 and Low Density Polyethylene

Composite number	Polymer matrix Type	Mixing temperature	Melt flow rate (g/10 minutes)	Melting point (°C)
4	LDPE Bralen VA-20-60	130	20	115
5	LDPE Bralen 200	130	200	115
6	LDPE Bralen 70-21	130	70	155

Again, The carnauba wax was mixed with the polymer matrix at the following concentrations:

a. 5g of yellow polymer matrix and 10g of Carnauba wax, yielding a 33% mixture

b. 5g of yellow polymer matrix and 15g of Carnauba wax yielding a 25% mixture

c. 5g of yellow polymer matrix and 20g of Carnauba wax, yielding a 20% mixture,

The figures all represent the samples as the concentration percentages

3.2 Rheology Measurement

The samples that were measured were inks that contain Polyethylene (PE) and Ethyl Vinyl Acetate (EVA) as the respective polymers used to disperse the pigments. The pigments accounted for 20% of the total weight of the ink samples. Compared with common practice, this is approximately double the recommended amount of pigment for a process color ink. A representative rotogravure ink might have 15-20% of a pigment base. This base dispersion contains nearly 50% solids dispersion. The rest of the ink consists of 45-50% vehicle and 35-40% solvent. The inks that were measured had viscosities that could not possibly be printed on a gravure proofing press. These inks displayed critical stress values, where the viscosity began to decrease with increasing stress, but the viscosities associated with the critical values were on the order of 10^5 Poise, while the correct printing viscosity for gravure printing is in the range of 10^{-1} Poise. This suggests that these inks were not viable for a press test. This may be attributed to the degree of polymerization of the PE or EVA inks. The cause might be attributed also to the 20% pigment by weight in the dispersions. The polymer chain length also greatly influenced how well the ink film will lay down on the substrate. All of the ink samples had good gloss, but this observation might be misleading because of the overly thick ink film. The rheological data for the base ingredients used in the polymer matrices are shown below in figures 9 and 10. The data shows that the viscosity of the polymers does not change as the stress changes. The rheology data (Figure 9) indicate that the Evatane polymer is not usable in HMI formulation because of the extremely high viscosity in the range of 50,000 - 55,000 P, and not decreasing with increasing stress forces. The next set of inks focused attention on the Elvax 210 and Elvax 220 polymers. The viscosity data for the LDPE seems more promising, with a viscosity in the range from 6500 to 8000 P. The oscillation in viscosity at the lower stresses may have been caused by edge effects on the rheometer. However, they are not significant for stress rates associated with the stresses imparted on ink between the doctor blade and the cylinder on the press, typically in the range of 10^3 to 10^4 sec^{-1}. Initially, the polymers were chosen with no prior knowledge of the viscosity characteristics of the polymers. The reason for this is that in the industries where these polymers are used, such as injection molding, a property such as viscosity, as it is measured for printing inks, is not an area of interest. It is of some interest to injection molding. The viscosity needs to high but finite, i.e. it needs to flow without running. This seems to indicate the need to find a material that could significantly lower the viscosity of the thermoplastic polymers.

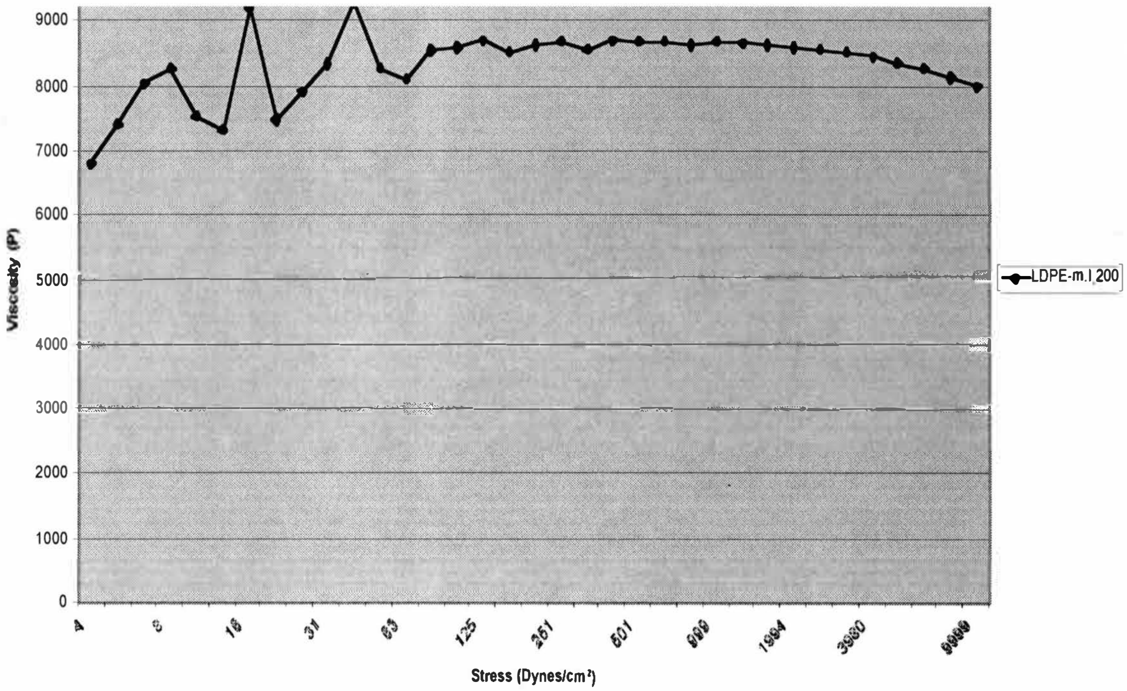


Figure 10: Viscosity v. Stress of LDPE with a Melt Index of 200 Used in HMI Formulations at 115C

The inks were then poured into an aluminum pan in order to solidify for easy transport to the rheometer lab. The result for three different temperatures for each of the three different formulations for each the PE and EVA. They were mixed as follows:

- 5g of yellow polymer matrix and 10g of Carnauba wax, yielding a 33% mixture
- 5g of yellow polymer matrix and 15g of Carnauba wax yielding a 25% mixture
- 5g of yellow polymer matrix and 20g of Carnauba wax, yielding a 20% mixture,

- The figures all represent the samples as the concentration percentages

This indicates that the viscosity can potentially be achieved for gravure printing if the temperature is increased. However, the rheometer was limited to 120°C, so the inks could not be heated up any more to check the effect on viscosity. In order to lower the viscosity, a carnauba wax was used. They were mixed under heating and then the rheology measurements were performed again. After the carnauba wax was mixed into

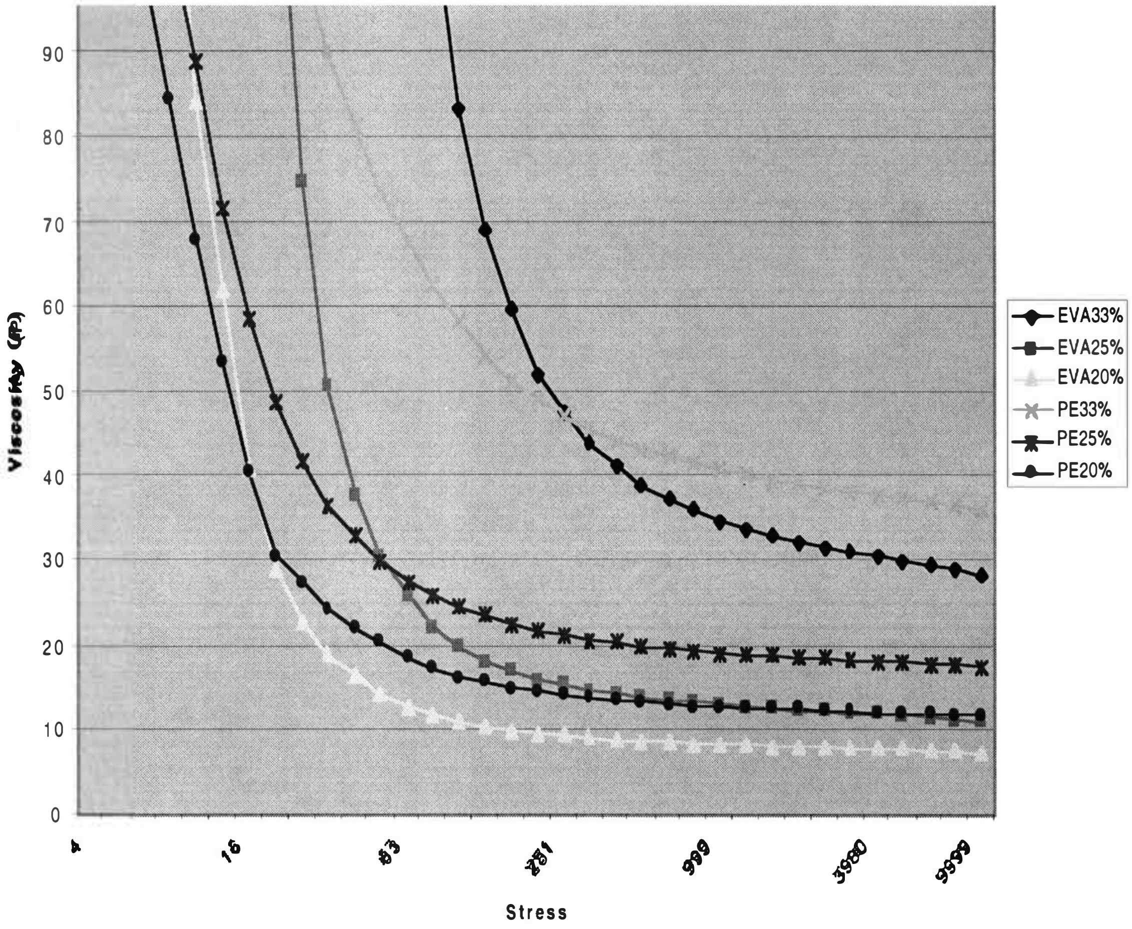


Figure 12 Viscosity v. Stress of HMI Formulations With Carnauba Wax at 95C

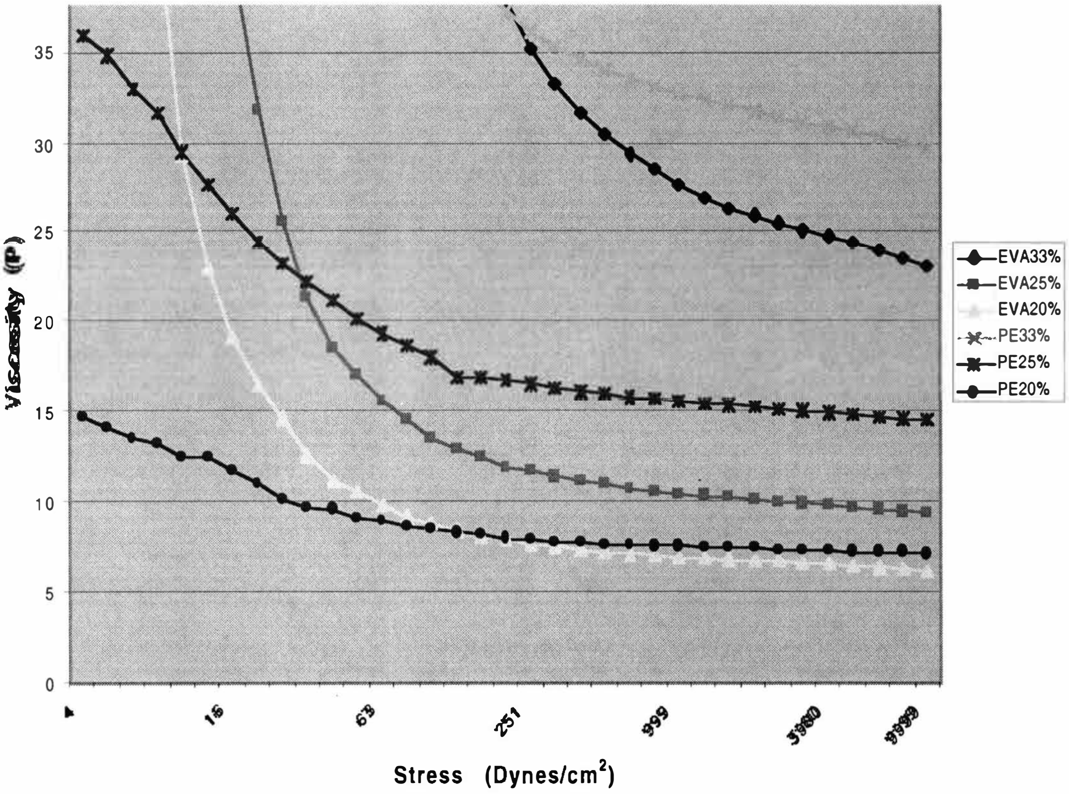


Figure 13: Viscosity v. Stress of HMI Formulations With Carnauba Wax at 100C

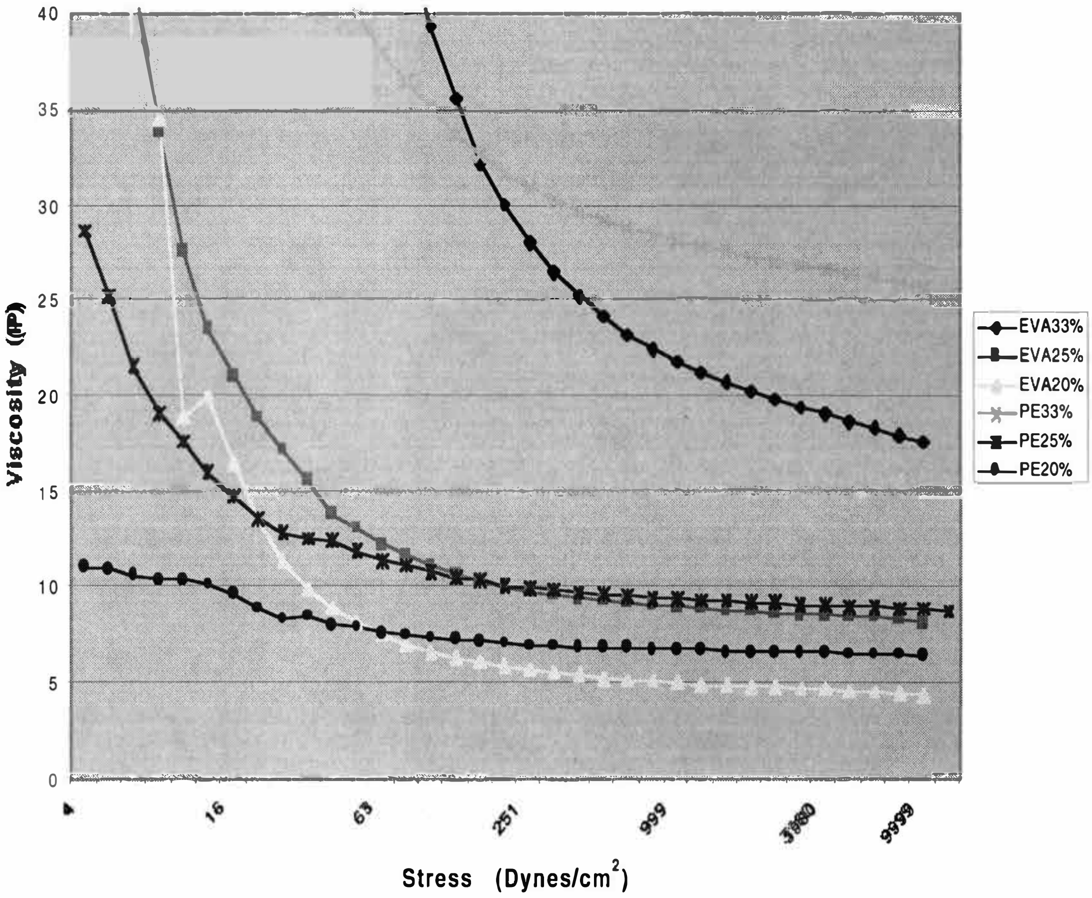


Figure 14: Viscosity v. Stress of HMI Formulations With Carnauba Wax at 105C

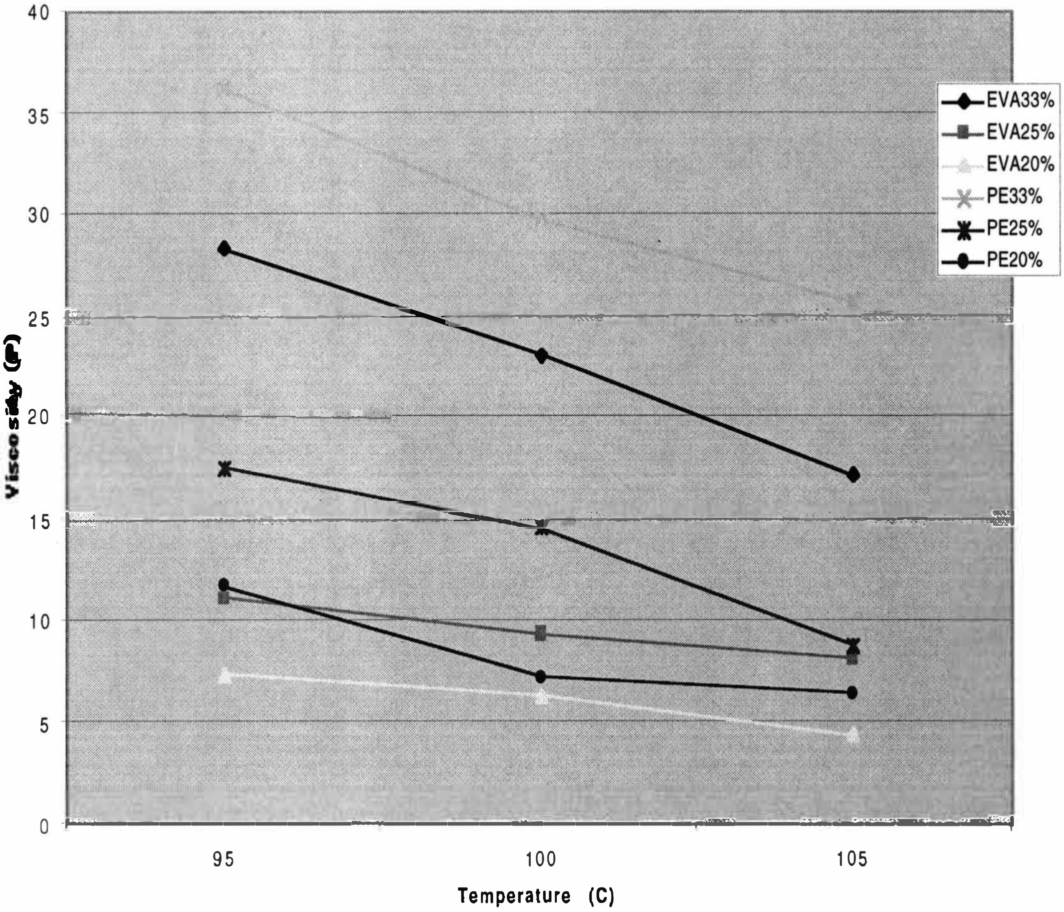


Figure 15: Viscosity v. Temperature of HMI Formulations With Carnauba Wax

3.3 Printability

Only the HMI formulations with Carnauba wax were printed. The printability study utilized the drawdown method with a #3 Mayer Rod. Three different substrates were used. SBS board, supercalendered paper (SCA), and light-weight coated paper (LWC). The density readings are shown in figure 16. The EVA inks had slightly higher densities than the PE inks, and in all of the HMI formulations, the density decreased as the amount of Carnauba wax increased, in both the EVA and PE samples as well as the different substrates. The PE and EVA inks had good gloss and little show through on the SBS board, which indicates that the inks did not migrate into the sheet. This might be attributed to the fact that the pigment ratio was too high in the ink and there was no chance for the pigment to migrate into the substrate. The density readings attained for the drawdowns of the PE and EVA yellow inks were high enough to indicate that the ink film was too thick. The inks were mixed in the following ratios:

- 5g of yellow polymer matrix and 10g of Carnauba wax, yielding a 33% mixture
- 5g of yellow polymer matrix and 15g of Carnauba wax yielding a 25% mixture
- 5g of yellow polymer matrix and 20g of Carnauba wax, yielding a 20% mixture,
- The figures all represent the samples as the concentration percentages

The drawdowns performed on the new inks showed excellent gloss and rub resistance, on the C1S board, and the printability data is shown in figures 16 through 20. The behavior of the rub resistance data for the SBS board can be attributed to the fact that the ink is held up out of the pores of the sheet. The SCA and LWC sampled both absorbed a good portion of the wax, which made showthrough a problem. These inks were, however, formulated for packaging, which uses more board substrates than paper. The EVA densities were sufficient, even at the 80% carnauba wax concentration, on all

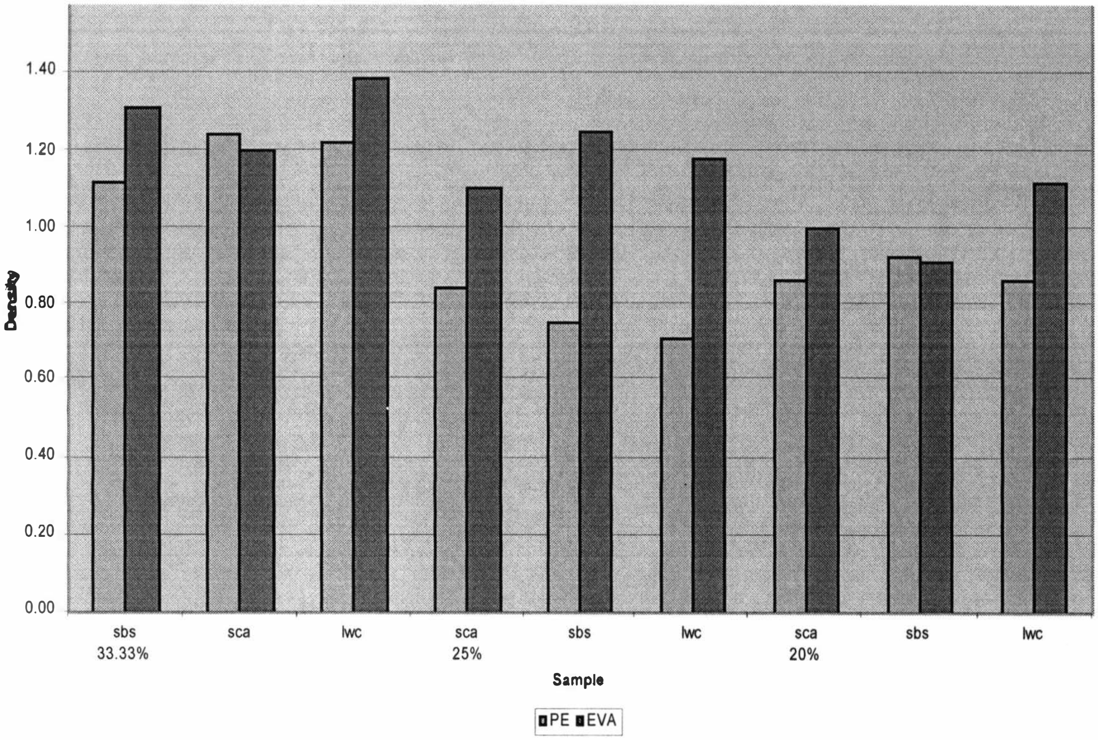


Figure 16: Reflective Density of Yellow HMI Formulations With Carnuaba Wax

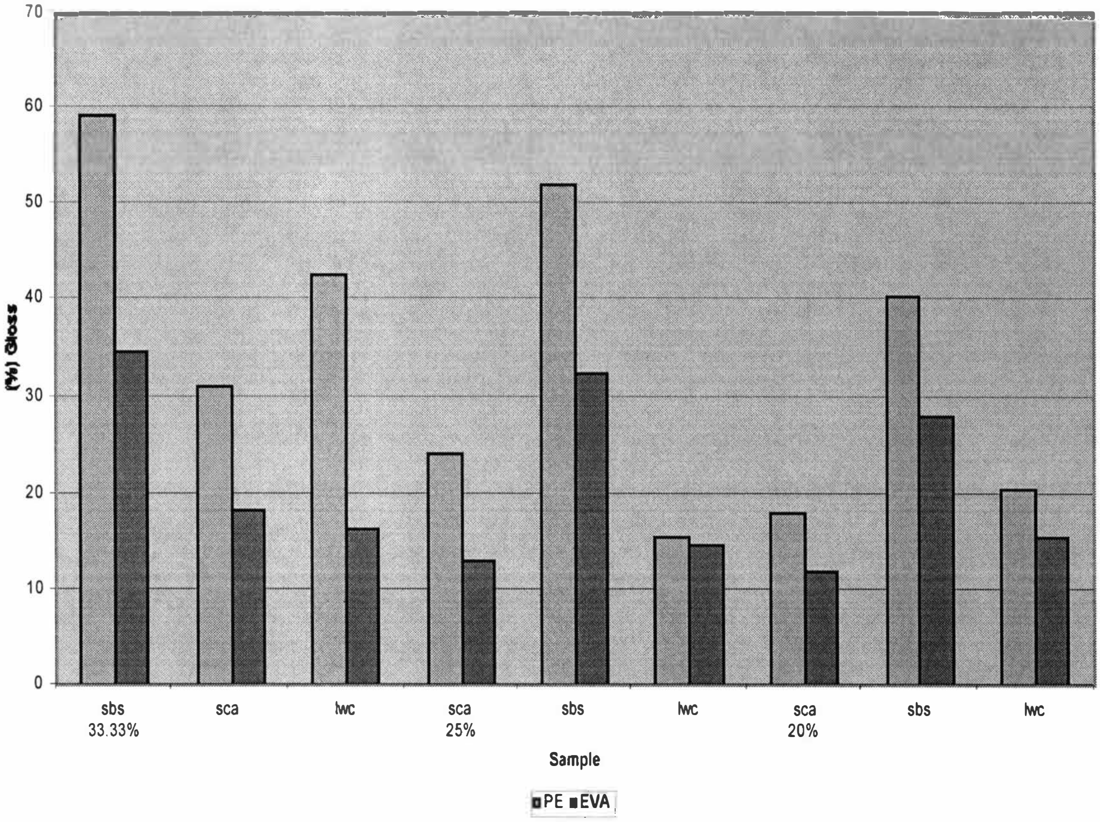


Figure 17: Print Gloss of Yellow HMI Formulations With Carnauba Wax

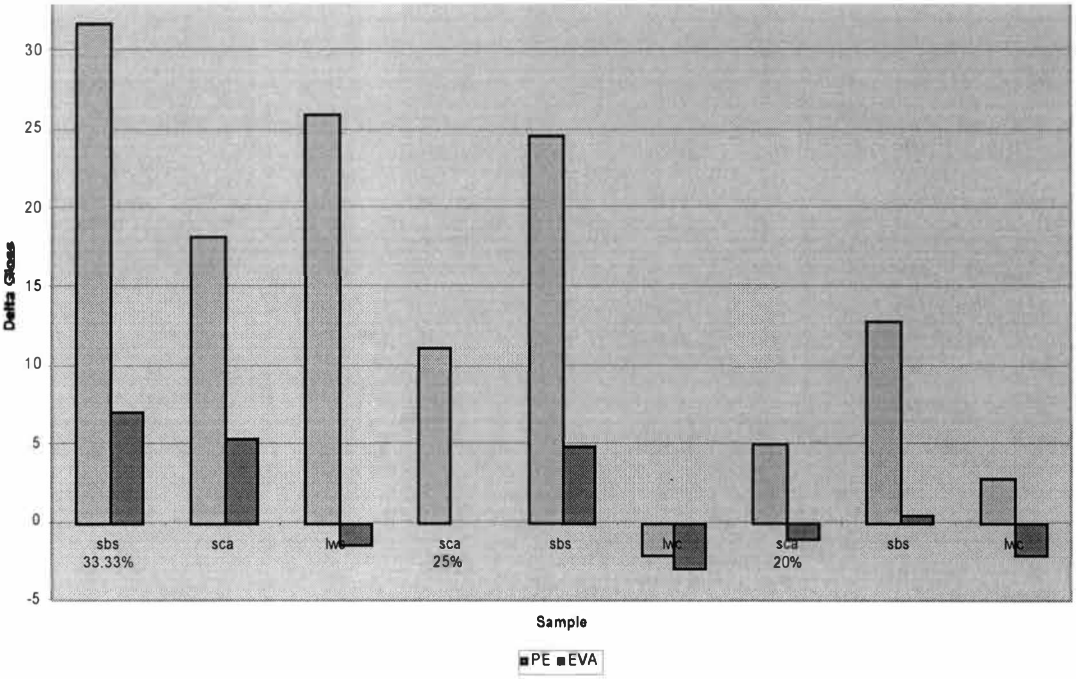


Figure 18: Delta Gloss of Yellow HMI With Carnauba Wax

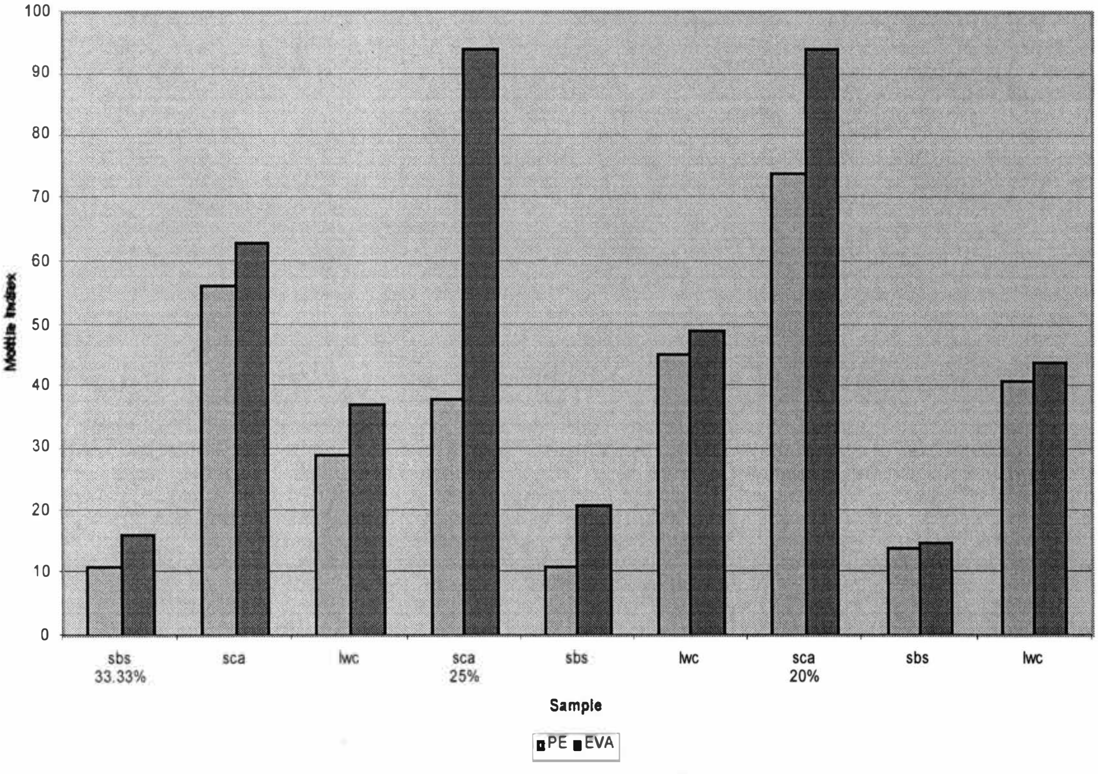


Figure 19: Mottle Index of Yellow HMI With Carnauba Wax

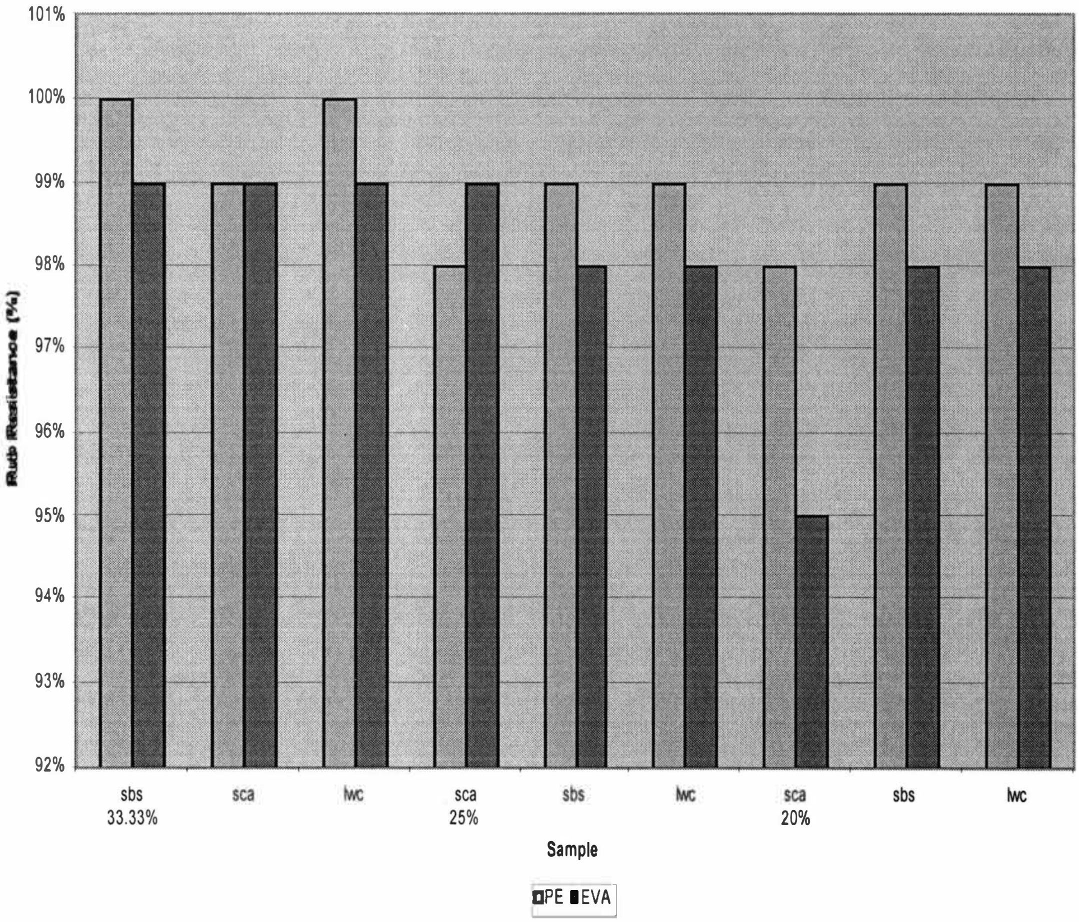


Figure 20: Rub Resistance of Yellow HMI With Carnauba Wax

three substrates. The PE HMI formulations had slightly low density readings for the 80% carnauba wax inks, around a 0.70 density, whereas the target density for yellow inks in gravure printing is around 0.95. The density data show that the SBS samples were better overall for the EVA drawdowns as compared to the PE drawdowns. However, the mottle test indicates that the PE samples were less mottled in appearance than the EVA samples, with the SBS samples having the lowest mottle values at around 11 units. The gloss readings were higher all around for the PE samples. The carnauba wax decreased the gloss as its concentration increased, the PE HMI samples on SBS board still had a gloss of about 40%, which is extremely good for this type of substrate. The gloss for the 80% carnauba wax formulation EVA sample on SBS was 28%. The

The gloss for the 80% carnauba wax formulation EVA sample on SBS was 28%. The specular gloss of the publication papers, SCA and LWC, were significantly lower, at 18% and 20% respectively. This indicates that there is a high amount of penetration into the open structure of the SCA and LWC substrate. The delta gloss readings were the highest on the SBS samples as well. This indicates that the lack of migration into the sheet highly contributed to the development of high gloss. The rub resistance was excellent overall, there was at least 95% resistance or better for all of the samples. The SBS samples lost very minimal ink, and the only spot to lose ink was the corners of the test sheets. These data indicate that the inks formulated have good end-use properties. When compared to various other attempts at hot melt ink formulation, there have been many obstacles to overcoming a lack of ink adhesion to the substrate. The inks that were made for this project displayed superior rub resistance to that of some commercial company research, which indicates a high amount of ink adhesion. The gloss readings indicate that the ink is being held on the surface of the SBS board, which is an important property for packaging ink. If the ink absorbs into the board to the point where it bleeds through the back of the sheet, it may come into contact with food product, which is a very undesirable property for packaging ink.

CHAPTER 4

CONCLUSION

The aim of this work was to formulate, analyze, and print hot melt ink formulations, based on PE and EVA chemistry. Polymer matrices were prepared in cooperation with the Slovak Technical University. The original inks were measured on the rheometer, but the viscosities were very high. Carnauba wax was determined to have a low enough viscosity to decrease the viscosity of the HMI formulations. The polymer matrix was mixed into the carnauba wax (33-20 % of original HMI), and then the rheology was tested again. After the rheological data indicated that the inks were low enough in viscosity, drawdowns were made and then the printability data were collected. The data indicate that the PE inks may have some viability in HMI formulation and printing. The new inks formulated using the carnauba wax showed excellent gloss properties on the SBS board in the printability study. The reflective densities of the samples were adequate in all of the samples except for the 80% carnauba wax concentration on the SCA paper. The yellow ink is almost viable as press ready ink. The PE is recommended over the EVA, because the EVA is not as temperature stable as the PE, and will degrade and yellow with a long exposure to heat. The next research projects should focus on the formulation of the magenta, cyan and black inks so that a process set can be formed and patent applications prepared. The need for better equipment that has the ability to test rheology is a pertinent topic for this paper. TA instruments makes a higher temperature attachment for the stress controlled rheometer that has the ability to heat to 180 degrees Celsius. This is a piece of equipment that will be necessary for the rheological data for the further ink formulations, and is available for use at Flint Ink Corporation

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