

Phase Change Inks for Rotogravure

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Abstract: The environmental and health problems caused by inks containing volatile organic compounds (VOC) call for new solutions in printing ink chemistry and technology. One of the approaches may be the hot melt ink, which is ink solid at ambient temperature and liquid in the moment of printing. Such ink contains no volatile solvent to be trapped in ink film or to produce VOC. In this work, hot melt ink for the rotogravure printing process based on ethylene vinyl acetate (EVA) chemistry was formulated, analyzed for rheological properties, and printed on publication and packaging substrates. The original inks based on ethylvinylacetate and polyethylene (PE) chemistry was too viscous for rotogravure. The polymer matrix was mixed into the carnauba wax and then the rheology was tested again. Carnauba wax significantly decreased the viscosity of hot melt formulations. Draw-downs were made on publication (supercalendered grade A and lightweight coated) and packaging (SBS board) substrates and then the printability data was collected. The EVA/carnauba wax inks showed slightly higher optical density than PE inks. Print gloss, delta gloss and rub resistance properties were better on PE inks. Also mottling was lower at PE inks. SBS board exhibited highest print and delta gloss and lowest mottle index. The deinking experiments of hot melt ink and commercial toluene based ink were done. Slightly better optical properties were found on LWC paper deinked from hot melt ink than on that deinked from toluene-based ink.

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Introduction

The hot melt inks, or phase-change inks found their utilization in digital printing technology. Colored waxes are brought into the contact with the substrate and a thermal head. The thermal head is digitally addressed and the arrays of pixels must heat up and cool down at frequency of around 3000 cycles per second to give acceptable printing speed (Thompson, 1998). 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. Phase-change inks have advantages over conventional inks because they do not contain volatile organic compounds - VOC's (Griebel, 1992a). However, this is not the only advantage of 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 (Griebel, 1992b).

The conventional hot melt colored ink used in a heat transfer layer of a heat transfer recording material contains an ink binder comprising a wax, a dispersant and a resin and a coloring component (Fujiyama, 1999). Waxes and polymers (resins) form semi- crystalline vehicles. These vehicles, when solidified, create large spherulitic structures. Control of the spherulite size during solidification is very critical for the image quality and durability. Large spherulites would lead to hazy and brittle prints. The spherulite size should be the same order as the wavelength of visible light.

The resins (polymers) contained in the vehicle ensure the adhesion of ink to the printed substrate, and simultaneously have the functions to control the viscosity of ink at the time of melting and to impart transparency to the ink by inhibiting the crystallization of wax. 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, in order not to decompose and form deposits on the printing head (Sawada, 2000). Many chemical families of resins can be employed in hot melt inks, such as: polyamide-, terpene-, acrylic-, polyethylene- or oxidized polyethylene-, epoxy -, urethane-, or isocyanate-derived resins. Structurally, they can be homopolymers, or heteropolymers, linear or crosslinked hybrid polymers, and/or reversibly crosslinked polymers.

Waxes are usually selected from the family of petroleum waxes, plant waxes, animal waxes, synthetic hydrocarbon waxes, higher fatty acid, higher alcohol, and their derivatives. The petroleum wax consists of paraffin wax and microcrystalline wax. The most important synthetic hydrocarbon waxes are a polyethylene wax and a Fisher-Tropsch wax. The main representatives of plant

waxes are candelilla wax and carnauba wax. The most important animal waxes are bees and lanolin wax.

Coloring agents that are incorporated in the ink composition include pigments and dyes. Any dye or pigment or combination of one or more dyes or pigments may be used as long as the colorant can be dispersed in the ink composition and is compatible with the other components of the composition. Colorant may be selected from pigments, dyes, metals, and metal oxides (Sawada, 1999).

Various additives may be added to phase change ink formulation. To prevent thermally induced oxidation from occurring in ink molten state, antioxidants are added to the formulation. Lightfastness components protect the printed images from oxidation (Breton, 2000), UV absorbers from UV degradation, crease agent from creasing. The biocide protects the hot melt inks from color and odor change, destabilization phenomena, pH and viscosity change. Corrosion inhibitors may be added to inhibit the corrosion of the metal that comes in contact with the phase change ink. The possible composition of phase change ink for digital printers is given in the **Table 1**.

Table 1: Composition of phase change ink for digital printing

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

In the history of rotogravure printing, water-based inks preceded solvent-based inks, but they were abandoned because of slow drying rates. Since the beginning of the 1960s, toluene has been used as a solvent in most rotogravure publication printing plants. Toluene was the most likely cause of the lung cancer (Wiebelt, 1999), genotoxicity (Peclova, 2000; Nise, 1998) and neurotoxicity (Seeber, 2000). For all of these health-hazard problems, water-based inks are coming into use again. The use of water-based inks for packaging and product gravure grew from 26% in 1993 to 50% in 1997 (Kasunich, 1998). There have been some technical problems related to the application of water based inks to the high press speed, such as relatively low drying rates, issues such as printability on a variety of substrates, and their cost/performance ratio. However, aqueous formulations have also serious environmental disadvantages, as they cause

greater water pollution and consume more energy (Schmidt, 1996). UV gravure inks are not yet a reality (Teng, 1998).

Phase change inks have not yet been accepted in the rotogravure printing industry because not enough research and development work have been done to formulate optimum performance hot melt inks. Therefore, the aim of this work was to formulate hot melt inks for the rotogravure printing process.

Experimental

Materials

Pigment chips: Magenta – Quinacridone PE Flush Red 122 L280013, Yellow – AAMX Yellow 13 L751349D28707, Pthalo Blue Green Shade L490714D59565, commercial pigment chips covered with polyethylene (Sun Chemical Co.) were used for inks formulation.

Polymers: EVAC copolymer A – 85 °C – melt index 400, EVAC copolymer AA – 85 °C – melt index 250, EVAC copolymer B – 105 °C, EVAC copolymer C – 120 °C, EVAC copolymer D – 124 °C, Carnauba Wax– from Michelman, Inc.

Additives: Slip agent – Structol.

Blending of Inks

Melt blending of polymer matrix with pigments (hot melt inks) was carried out using a Brabender Plasticorder fitted with a W50 chamber and cam blades. Mixing time was 10 minutes, mixing torque data was reported after the first minute of mixing after stabilization of the torque response. Mixing temperature was varied from 120 to 190°C. All composite samples were compression molded into plates of 3 mm thickness for further printing and rheology measurement.

The polymer matrix plate (EVAC A with pigment) 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. A 33.3%, a 25%, and 20% dispersion of EVAC A with pigment and the Carnauba wax were prepared.

Printing and Printability Analysis

The drawdowns were done using a Meyer rod #3. The following printing substrates were used: Light weight coated –33 lb/ream (LWC), Solid Bleached Sulfate board – (SBS), Super-calendered A grade (SCA) – 34 lb/ream.

Printability analysis was done by measuring optical density (X-Rite 408 reflection densitometer), specular print gloss and delta gloss (Gardener gloss meter with 60 degree geometry), rub resistance (Sutherland rub tester), and mottle index (Tobias Mottle Tester).

Rheology

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 to achieve the necessary temperatures for the inks to be liquefied. The following conditions were used: Sweep Mode: Logarithmic; Initial Stress = 0.1 dynes/cm²; Final Stress = 10000 dynes/cm²; Points per decade = 10; Maximum time per data point: 10 sec; Temperature: 85 °C, 90 °C, 95 °C, 100 °C, 105 °C, and 110 °C, respectively. Delay = 180 sec (to normalize the sample).

Deinking

The samples (pieces ca 5x5 cm) were soaked in the water (50 °C) for 10 min. Samples were put into a laboratory mixer (Waring Model 47 BL84 CB6 Heavy Duty Blender). The repulping was done at a temperature of 50 °C at 2.5% consistency at the lowest RPM. After 1 minute of repulping the pH was adjusted with NaOH to the value of pH = 10.0. The repulping was continued for 4 minutes at the same pH. The final temperature was 50 °C, due to the heat generation during the agitation process.

The flotation cell (Adirondack, Format TM Flotation Deinking Cell, 29.1 L) was used at a consistency of pulp slurry of approximately 0.7%. The temperature was adjusted with direct steam to 40 °C. The slurry circulated at 57 L/min. The feed sample was taken. Non-ionic surfactant was added (Lionsurf 729, 0.125% on dry solids) and the slurry was allowed to circulate for 5 minutes. After 5 minutes of circulation the air flow was opened with the rate of 225 L/min. The foam from the center of the flotation cell was collected and weighed. After 10 minutes of flotation the air input was closed and the accept sample was taken.

Analysis of Deinked Pulp

Handsheets from slurry before and after flotation were made in accordance to TAPPI Standard T 205. Brightness was measured in accordance to TAPPI Standard T 452. Rejects were not diluted. The pads from rejects were formed by filtering the samples (cca 75 mL) using a Buchner funnel (Whatman 42 Ashless Filter Paper). The solids were determined by drying the samples in a laboratory CEM Lab Wave 900 microwave.

Results and Discussion

The polymer blends for hot melt inks (HMI) for rotogravure printing were prepared on the basis of ethylene- vinyl acetate (EVA) or polyethylene (PE) chemistry. The starting formulations were based on 20 wt. % of pigment (in this case Yellow 13) and EVA (PE) matrix. Properties and processing conditions of polymers are given in the **Table 2**.

Table 2: Selected properties of the polymers chosen for starting formulations

Polymer Matrix Type	Melt Flow Index (g/10 minutes)	Melting Point [°C]	Ink Blending Temperature [°C]
Elvax 210	365-440	85	100
Elvax 220	134-180	105	120
Evatane 28-40	27-29	125	140
LDPE Bralen	200	130	200

The commercially available thermoplastic polymers are usually rheologically characterised by the manufacturer using the melt flow index (MFI). It is a single-point viscosity measurement at a relatively low shear rate and temperature (Shenoy, 1996). Although there exists an inverse relationship between zero shear viscosity and MFI, the addition of pigment changes the whole situation. Therefore, the measurement of the ink viscosity at the shear rates close to those achieved at the moment of printing was done using DSR 5000 Stress Rheometer. The hot melt ink formulations using Evatane 28-40 had viscosity oscillating in the range of 45,000-50,000 P and Elvax 220 in the range of 7, 000-9,000 P (**Fig. 1**) and LDPE Bralen had viscosity 6,500-8,000 P (data not shown). The lowest viscosity range (3,000-3,500 P) was found at ink formulated with Elvax 210 polymer. However, all of these HMI formulations exhibited a much higher viscosity than that used for the gravure printing.

Therefore, the next goal was to reasonably decrease the viscosity of HMI. This aim was achieved by blending starting formulations with the Carnuba wax. The Carnuba wax was chosen because of its relative low melting range (82-86°C). It contains mainly fatty esters (80-85%), free alcohols, (10-15%), acids (3- 6%),

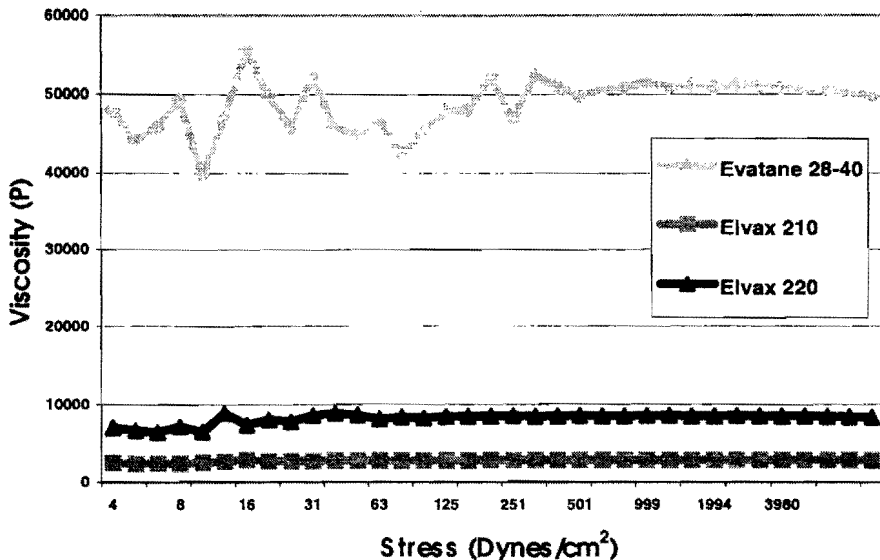


Figure 1: Viscosity vs. stress of EVA polymers. Measurements were done at 95 °C.

hydrocarbons (1-3%), esterified fatty dialcohols (up to 20%), hydroxylated fatty acids (up to 6%) and cinamic acid - up to 6% (Shenoy, 1996). The rheology of Carnauba wax was measured at 95°C (Fig. 2). Steep viscosity drop was found at stresses higher than 12 Dynes/cm² to 2P at 40 Dynes/cm² and then dropping only slightly with increasing shearing rates. The Carnauba wax was mixed with the starting formulation polymer matrix at the following concentrations: 5g of yellow polymer matrix Elvax 210 (LDPE Bralen) and 10g of Carnauba wax, yielding a 33% mixture; 5g of yellow polymer matrix Elvax 210 (LDPE Bralen) and 15g of Carnauba wax yielding a 25% mixture; 5g of yellow polymer matrix Elvax 210 (LDPE Bralen) and 20g of Carnauba wax, yielding a 20% mixture. All of the figures represent the percentage weight.

The viscosities of the hot melt formulations measured at all three temperatures (95-105°C) showed a similar trend – steep drop of the viscosity to almost constant value, not changing with further stress increase from about 250 Dynes.cm⁻². For example, the 25% Elvax blend with Carnauba had 75 P viscosity at 95 °C and at the shearing stress of 35 Dynes. cm⁻² and this value dropped to the value of 12 P at the shearing stress of 250 Dynes. cm⁻² (Fig. 3). This viscosity can be even lowered by the temperature increase (Fig. 4). Temperature rise of 10 degree reduced the viscosity of this hot melt ink formulation from 12 to 8 P (Fig. 4).

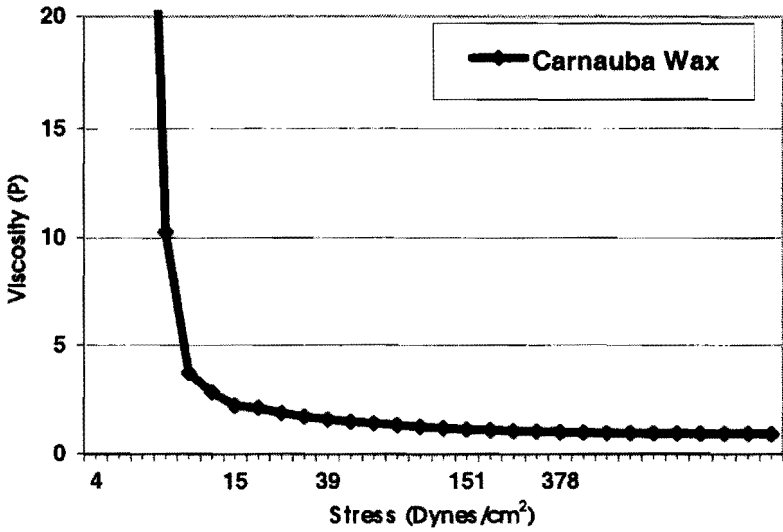


Figure 2: Viscosity vs. stress of carnauba wax used for HMI formulations measured at 95 °C

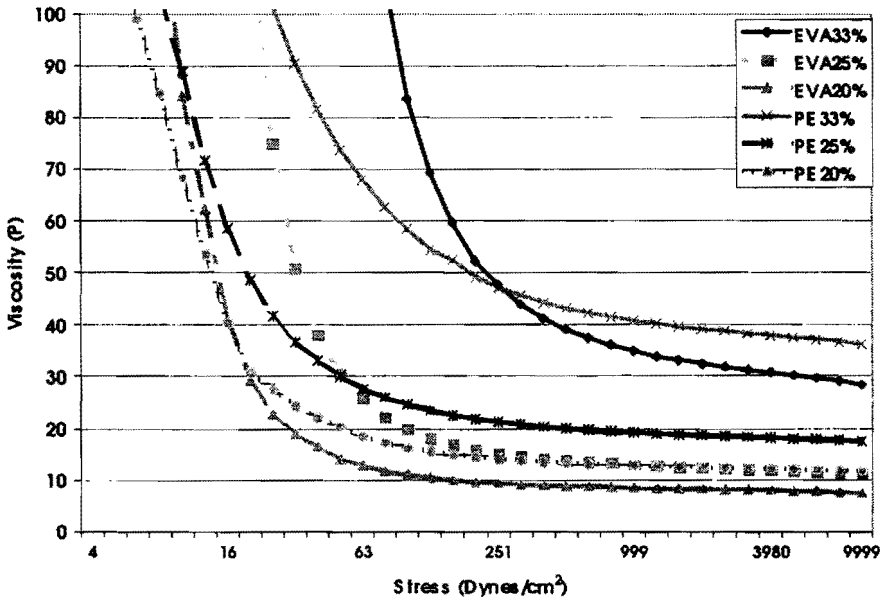


Figure 3: Viscosity vs. stress of HMI formulations with carnauba wax at 95 °C

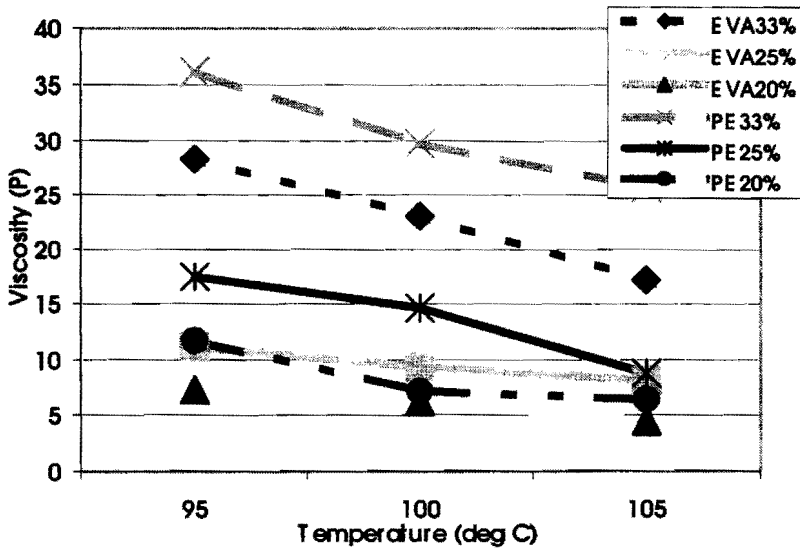


Figure 4: The change of viscosity of Elvax 210/carnauba HMI formulations due to the temperature. The viscosity measurement was taken at constant stress of 250 Dynes.cm⁻².

These blends were used for printing trials. Three substrates were printed - lightweight coated (LWC), supercalendered (SCA) and Solid Bleached Sulfate board - (SBS). The print density (Fig. 5) was excellent even after blending with the Carnauba wax. EVA formulations had slightly higher reflective densities than LDPE formulations on all substrates tested and at all formulations. Print gloss (Fig. 6) was higher on PE than EVA formulations (59 to 40% on SBS decreasing with increasing Carnauba wax content). This is probably due to excellent ink holdout properties- due to phase change it does not have the ability to penetrate into the paper pore structure. Delta gloss (Fig. 7) was much higher in PE formulations (32 to 12% decreasing with increasing wax content). Negative delta gloss was found at LWC and SCA when printing with EVA inks (Fig. 7). Mottling was quite low at all inks and substrates. However, mottling was in all cases slightly higher on EVA inks than on LDPE inks and this was true for all substrates and formulations tested (Fig. 8). Mottle index was 15-95 at EVA, which is much lower than usually obtained when printing with standard toluene inks (Pekarovicova, 2000). Mottling was noticeably lowest at SBS board with all ink formulations (Fig. 8). Adhesive and rub resistance properties

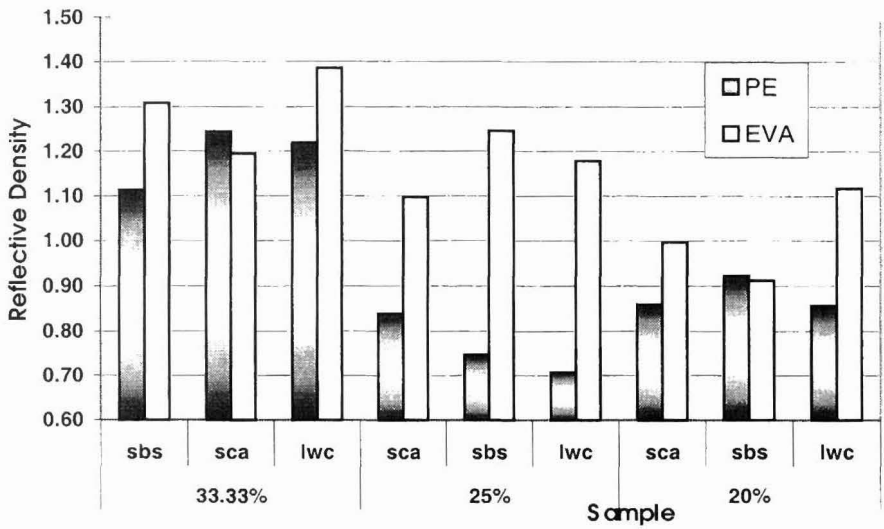


Figure 5: Reflective density of solid HMI print at different paper substrates

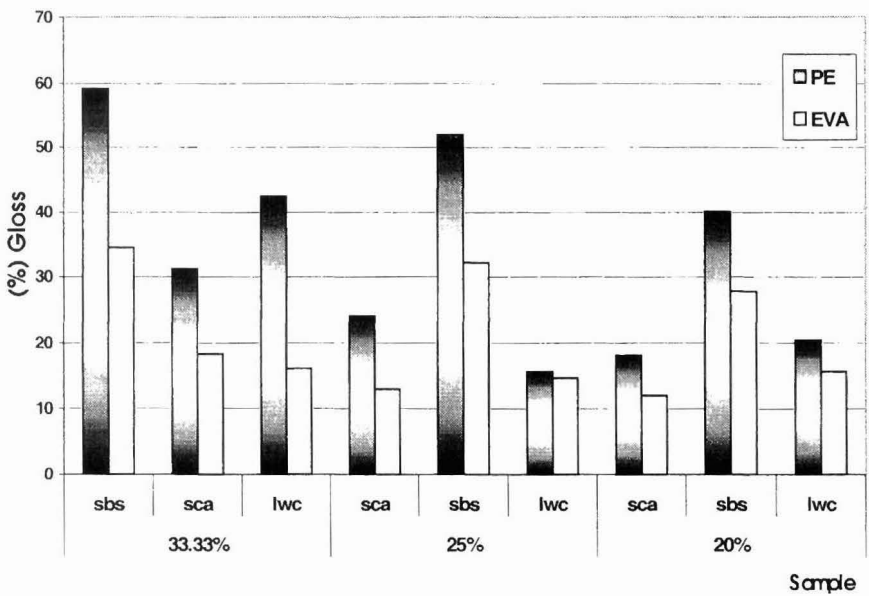


Figure 6: Specular gloss of solid HMI print on different paper substrates

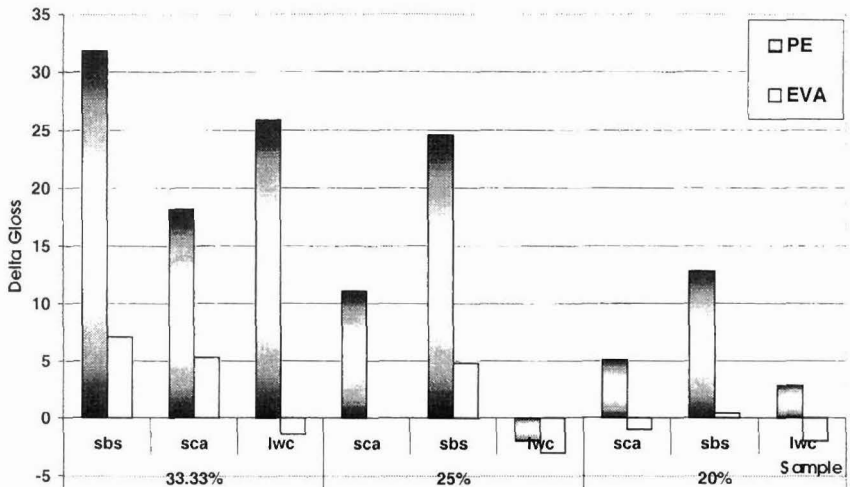


Figure 7: Delta gloss of yellow HMI with carnauba wax at different paper substrates

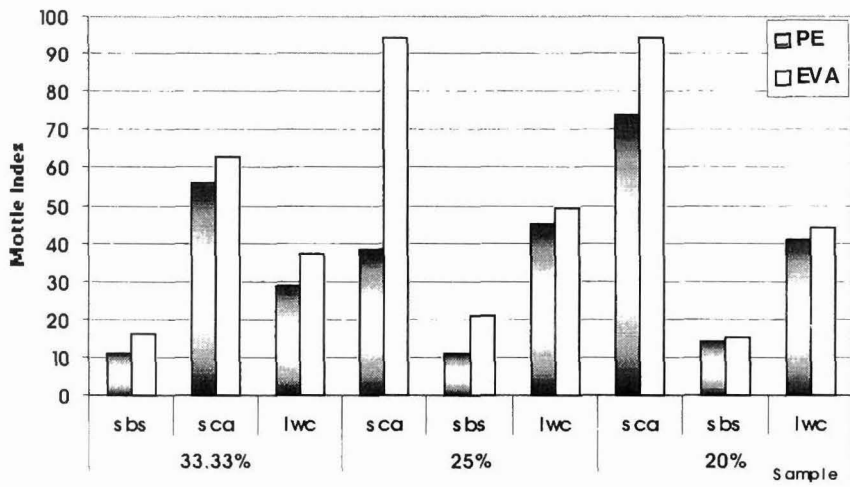


Figure 8: Mottle index of yellow HMI with carnauba wax at different paper substrates

were slightly better on LDPE inks (Data not shown). LDPE formulations had rub resistance in the range 100%- 98%, being worst at SCA substrate (98%). Rub resistance of EVA inks was 99-98%. However, ink show-through was observed on publication grades (LWC and SCA), which may be connected with slow printing speed of draw-down technique of printing (Data not shown).

Overall, very good printability results were achieved. HMI resulted in sufficient print density, very high print gloss, low mottling and excellent rub resistance. Especially, specular gloss values are very promising. Ink holdout is better than in conventional inks, due to phase change of HMI. Ink does not penetrate into pore structure of substrate. However, further work is necessary to tune up the inks viscosity, especially when process colors will be printed.

Flotation deinking of commercial toluene based ink printed samples on LWC substrate and samples printed with EVA/Carnauba hot melt ink on the same substrate were carried out. The deinking experiments were performed in Adirondack, Format™ Flotation Deinking Cell, at a consistency of approximately 0.7% with the addition of non-ionic surfactant Lionsurf 729. GE

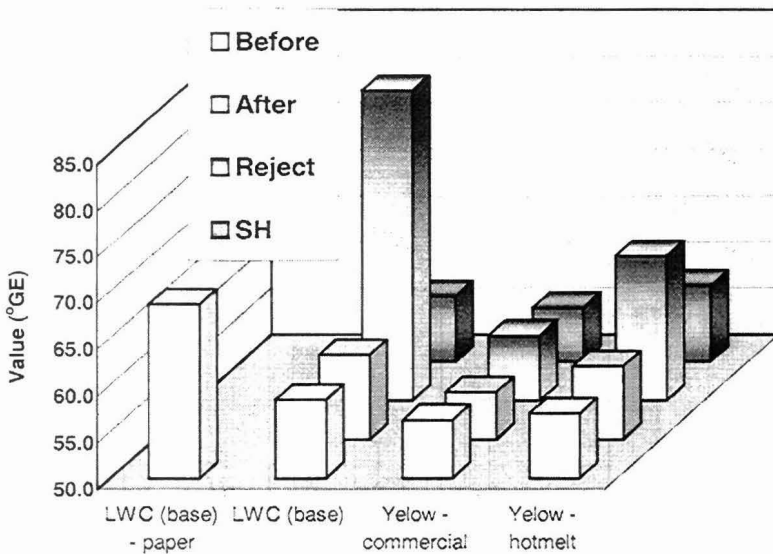


Figure 9: Comparison of LWC paper brightness after deinking yellow EVA/carnauba hot melt ink formulation and commercial toluene-based yellow ink (SH= side hill accepted fiber fraction)

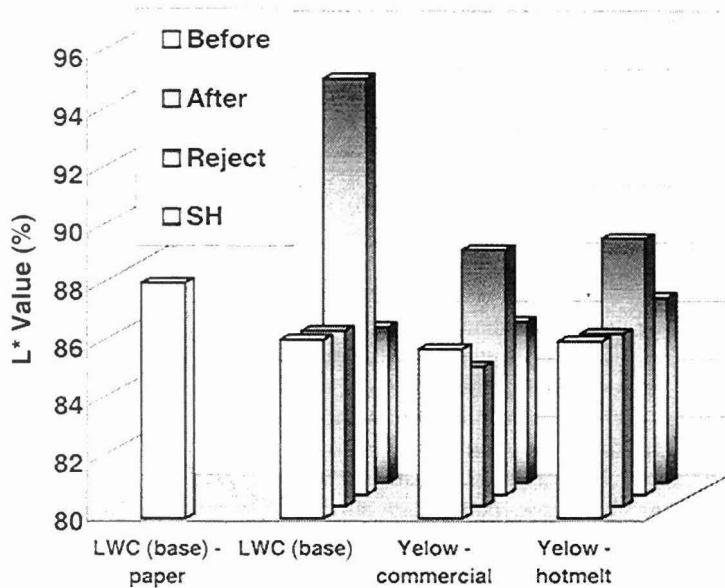


Figure 10: Comparison of LWC paper L* value after deinking yellow EVA/carnauba hot melt ink formulation and commercial toluene-based yellow ink (SH= side hill accepted fiber fraction)

brightness of base LWC sheet was much higher than that of repulped LWC, most likely due to the filler loss (**Figure 9**). GE brightness of sample printed with HMI after flotation deinking was higher than that found on sample printed with commercial toluene-based ink. CIE L*a*b* values of deinked pulp accept and reject were measured, too. The most meaningful is value L* depicting lightness of the substrate. The higher the L* value, the lighter the object is. CIE L* value of LWC paper after flotation deinking was higher than L* for deinked LWC paper printed with commercial toluene-based ink (**Figure 10**).

CIE b^* value (yellowness) of paper printed with HMI after flotation deinking was lower than that of paper printed with toluene-based ink (data not shown). It means, that the deinked HMI substrate was less yellowish than the substrate printed with commercially available yellow toluene ink. All these factors show that it is possible to recycle and de-ink the HMI printed paper. Somewhat better optical properties were found on hot melt ink deinked LWC paper than on toluene-based ink printed and subsequently deinked LWC.

Conclusion

The polyethylene and ethylene vinyl acetate hot melt ink formulations were made. The Elvax 210 was found to be the most suitable polymer for hot melt ink formulation from all EVA polymers tested and polyethylene PE - Bralen SA 20 was the best of all polyethylenes tested. However, their viscosity was too high for gravure printing. To reduce the viscosity of HMI formulations, Carnauba wax was used. Printability analysis showed very good reflective density, excellent print gloss, low mottling of HMI, and excellent rub resistance. The high print gloss is probably due to decreased ability of the ink to penetrate into the substrate, so that good ink lay is achieved. Overall, PE formulations had slightly better printability properties than EVA formulations. Deinking of hot melt inks was compared to the deinking of commercial toluene-based rotogravure ink. Hot melt inks were deinked in flotation cell and handsheets were tested for GE brightness and CIE $L^*a^*b^*$ values. Somewhat better optical properties were found after deinking of LWC paper printed with HMI compared to LWC paper printed with toluene-based ink.

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