VEGETABLE OIL BASED SHEETFED AND HEATSET INK FORMULATIONS AND COMPARISON OF VOC TEST RESULTS WITH COMMERCIAL INKS

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Abstract: Vegetable oil based sheetfed and heatset inks are formulated in the absence of volatile organic chemicals (VOC). Properties of these inks (viscosity, tack, drying time) are evaluated and reported. Comparison of VOC test results show that these inks have lower VOC values than both commercial sheetfed and heatset inks. Also comparison of VOC test methods are reported and discussed.

Introduction

Conventional printing inks used in sheetfed and heatset applications are multicomponent systems comprising: (a) the pigment; (b) a hydrocarbon and/or alkyd resin; (c) a hydrocarbon solvent; and (d) optional additives.

In recent times, such inks have been formulated with some soybean oil so that the formulation and printer could use the familiar SoySeal. The SoySeal trademark was developed by Monsanto Agricultural Company to indicate the presence of soybean oil in various agricultural chemicals. Monsanto officials assigned the rights to the trademark to the American Soybean Association (ASA) in January 1989. ASA has used the SoySeal to indicate industrial uses of soybean oil, such as in printing inks (Iowa Soybean Association). For the ink manufacturing company to be eligible to apply the "Contains Soy Oil" SoySeal to its product containers, the soy ink product must meet certain minimum requirements for soybean oil content, which is 20 and 7 percent of total formula weight for sheetfed and heatset inks, respectively.

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The current United States market for sheet-fed inks is greater than 100 million pounds and for heatset inks greater than 400 million pounds (Rauch Associates, Inc). The worldwide market for these inks is estimated to be at least twice that of the domestic market . Because of this significant potential market, we formulated sheetfed and heatset web offset inks using 100% vegetable oil based vehicles (Erhan and Bagby, in press.).

Experimental

Materials

Carbon black (Regal 400 and Regal 250) was obtained from Cabot Co., Boston, MA. Carbon black dispersions (Kerley Soy 40, Kerley 40⁺ and Kerley Super 36) were obtained from Kerley Ink, Broadview, IL.

Methyl linoleate and methyl linolenate were purchased from NuCheck Prep., Elysian, MN. Linseed oil methyl ester was purchased from Archer Daniel Midland, Red Wing, MN. Sunflower and tung oil methyl esters were prepared in our laboratory.

Methods

Premixing of the pigment, vehicle and additives was done with a Shar High Speed Disperser, Model D-10P, at 2500 rpm for 10 min. Dispersion of the pigments was completed with a water cooled three roll mill (Brazington). Proper dispersion was assured by checking each formulation with a "NPIRI Production Grindometer" using ASTM 1316-87. Viscosities of the inks were measured with a Laray Falling Rod Viscometer, model VM .01. The apparent viscosity at 2500 s-1 was calculated by Power Log method using ASTM D 4040-81. Tacks of the inks were measured with an Electronic Inkometer, Model 101. The method of ASTM D 4361-84 was used to obtain the apparent tack values at 1200 rpm and 90.0 ± 0.1 °F. Tack values were reported at 1 min.

A "Little Joe" offset proof press, model HD was used to obtain the sheetfed prints. Wedge plate (Model FPBAA-C) was used in place of Little Joe press plate to obtain the print at different film thicknesses (Fetsko et al. 1962). Set-off was tested after 2 and 5 minutes of printing by placing a clean paper on the blanket roller of the press and rolling on the print. Set-off was compared with commercial sheetfed ink samples. Promising candidate ink formulations were used in pilot scale runs on a Hamada 19 inch x 26 inch sheetfed single color press with conventional damping. In the first run, printing was conducted on 17 inch x 22 inch sheets of kenaf bond paper. Upon printing both sides, no setoff was noticed, thus providing evidence of adequate dryness. Hold out of color was excellent and very consistent throughout the run. It was not necessary to carry a quantity of ink on the rollers to obtain a solid coverage of color. The second run was conducted on 70 pounds enamel coated paper. The drying time was comparable to conventional oil-based inks.

Drying tests for heatset inks were conducted on the Prufbau Printabililty Tester. A 1 μ film of the ink was printed on coated heatset paper at 600N pressure, 1.0 m/s, distributing ink on a rubber covered cylinder. The print was dried on the Sinvatrol Laboratory Heatset Dryer Set at 300°F and 0.3 m/min, the print was given 1 pass, 5 passes or 10 passes. The point at which the print was dry was determined by placing a strip of newspaper on top of the print and passing the printed paper and newspaper together through the Prufbau in contact with a metal cylinder at 800N and 1.0 m/s, and then examining the print for signs of ink set-off from the newspaper. This test was conducted on the print before and after 1, 5 or 10 passes on the Sinvatrol.

To test for VOC, a sample of the ink was heated under controlled conditions, and the amount of weight loss was measured by the difference of weight before and after heating. The most commonly used test method is EPA Method 24. This method specifies heating the sample at 110°C for 1 hour in a forced air oven. Method 24A specifies a test condition of 120°C for 4 hours under partial vacuum (~510 mm Hg) or 120°C for 24 hours in a forced air oven. Bay Area Method 30, specifies heating the sample at 40°C for 1 hour in forced air oven. Experiments were done in triplicate on four different days and average values were reported.

Results and Discussion

We formulated vegetable oil-based printing inks and completely eliminated petroleum based resins and oils. A broad range of viscosity and tack values are possible. Thus, formulations can be prepared that are suitable for both sheetfed and heatset web offset applications. Drying properties of the vehicles used in the formulations are given in Table 1. Ink vehicles reported in Table 1 were formulated to comprise: 77.05% heat bodied soybean oil (Erhan and Bagby, 1991) with Gardner-Holdt viscosity of Z_3-Z_4, 8.56% heat bodied soybean oil with Gardner-Holdt viscosity of Z_1-Z_2, 13.67% alkali refined soybean oil and 0.72% monoester (Erhan and Bagby, in press). The blended heat bodied oils were selected to give the equivalent of 85.61% heat bodied soybean oil with Gardner-Holdt viscosity of Z_2-Z_3. Each formulation was evaluated both with and without the addition of 2% Cobalt-drier added as a 6% solution.

The drying properties of the vehicles were evaluated in the Prufbau Printability Tester as described in Methods. The vehicles that dried immediately before the first dryer pass were considered suitable for sheet-fed inks. In some cases the vehicle was dry before the first dryer pass, but was slightly wet afterwards. This is attributed to heat softening of the vehicle during drying and is not considered a significant drawback to the use of such vehicles for heat set applications.

The pigment is blended into the vehicle until a uniform dispersion is obtained. Additives that may be formulated into the inks include driers, waxes, antioxidants, rheological modifiers and the like. The thickening effect of the pigment on the base vehicle was considered in preselecting a vehicle viscosity. Formulated inks were characterized by viscosities in the range of about 80-150 poises and tacks in the range of about 8-30 g-m. The typical viscosity for a sheetfed ink is in the range of about 80-140 poises and about 100-150 poises for a heatset web offset ink. Tack values for the sheetfed inks are about 8-17 g-m, and about 8-30 g-m for heatset inks.

Table 2 shows the average % VOC of the commercial and USDA's black sheetfed inks. Results were tabulated from three different methods: EPA Method 24, EPA Method 24A and Bay Area Method 30. EPA Method 24 is the more widely used, but the other methods were tested for comparison. In Method 24A, samples are placed in a forced air oven at 120°C for 24 hours or a vacuum oven for 4 hours. VOC's values from reaction conditions of 120°C and 24 hours in forced air oven were higher for all inks. The third method, Bay Area Method 30 resulted in the lowest VOC values for all inks tested. Table 3 tabulates the average % VOC (using Method 24) for commercial and USDA's experimental black heatset web offset inks. Also by using Method 24, pigments used for both sheetfed and heatset ink formulations were tested, and results are tabulated in Table 4. Overall data showed that USDA's soy oil based inks contained the lowest % VOC, followed by commercial soy based inks. Sheetfed inks had a lower % VOC than heatset inks in all cases. USDA's inks were selected to include different types of pigments in the formulations. Formulation with Regal 250 and Regal 400 carbon black gave the lowest % VOC followed by Kerley Soy 40, Kerley 40^+ and Kerley Super 36. These results once again demonstrated the advantage of using more soybean oil in the sheetfed and heatset ink formulations.

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Table 1

Vehicle[a]	Ester	Cobalt Drier 2%	Dryer Pass[b] 0	1	5	10
1	Methyl linoleate	no	-	-	-	+
2	Methyl linoleate	yes	+	+		
3	Methyl linolenate	no	+	sl		
4	Methyl linolenate	yes	sl	+		
5	Linseed oil, methyl ester	no	-	-	-	+
6	Linseed oil, methyl ester	yes	+	+		
7	Safflower oil, methyl ester	no	+	sl	vsl	vvsl
8	Safflower oil, methyl ester	yes	sl	+		
9	Tung oil, methyl ester	yes	+	+		

[a] 77.05% Z_3-Z_4 heat bodied soybean oil; 8.56% Z_1-Z_2 heat bodied soybean oil; 13.67% alkali refined soybean oil; 0.72% monoester.

[b] "-" = wet; "+" = dry; "sl" = slightly wet; "vsl" = very slightly wet; "vvsl" = very, very slightly wet; no entry indicates that the ink was not evaluated at that pass level.

Table 2

Percent Volatile Organic Compounds (VOC) Analysis of Sheetfed Inks

Ink	Percent VOC			
	EPA Method 24[a]	EPA Method 24A[b]		Bay Area Method 30[c]
		I[d]	II[e]	
USDA I[f]	1.79	6.91	2.46	0.85
USDA II[f]	2.59	6.83	2.66	0.94
USDAIII[f]	5.25	9.90	7.31	1.35
Commercial I[g]	14.59	23.71	21.47	1.35
Commercial II[h]	22.92	26.96	24.87	2.01
Commercial III[h]	19.68	29.21	28.71	3.98

[a] ASTM D-2369-92; [b] ASTM D-2369; [c] ASTM D-5328-92; [d] 120°C, 24 hr, forced air oven; [e] 120°C, 4 hr, vacuum oven; [f] USDA I, II, III--Sheetfed ink formulations with vehicle 2 (Table 1) and 400R, Kerley Soy 40 and Kerley 40+ (Table 4), respectively; [g] Commercial sheetfed ink--soy based;[h] Commercial Sheetfed ink--petroleum based, from two different manufacturers.

Table 3
Percent Volatile Organic Compounds (VOC) Analysis of Heatset Inks

Ink	Percent VOC EPA Method 24[a]
USDA I[b]	1.28
USDA II[b]	8.60
Commercial I[c]	31.96
Commercial II[c]	28.36
Commercial III[d]	35.15
Commercial IV[d]	30.67

[a] ASTM D-2369-92.
[b] USDA, II--Heatset ink formulations with vehicle 2 (Table 1) and 250R and Super 36 (Table 4), respectively.
[c] Commercial I, II--Heatset inks--soy based, from two different manufacturers.
[d] Commercial III, IV--Heat inks, petroleum based, from two different manufacturers.

Table 4
Percent Volatile Organic Compounds (VOC) Analysis of Pigments for Sheetfed and Heatset Ink Applications

Pigment	Percent VOC EPA Method 24[a]
Regal 250[b]	0
Regal 400[b]	0.50
Kerley Soy 40[c]	1.06
Kerley 40[c]	12.78
Kerley Super 36[c]	16.44

[a] ASTM D-2369-92.
[b] Carbon black (Cabot Co., Boston, MA).
[c] Carbon black dispersion (Kerley Ink, Broadview, IL).