



Hot-Melt Inks for Rotogravure: Formulation, Printability and Rheology

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Graduate Student Award
2002 GEF/Sun Chemical Technical Essay Contest**

Abstract

A new generation of phase change or hot-melt ink was formulated that is solid at ambient temperatures and liquid at the moment of printing. Inks were formulated on the basis of EVA (Ethylene Vinyl Acetate Chemistry) and printed using a K-Printing Proofer. Selection of the best formulations was done on the basis of the inks' rheologies. Screened inks having the best properties were printed on the K-Printing Proofer. More detailed printability analysis was done after printing, including reflective density, specular gloss, and rub resistance. The rheology of the best formulation was studied and compared to conventional rotogravure inks.

Introduction

Gravure inks are made by blending pigments, solvents, resins (or binders), and other 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 (U.S. EPA, 1994). Gravure ink frequently uses materials containing VOCs (Volatile Organic Compounds), and some may contain HAPs (Hazardous Air Pollutants). Small printing facilities may not have an environmental impact by themselves; however, when combined with other sources of pollution, they can affect the overall environmental quality (U.S. EPA, 1994).

Toluene, one of the frequently used vehicle solvents by ink manufacturers, is a VOC that causes acid rain, smog, air toxins, ozone formation, and global warming (U.S. EPA, 1994, 1999, 1997). VOCs can be highly flammable, can result in toxic and narcotic effects when inhaled, and can contribute to the formation of tropospheric ozone and smog, resulting in differences in weather patterns (U.S. EPA, Chap.1: Health and Welfare Concerns). Due to ozone exposure, there are increased admissions to hospitals and emergency rooms for respiratory problems. Ozone exposure can also lead to respiratory infections, irreversible changes in lung structure and lung inflammation, and can aggravate pre-existing respiratory diseases such as asthma.

A better way to reduce pollution is to prevent it in the first place. Pollution prevention includes using raw materials more efficiently and replacing toxic materials with non-toxic ones (U.S. EPA, 1999). Using hot-melt inks (HMI) could possibly be the solution. These inks do not need a drying system; therefore, the paper web can be shortened, saving white paper waste and reducing the makeready printed waste and press running waste. Money is also saved on the drying system's operation and maintenance. Current technology is able to trap and recover up to 93 percent of the solvent being used, but the rest is being emitted into our environment. The use of HMIs will eliminate the creation of VOCs.

Rotogravure hot-melt inks are based on waxes, resins, vehicles (optional), and antioxidants (optional). Table 1.

Waxes can be used in the mixture of two or more, and contained in the ink composition in an amount ranging from 5 to 95 percent by weight. If it is less than 5 percent by weight, properties of other additives may come out overall, and the ink composition may have a higher or unsettled melting point, which will tend to make the ink composition not melt sharply. If it is more than 95 percent by weight, the ink may have an insufficient melt viscosity, so that it may adhere to printing paper with difficulty (Sawada, Hidemasa, 1999). Waxes are usually selected from the family of petroleum waxes, plant waxes (carnauba wax), animal waxes, higher fatty acids, synthetic hydrocarbons, and their derivatives (Malhotra, Shadi L. 2000).

Resins ensure the adhesion of ink to the print substrate, control ink viscosity at the time of melting, and impart ink transparency by inhibiting the crystallization of wax. Resins used in phase-change inks generally have melting points in the range of about 60°C to 140°C. They should be thermally stable in a molten state so that gaseous products are not generated (Sawada, Hidemasa, 2000). Resin is present in the ink composition in an amount ranging from 5 to 60 percent. If it is less than 5 percent by weight, the ink composition cannot ensure a sufficient melt viscosity, and if it is more than 60 percent by weight, the ink may have a high melt viscosity, making it difficult to perform good ink ejection at operation temperature (Sawada, Hidemasa, 1999). Resins for phase-change inks are usually selected from the family of amide resins, urethane resins, terpene resins, polyamide resins, and isocyanate-derived resins.

Hot-melt inks contain low molecular weight vehicles such as alcohol compounds. These vehicles deliver homogenous dissolution of dyes, good flow properties, sharp melt/solidification properties, and good edge definition and dot size. A very sharp melting point is achieved that, if desired, can be manipulated within a small temperature range. Vehicles might also be formulated using cyclic alcohol and aliphatic/aromatic alcohol.

Antioxidants are used to prevent thermally induced oxidation from occurring in the molten state during printing. The amount of antioxidant used is usually 0.1 to 1.0 percent by weight of the ink composition (King, Clifford R. 2000). They protect the images from oxidation and also protect the ink components from oxidation during the heating portion of the ink preparation process (Malhotra, Shadi L., 2001b). Generally used antioxidants

are pyrocatechol, eugenol, guaiacol, and butylated hydroxytoulene (Pekarovicova, Alexandra, 2001).

A lot of work has been done in hot-melt inks for digital printing processes; however, there is also a need to implement new, environmentally safe inks into rotogravure printing. The aim of this work was to formulate hot-melt inks for rotogravure and test their rheological and printability properties.

Experimental

Ink Components Used in Formulation of Hot-Melt Ink.

Pigments: Polyethylene flushes of pigments were used for all hot-melt ink formulations:

Diarylide yellow: AAMX Yellow 13 Polyethylene Flush (Sun Chemical Corporation, Product: L75-1349, 2000), Quinacridone Magenta: Polyethylene Flush Red 122, specific gravity: 1.4-1.5 (Sun Chemical Corporation, Product: L28-0013, 2000), Phthalo Blue Green Shade Copper: Trade name: Phthalocyanine15, Polyethylene Flush, specific gravity: 1.25 (Sun Chemical Corporation, Product: L49-0714, 2000).

These pigments display excellent transparency and color strength and are suitable for rotogravure ink formulations.

Polymer: EVA Polymer 2528 (ExxonMobil Chemical Co., 2000) was used for the formulation of the hot-melt inks. It is an ethylene-based polymer containing 27.5-wt percent Vinyl Acetate. It yields excellent adhesion properties, has excellent flexibility, exhibits good clarity and gloss, and can operate over a wide range of temperatures. It has excellent impact resistance, elasticity, and environmental stress cracking.

Physico-chemical properties:

Melt viscosity: 190°C.
Specific gravity: 0.937.
Refractive Index: 1.483.
Softening point: 169°C.
Tensile strength: 142°F.
Elongation: 100%.
Hardness: 48 shore.

Wax: Carnauba wax (Michelman Co., 2002) was used with an EVA copolymer for hot-melt ink formulation, mainly for the adjustment of melt viscosity. Carnauba wax increases lubricity, hardness, and scuff resistance without sacrificing finish, gloss, and clarity. It easily incorporates into coatings with simple stirring. High-speed mixing equipment may be used without affecting physical properties.

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

Components	Literature Source
Viscosity modifier Lowers Viscosity (Conc. 5 - 20 %)	Banning, Jeffery H., 2000
Antioxidant Prevents Oxidation (Conc. 1 - 10 %)	Kovacs, Gregory J., 1999
Resin/Polymers Imparts Adhesion (Conc. 5 - 60 %) Urethane resin, Urethane/Urea resin Acrylic resin Polyamide resin Polyethylene resin, Oxidized polyethylene Terpene resin, Terpene phenol resin, Polyester resin, Branched polyester Ethylene Vinyl Acetate resin Reversibly-crosslinked polymer Epoxy resin Isocyanate-derived resin	Banning, Jeffery H., 2000 Mizobuchi, Yoshikazu, 2000 Titterington, Donald R., 1999 Boils, Danielle C., 2000 Nishizaki, 2000 Baker, Richard, 1999 Fujiyama, Jitsunori, 1999 Matzinger, Michael D., 1999 Macholdt, Hans-Tobias, 2000 Titterington, Donald R., 2000
Wax Acts as Ink Vehicle (Conc. 5 - 60 %) Amide wax, Diamide wax Petroleum wax, Polyethylene wax Polyethylene oxide wax Colored urethane wax Fisher-Tropsch wax Montan ester wax Alcoholic wax, Ketone wax Maelic anhydride modified wax Isocyanate-derived wax Oxazoline Carnauba wax, Candela wax, Bees wax	Sawada, Hidemasa, 2000 Banning, Jeffery H., 2000 Sawada, Hidemasa, 2000 Titterington, Donald R., 1999 Matzinger, Michael D., 1999 Inaishi, Kouji, 1999 Sawada, Hidemasa, 1999a Sawada, Hidemasa, 1999b Titterington, Donald R., 1999 Boils, Danielle C., 2000 Matzinger, Michael D., 1999
Plasticizers Provides Flexibility (Conc. 1 - 15 %)	Wong, Raymond W., 2001

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

Components	Literature Source
Lightfastness antioxidant Protects Ink from Thermal Degradation (Conc. 1 - 10 %)	Breton, Marcel P., 2000 a
Low-molecular compound Acts as Ink Vehicle (Conc. 5 - 60 %) Liquid cyclic vehicle Triblock copolymer vehicle Water Non polymeric ester compound Thermoplastic vehicle Ketone Saturated fatty acid, Unsaturated fatty acid	Goodbrand, H. Bruce., 2001 Maekawa, Tsutomu, 2001 Lesani, Fereshteh, 2001 Malhotra, Shadi L., 2001 b Williams, Kevin G., 1993 Malhotra, Shadi L., 2000 Sawada, Hidemasa, 1996
Alcohol compound Acts as Ink Vehicle (Conc. 0.5 - 49 %) Cyclic alcohol Aromatic alcohol Higher alcohol-Tetracosyl, Octacosyl Monohydric aliphatic/aromatic alcohol Amino alcohol	Breton, Marcel P., 2000 a King, Clifford R., 2000 Matzinger, Michael D., 1999 Mizobuchi, Ypshikazu, 2000 Malhotra, Shadi L., 1999
Thiourea/ Carbamate compounds Creasing Agent (Conc. 1 - 98 %)	Malhotra, Shadi L., 2001a
Lightfastness UV absorber Protects Ink from Thermal Degradation (Conc. 1 - 10 %)	Goodbrand, H. Bruce, 2001
Lightfastness compound Protects Image from Electromagnetic Radiation (Conc. 10 - 0.5 %)	Breton, Marcel P., 2000 b
Conductivity enhancing agent Acts as Corrosion Inhibitors (Conc. >5 %)	Matzinger, Michael D., 1999
Biocide Prevents Microbial Growth (Conc. 0.01 - 5 %)	Paine, Anthony J., 1999
Pigments Adds Color (Conc. 0.1 - 20 %)	Wong, Raymond W., 2000

Physico-chemical properties:

Specific gravity: 0.99-1.00.

Particle Size: 10 μ .

Melting Point: 83-85°C.

Alcohol compound: 1-Octadecanol, 95% (Aldrich Chemical Co.) is capable of dissolving other materials without significantly changing any physical properties. It does not undergo any chemical state changes, which allows dissolving the ink resin.

Physico-chemical properties:

Molecular weight: 270.50.

Specific gravity: 0.812.

Melting point: 58-60°C.

Hot-melt Ink Formulations

Hot-melt ink blending was carried out using a Barablender Plasticorder fitted with a W50 chamber and cam blades. The mixing time was 20 minutes, and the mixing torque was reported after the first minute of mixing after stabilization of the torque response. The mixing temperature was varied from 90-115°C. All composite samples were compression molded into plates of 3-mm thickness for further blending and testing.

Composite 1: Pigment (AAMX Yellow)

Composite 2: Pigment (Polyethylene Flush Red)

Composite 3: Pigment (Pathalo Blue - Green shade)

The polymer matrix and pigment were melted in the Carnuba Wax and Octadecanol 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. The polymer matrix was mixed in the following proportion to yield the 64 percent concentration of polymer matrix.

Rheology Measurement

A steady stress sweep was performed on the DSR 5000 Stress Rheometer. The formulations were tested to quantify the rheological properties of the ink. A 25-mm parallel plate in conjunction with a Peltier plate-heating system was used to achieve the necessary temperature for the inks to be heated and liquified and for the test to be performed.

The following conditions were set on the Rheometer in order to complete the testing:

Geometry type:	Parallel Plates
Diameter:	25.0 [mm]
Gap:	0.535 [mm]
Sweep Mode:	Logarithmic
Initial Stress:	3.19 [dynes/cm ²]
Final Stress:	1.58e + 05 [dynes/cm ²]
Points per decade:	10
Maximum point/data point:	15 sec
Temperature:	115°C
Delay:	180 seconds (to equilibrate sample)

Steady Stress Sweep Test

In this test, a range of stress levels, each at constant amplitudes, 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 sweep stress 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.

Printing (Drawdowns)

The drawdowns were done using a laboratory K-Printing Proofer. In this process, ink was transferred from an electromechanically engraved printing plate directly onto the substrate, which was attached to the rubber-covered

impression roller. Doctor blade and roller adjustments were made via micrometers, allowing repeatable settings before drawdowns.

Printing plate used: Double 8 Wedge Plate (150 lines/inch), Dot area: 100-60 percent. K-Proofer was pneumatically driven, using an air-supply pressure of 80 psi.

Table 2: Characterization of composites based on 2 wt. percent of pigment and Ethylene Vinyl Acetate Copolymer Matrix

Composite Number	Ingredients	Percent [%]	Mixing Temperature(°C)	Melting Point (°C)
1	Carnauba Wax	10	70	85
2	1-Octadecanol, 95%	24	80	60
3	Polymer MVA 2528	64	100	76

K-Printing Proofer Draw-Down Steps:

- A. Mount the substrate on the rubber impression roller with the help of adhesive tape.
- B. Adjust the doctor blade angle to a 45° angle.
- C. Heat the engraved plate and doctor blade with heated coils.
- D. After heating the plate to approximately 85-95°C, the heated ink is poured on the engraved plate, just ahead of the doctor blade.
- E. Now take a drawdown. As the doctor blade moves forward, the ink over the engraved plate is metered off, and ink fills the tiny cells of the plate.
- F. As the doctor blade moves ahead, an impression roller with the loaded substrate is simultaneously brought in contact with the plate. At the point of contact, ink is drawn out of the cells onto the substrate by capillary action.
- G. The drawdowns were made with the LWC, SCA, and SBS substrates.

The Substrates for Printing

SBS (Solid Bleached Sulfate Board), LWC (Lightweight Coated), SCA (Supercalendered A) commercial paper/board substrates were used because they cover the basic spectrum of materials used in the gravure industry. These substrates also demonstrated the effects of different porosity, smoothness, and compressibility. Once the drawdowns were completed for all of the substrates, basic printability tests were performed on all the samples.

Printability Analysis

Reflective Density (X-Rite 408 Reflection Densitometer)
Reflective density was determined by using an X-Rite 408 reflection densitometer. A reflection densitometer measured the amount of light that was reflected from an image. The incident light was projected at an angle of 45°, while the light-sensitive densitometer head was located at 90°. Ten measurements were taken and the average was compared in the graph.

Specular Gloss (Gardener Gloss Meter)

Specular gloss was determined by the Gardener gloss meter with 60° geometry. It measured the percentage of perfect reflectance of the ink film and the substrate. The gloss was measured in both the machine and cross directions on both the solid printed and unprinted regions. The paper gloss was then subtracted from the printed gloss, and the delta gloss was the difference. Ten measurements were taken in the solid areas, and another ten measurements were taken on the paper in order to determine delta gloss (Ink gloss - Paper gloss) and then plotted in a graph for comparison.

Rub Resistance (Sutherland Rub Resistance Tester)

A rub-resistance test was performed on a Sutherland ink-rub tester. First, the density of a solid patch needed to be determined. The solid patch of print was attached to a 4-lb. block. Then, an unprinted sample of the exact same substrate was secured below the 4-lb. weight. The two samples were rubbed together for fifty strokes, and then the density was taken again. The rub resistance value was calculated using the following formula:

Density of solid - Density of rubbed/Density of solid
100 %.

Results and Discussion

The hot-melt ink formula was based on an ethylene vinyl acetate copolymer (Polymer 2528). Pigment chips were used as the colorant. A low molecular media used was 1-Octadecanol, 95 percent and carnauba wax. The rheology of the formulated inks was done on a Dynamic Stress Rheometer.

The rheological data of the base ingredients used in the composition was measured at 115°C and is shown in Figure 1. The data shows that the viscosity of the polymer did not change as the stress changed, illustrating that the MVA 2528 polymer has a high viscosity in the range of 102-103 poise, and its viscosity does not decrease with increasing stress force.

The carnauba wax rheology was measured in Figure 1. The viscosity of the carnauba wax started decreasing in the first 10 dynes of stress steps between 100-101 at 10 [dynes/cm²], and then it decreased to below 1 poise at around 50 [dynes/cm²]. The carnauba wax viscosity data seems very promising with a viscosity in the range from 10-1 - 100 poise. It was decided that this wax could be used for the HMI ink formulation, along with the EVA polymer.

The rheological data in Figure 1 indicates that the 1-Octadecanol, 95 percent is usable in HMI formulations because of the 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 the stress steps, showing shear thickening with increasing stress, but it was still used in the HMI formulation because it showed and maintained very low viscosity for HMI.

Next, the rheology of finished inks was measured at 115°C. The formulation of these inks is listed in Figure 2. These inks displayed critical stress values, where the viscosity began to decrease with increasing stress. But the viscosities associated with the critical values were in the order of between 102-103 poise, while the correct

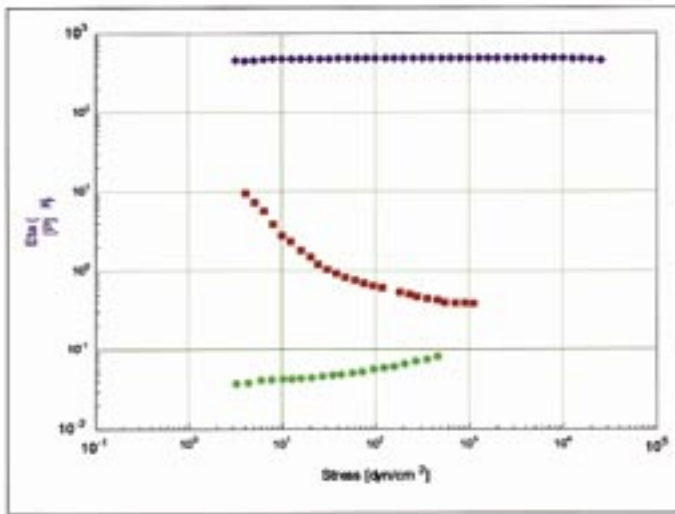


Fig. 1: Viscosity v. Stress of Hot Melt Ink Ingredients
 (■ Polymer 2528, ■ Carnauba Wax, ● 1-Octadecanol)

printing viscosity for gravure printing is in the range of 10-1 poise. This suggests that the inks have high viscosity, the cause of which might be attributed to the degree of polymerization of EVA, 64 percent polymer by weight in the dispersion or shear thickening of 1-Octadecanol, 95 percent at increasing stress. The laboratory data indicate that the hot-melt ink had a tendency to decrease in viscosity with temperatures over 115°C (Data not shown). However, it was not possible to prove that at the Stress rheometer, due the manufacturer's recommendation for used temperature range.

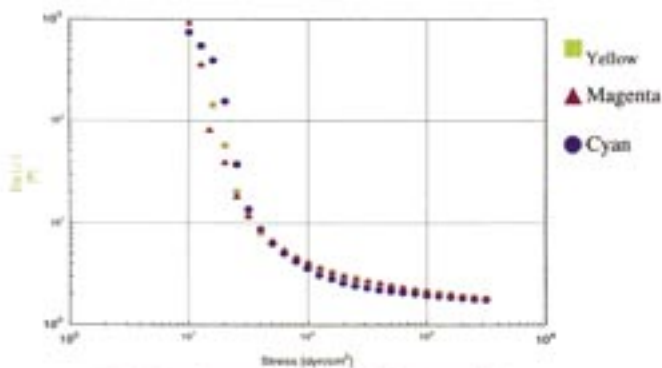


Fig. 2 Viscosity v. stress of Hot Melt Ink Formulation

Figure 3 shows that 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 low on SCA and SBS. The density values reached at LWC match the target densities [0.90 for Yellow, 1.30 for Magenta, and 1.35 for Cyan] recommended for publication gravure.

Theoretically, hot-melt ink formulations should have excellent gloss properties due to very good ink holdout on the printing substrate surface. This was proven in previous work done here at WMU. Current hot-melt ink formulations have the highest gloss values at yellow ink,

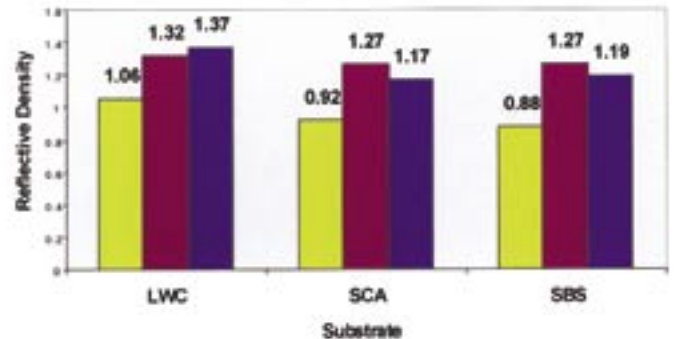


Fig. 3 The Reflective Density of Hot Melt Ink on Different Paper Substrates

■ Yellow Ink, ■ Magenta Ink, ■ Cyan Ink

then at magenta, and lowest at cyan ink, having values in the range of 4.4 to 3.1 percent. SBS board showed the overall highest specular gloss (Figure 4.). The gloss was between 40-45 percent for Yellow, 37-45 percent for Magenta, and 30-35 percent for Cyan, lower on LWC and SCA than on SBS board. The reason why the gloss values were quite low on all substrates was due to insufficient printing plate temperature at the moment of printing.

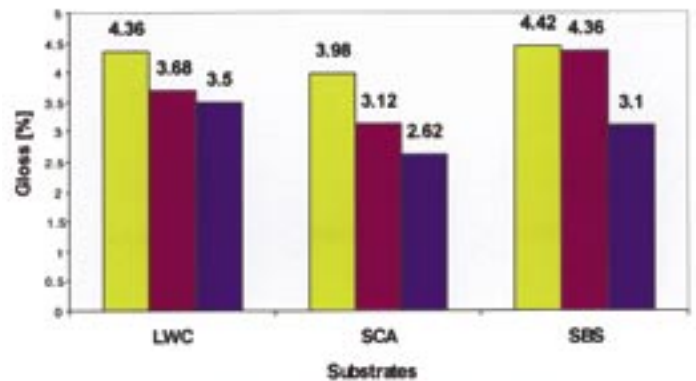


Fig. 4 The Gloss of Hot Melt Ink on Different Substrates

■ Yellow Ink, ■ Magenta Ink, ■ Cyan Ink

The rub resistance of hot-melt ink is illustrated in Figure 5. LWC, SCA, and SBS showed excellent rub resistance—i.e., between 95-98 percent for Yellow; 70-85 percent for Magenta; and 80-85 percent for Cyan. The LWC and SCA sample lost minimal ink. The worst rub resistance was observed on magenta ink. The data indicate that the inks formulated have good end-use properties. The inks displayed superior rub resistance as compared to that of some commercial company research, which indicates a high amount of ink adhesion. The sample that proved to be too porous showed normal to excellent rub resistance.

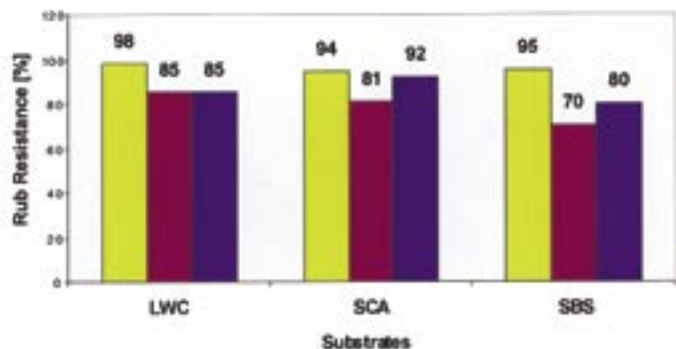


Fig. 5 The Rub Resistance of Hot Melt Ink on Different Substrates

Yellow Ink, Magenta Ink, Cyan Ink



Hrishikesh Bhide is a graduate student at Western Michigan University (WMU), Kalamazoo, Michigan, pursuing a Master of Science degree in Paper and Printing Science and Engineering, with a tentative graduation date of April 2003.

Born and brought up in Bombay, India, he pursued his diploma in Printing Technology from the Maharashtra Institute of Printing Technology (M.I.P.T) Pune, and his undergraduate degree in Printing and Graphic Communication from the University of Pune, India. At WMU, Hrishikesh realized he was attracted by the United States gravure inks industry and started working part time at the Department of Printing under the guidance of Dr. Alexandra Pekarovicova. There, he has had a chance to learn more about "Hot Melt Inks for Rotogravure" and conducted formulations, rheology, and printability analysis in the department research lab.

Hrishikesh joined the TAGA student chapter in 2002 and had his graduate research paper considered as a winning entry in the TAGA Dusty Rhodes/Graduate Paper writing competition. In addition to his interest in printing and paper technology, he likes to listen to music and swim. He also likes to write review papers in the field of printing and graphic communication.

Conclusion and Recommendations

The aim of this work was to formulate, analyze, and print hot-melt ink formulations, based on EVA chemistry. The rheological data indicated that present hot-melt inks have higher viscosity at 115°C than recommended for rotogravure printing. However, their viscosity rapidly decreased with increasing temperature. After printing on a laboratory gravure K-Proofer, the inks showed excellent reflective density and rub-resistance properties. The gloss properties were quite low, due to insufficient printing plate temperature at the moment of printing. The next research should focus on the formulation of hot-melt ink with polymers with even lower viscosity. 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.

Acknowledgement

This research has been approved by grant from the Eppley Foundation for research. The author would like to extend thanks for funding this work.

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