VEGETABLE OIL-BASED VEHICLES, NEWS INK FORMULATIONS AND THEIR PROPERTIES

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Abstract: Our objectives for this study were to produce vegetable oil-based printing ink vehicles that did not require petroleum components. Modified soybean oil was used for formulating nearly 150 paste news inks. Physical properties of these inks meet or exceed the industry standards for lithographic and letterpress newsprint applications. Elimination of petroleum-based resin and reduced amount of pigment usage, due to the light vehicle color, provide a competitively priced alternative to petroleum-based inks.

The apparent weight average molecular weights (Mw) of ink vehicles made from representative vegetable oils, such as soybean, sunflower, cottonseed, safflower and canola oils were compared by gel-permeation chromatography (GPC) and a correlation between viscosity and apparent Mw of these vehicles was established.

Introduction

The petroleum shortages in the 1970's stimulated research on identifying alternative and renewable materials for preparation of printing ink vehicles and ink formulations. Because of their well known characteristics of being nonvolatile and biodegradable, vegetable oils were an obvious choice for further investigation. Inks containing vegetable oils have been formulated for various applications (Ono et al., 1961; Kuzuwata and Koko, 1963; Gupta et al., 1984; Kobayaski and Nozaki, 1978). In the early 1980's, the American Newspaper Publishers Association (ANPA) developed a series of ink formulations comprising a blend of "gilsonite" and tall oil fatty acids together with carbon black pigment (Moynihan and ANPA, 1983a; Moynihan and ANPA, 1985b; Moynihan and ANPA, 1985c). Acceptance of these inks by the industry has been limited by the cost and availability of tall oil and the difficulty of equipment cleanup caused by the "gilsonite."

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Later in 1985 ANPA introduced a vegetable oil-based ink vehicle suitable for lithographic news ink, comprising alkali-refined soybean oil, a hydrocarbon resin and pigments (ANPA, 1988). While the colored inks have become commercial, widespread acceptance of black ink has been inhibited by cost. Both the black and color inks contain 20-25% hydrocarbon resin. Thus, the industry has continued to seek vegetable oil-based nonpetroleum ink.

Because of its general availability and favorable price relative to other commodity oils, soybean oil was emphasized in our studies. Also, other vegetable oils of various iodine values (I.V.) and fatty acid contents were evaluated to determine the influence of unsaturation on preparation and properties of the vehicles. For our studies, we selected alkali-refined soybean, cottonseed, canola, safflower and sunflower oils. Alkali refining removes gums, waxes and free fatty acids. The presence of one or more of these materials may interfere with desirable properties of the vehicles and the ultimate ink formulations. All tend to reduce hydrophobicity properties desired in certain ink formulations.

The vehicles were prepared from vegetable oils by two methods (Erhan and Bagby, 1991). In the first method, vegetable oils were heat polymerized at a constant temperature in nitrogen atmosphere to a desired viscosity. In the second method, the heat polymerization reaction was permitted to proceed to a gel point, and then the gel was mixed with vegetable oils to obtain a desired viscosity.

The apparent weight average molecular weights (Mw) of both the heat-bodied vehicles and the gels were determined by Gel Permeation Chromatography (Erhan and Bagby, 1992).

We describe here soy and other vegetable oil ink formulations (11) that are cost competitive with petroleum-based inks and meet or exceed industry standards in regard to ruboff resistance, viscosity and tack.

Experimental

Materials

Alkali-refined soybean oil was obtained from Riceland Foods, Stutgard, AR and Archer Daniels Midland, Decatur, IL. Alkali-refined canola oil and cottonseed oil were purchased from Bunge Oil, Bradley, IL. Alkali-refined sunflower oil was obtained from Archer Daniels Midland, Decatur, IL. Alkali-refined safflower oil was obtained from Pacific Anchor Chemical Co., Cumberland, RI. Polystyrene standards were obtained from Polymer Laboratories LTD and had the following specifications. [Peak Average Molecular Weight (Mp) and Molecular Weight Distribution (MWD)]: 580, 1.14; 1320, 1.09; 3250, 1.04; 9200, 1.03; 28500, 1.03; 66000, 1.03; 156000, 1.03; 435500, 1.04; 1030000, 1.05; 2250000, 1.04; and 2880000, 1.04.

Carbon black (Elftex 8) was obtained from Cabot Co., Boston, MA. Sunbrite yellow AAA (Sun 273-3556), Lithol Red (Sun 210-4200), Lithol Rubine (Sun 219-0688) and Blue 15 (Sun 249-2083) were purchased from Sun Chemical Co., Cincinnati, OH.

Butylated hydroxytoluene (BHT) was provided by Eastman Chemical Co., Kingsport, TN. Bentone 128 was provided by NL Chemical, Inc., Hightstown, NJ. Hydrite R was obtained from Georgia Kaolin Company, Inc., Union, NJ.

Methods

Vehicles were prepared in a four-necked reaction flask equipped with a mechanical stirrer. Two major methods were used in preparation of polymers. (1) Alkali-refined vegetable oil was polymerized with stirring at $330\pm3^{o}C$ under nitrogen atmosphere to the desired viscosity. Some polymers prepared by this method were used directly as vehicles, others having Gardner-Holdt viscosities as high as Z_8-Z_9, were admixed with low viscosity polymers and/or unmodified, alkali-refined vegetable oil at 65-75^{o}C in a reaction flask equipped with a mechanical stirrer. (2) Heat bodying was continued until the oil gelled. The reaction was discontinued at the transition point when clumps of gel began to climb up the shaft of the mechanical stirrer. The gel was blended in various ratios with unmodified alkali-refined vegetable oil at 330±3^{o}C. The heating softened the gel and promoted blending. Agitation was continued until a smooth vehicle was obtained. The proportions of the gel and unmodified oil determined the resultant vehicle viscosities.

The viscosities of all vehicles were determined by a Gardner-Holdt Bubble viscometer following ASTM D-1545-63.

The color of the vehicles was evaluated using the Gardner Color Scale by ASTM D-1544-63.

The apparent Mw of all heat-bodied vehicles and gels were determined by GPC. The samples were dissolved in tetrahydrofuran (THF) (0.4% w/v), filtered through 0.5 μ teflon filters, and then injected into the HPLC (Model 8100 Spectra Physics). Chromatography operating conditions were: flow, 1 mL/min; over temperature, 40^{o}C; column, 30 cm, 7.5 mm, PL-Gel 5 μ mix; detector, differential refractive index (Model 6040, Spectra Physics); and injection volume, 50 μL.

Premixing of the pigment, vehicle, and additives were done with a Shar High Speed Disperser, Model D-10P, at 2500 rpm for 20-30 min. Dispersion of the pigments were completed by an Eiger Mini Mill, loaded with 2-mm chrome steel balls, operated at 3500 rpm for 10 min.

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 2500s^{-1} was calculated by the Power Log Method using ASTM D4040-81.

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^{o}F. Tack values were reported at 1 min.

A commercial Hamilton Beach mixer was used for the water tolerance test. Fifty grams of ink were mixed with 50 g deionized water at 90.0 rpm, for exactly 5 min. Unemulsified water was poured off. An acceptable range of water retention for lithographic inks is 10 to 18 g (12).

A "Little Joe" offset proof press, Model HD was used to obtain letterpress prints. Absolute print densities were measured using an "X-Rite 428 computerized Color Reflection Densitometer.

Several formulations, considered to be candidates for offset lithography, were scaled up and evaluated on ANPA's commercial, pilot offset web press.

Ruboff resistance of these prints were evaluated by the ANPA-NAPIM Ruboff Standard Test Procedure. The amount of ruboff is reported as the percent blackness of a stain that results by pulling a tissue weighted with a 1 psi pressure, over the surface of a printed sheet. Blackness densities were measured with an "Applied Color Science Spectrometer, Model 1101 (Princeton, NJ) and calculated from the following:

$$\% \text{ Blackness} = \frac{\% \text{ R (tissue)} - \% \text{ R (rub stain)}}{\text{R (tissue)}} \times 100$$

% R = percent reflection at 560 nm

The percent improvement determines the rate of pigment fixation on the newsprint by either penetration into the sheet or resin hardening. Blackness of less than 6% after 2 hr is considered characteristic of an ink with good ruboff resistance.

Results and Discussion

The vehicles that we prepared typically had viscosity values in the range of G-Y on the Gardner-Holdt Viscometer Scale or about 1.6-18 poises (Mattil et al., 1964). These viscosities correspond to apparent weight average molecular weights (Mw) of about 2600-8900 (Erhan and Bagby, 1992).

Presumably, the molecular weight and viscosity increases are due to the triglycerides undergoing Diels-Alder Reaction (House, 1971). At the temperature of heat bodying, double bonds migrate and conjugate (Powers, 1950). Oils with conjugated unsaturation polymerize much more rapidly than those without conjugation. Characteristics and composition of oils used in this study can be seen in Table 1. During heat bodying, conjugated dienes of one fatty acid can form a 6-membered ring by reaction with a double bond of another fatty acid. If these fatty acids come from different triglycerides, the viscosity and molecular weight will increase in the system. In later stages of heating, a conjugated group can add to the previously formed ring structure. Triglyceride, consisting of three fatty acids at which addition may occur, introduces the possibility of forming very complex structures and very large molecules. Thus, the reaction time necessary to reach a desired viscosity depends on mass, structure of the reactants, rate of heat transfer and agitation. Gelling times for safflower (I.V. = 143.1), soybean (I.V. =127.7), sunflower (I.V. = 133.4), cottonseed (I.V. = 112.9) and canola (I.V. =110.2) oil were 110, 255, 265, 390 and 540 min, respectively. Although iodine values of cottonseed and canola oil are similar, canola oil with its high oleic acid content requires a longer time to gel.

Heat-bodied oils of different viscosities may be blended to produce a desired vehicle viscosity. Table 2 shows the component properties and viscosities of six vehicles that are prepared this way.

The viscosities of vehicles prepared by blending different proportions of the gel and unmodified oil can be seen in Table 3. Apparent Mw values of the vegetable oil derived gels are given in Table 4. The differences in apparent Mw at the gel points suggest a decrease in the size of the gel particles as one goes from soybean oil to sunflower oil. The principal advantage of these vehicles is that the gel can be prepared and stored as a stock material for subsequent custom blending of vehicles over a broad viscosity range.

TABLE 1
Characteristics and Composition of Vehicle Oils

	Canola	Cottonseed	Soybean	Sunflower	Safflower
Iodine Number	110.2	112.4	127.7	133.4	142.3
Saponification Number	188.2	194.9	190.2	190.6	190.0
Fatty Acid Composition, %					
$C_{14:0}$	0.2	0.8	0.1	---	---
$C_{16:0}$	4.2	23.4	10.2	6.0	6.6
$C_{16:1}$	0.2	0.5	0.1	---	---
$C_{18:0}$	2.1	2.4	4.3	5.2	2.4
$C_{18:1}$	63.7	17.7	25.2	19.7	16.8
$C_{18:2}$	19.6	54.1	52.7	66.0	72.2
$C_{18:3}$	5.1	0.3	6.0	0.2	0.5
$C_{20:0}$	1.4	0.3	0.3	0.4	0.3
$C_{20:1}$	1.6	---	0.2	0.5	---
$C_{22:0}$	0.4	---	0.4	0.9	0.4
$C_{22:1}$	0.3	---	---	---	---

TABLE 2
Heat-Bodied Oil Blends[a]

Vegetable oil component (% w/w)			
Heat bodied 1	Heat bodied 2	Unmod.[b] 3	Vehicle viscosity[c]
25.0 (X-Y)[d]	75.0 (G-H)	0.0	M-N
15.0 (X-Y)	85.0 (I-J)	0.0	M-N
50.0 (X-Y)	0.0	50.0	M-N
34.0 (Z_8-Z_9)	26.6 (U-V)	39.4	M-N
70.0 (Z_3-Z_4)	0.0	30.0	W-X
32.5 (Z_8-Z_9)	0.0	67.5	W-X

[a]Heat-bodied oils were prepared by using either of soybean, sunflower, safflower, cottonseed and canola oils.

[b]"Unmod." refers to unmodified alkali-refined vegetable oils.

[c]Gardner-Holdt Viscosity Scale.

[d]Letter values in parentheses represent Gardner-Holdt viscosities of heat-bodied oils.

TABLE 3
Gel-Oil Blends[a]

Composition (% w/w)		Vehicle
Gel	Oil	viscosity[b]
21.5-22.5	78.5-77.5	M-N
43.0-45.0	57.0-55.0	V
45.0-47.0	55.0-53.0	W
47.0-50.0	53.0-50.0	W-X
51.0-53.0	49.0-47.0	X-Y

[a]Gel-oil blends were prepared separately with soybean, sunflower, safflower, cottonseed and canola oil.

[b]Gardner-Holdt Viscosity Scale.

TABLE 4
Gel Molecular Weights

Gel	AMw
Soybean	60423
Canola	44924
Cottonseed	38266
Safflower	31772
Sunflower	15055

Vehicles, prepared by these technologies, are compatible with pigments for producing the four colors commonly used in the newspaper printing industry; namely, black, cyan, magenta and yellow. As shown in Table 5, these vehicles are characterized by an exceedingly light coloration. Except for canola, they have values on the Gardner Color Scale of about 6 or less and typically are in the range of about 2-4. This property permits some reduction in the amount of pigment required for colored inks as compared to the pigment levels required by the much darker commercial vehicles having Gardner Color Scale values of about 14 and greater.

Properties of inks formulated with soybean, cottonseed, canola, safflower and sunflower oils are characterized by viscosities in the range of about 5 to 46 poises and by tack values of about 2 to 7 gram-meter (g-m). The typical viscosity for a black lithographic newsink is in the range of about 13 to 24 poises and about 5 to 12 poises for a black letterpress newsink. Tack values for lithographic inks are about 3.5 to 4.8 g-m and about 2.6 to 3.4 g-m for letterpress. The thickening effect of the pigment on the base vehicle should be considered when preselecting a vehicle viscosity. Because of the vehicle system we use (Erhan and Bagby, 1991), it is fairly easy to tailor the viscosity and tack values of the formulated inks. These inks, with a large range of viscosities and tack values, are suitable for both letterpress and lithographic applications. A variety of additives may be formulated into the inks including driers, lubricants, antioxidants and the like.

The water take up for lithographic ink performances was also tested, and the range of 20-30% water take up was well within the acceptable range of 20-36% (Surland, 1980). Inks having these properties were also characterized by acceptable or superior ruboff values. Ruboff values as percent blackness are shown in Table 6. As shown in Table 7, these formulations were chosen to represent a wide range of viscosity and tack properties. The majority showed blackness of less than 6% after 2 hr, thus they demonstrate good rub resistance. The percent improvement is less important than having the minimal percent blackness after 2 hr of printing. All

TABLE 5
Vehicle Color Evaluation

Vehicle viscosity[b]	Vehicle color[a]					
	Soybean[c]	Cottonseed	Canola	Safflower	Sunflower	Commercial (soybean)[d]
W	4	5	6-7	3	3-4	
W-X	4	6	7	3-4	4	
X-Y	4	6	7	3-4	4	
						14

[a]Gardner Color Scale.

[b]Gardner-Holdt Viscosity Scale.

[c]Soybean oil viscosities of G-V have color values in the range of 1-4.

[d]Commercial soybean oil vehicle contains 22-27% Picco resin (ANPA, 1988).

TABLE 6
Ink Ruboff Resistance Evaluation

Experiment number	Ruboff values as percent blackness: Initial	Ruboff values as percent blackness: After 2 hr	Improvement (%)
7	10.6	6.5	39
15	8.4	5.2	38
17	7.3	7.0	5
22	7.4	7.0	5
23	6.3	10.4	-65
24	8.2	6.6	20
25	6.0	5.5	8
26	7.4	5.8	22
27	5.7	7.4	-37
29	8.6	5.9	31
30	8.4	5.6	33
31	5.3	4.6	13
44	6.6	5.2	21
45	5.1	4.4	14
46	6.8	4.5	34
47	4.3	4.2	2
ANPA soy ink 1[a]	14.1	8.4	40

[a]Reference ANPA, 1988.

TABLE 7
Ink Formulations with Soybean Oil

Experiment number	Vehicle viscosity[a]	Pigment (% w/w)[b]	Ink tack (g-m)[c]	Ink viscosity (poises)[d]
7[e]	T-U	19.8	4.1-4.2	16.58
15	V	19.8	5.0	23.38
17	V	17.0	4.6	20.95
22	W	15.0	4.7	19.46
23	W-X	19.8	6.7	33.78
24	W-X	15.0	5.4	23.38
25	W-X	12.0	4.6-4.7	18.80
26	W-X	11.0	4.3-4.4	18.37
27	W-X	10.0	3.9-4.0	14.56
29	X-Y	12.0	5.2-5.3	24.85
30	X-Y	10.0	4.8-4.9	22.48
31	X-Y	8.0	4.6-4.7	21.10
44[f]	W-X	12.0	4.5	20.38
45	W-X	10.0	3.9-4.0	16.60
46	X-Y	12.0	5.2-5.3	24.14
47	X-Y	10.0	4.9	21.47
ANPA Soy Ink[g]	M-N	19.8	3.6	16.45

[a]Gardner-Holdt Viscosity Scale. [b]Carbon black ("Elftex 8").
[c]Measured by "Electronic Inkometer." [d]Measured by "Laray Falling Rod Viscometer." [e]Vehicles in experiment 7 to 31 were prepared by Method 1.
[f]Vehicles in experiment 44 to 47 were prepared by Method 2.
[g]Reference ANPA, 1988.

formulations tested with the exception of one had ruboff values lower than that of ANPA's soy oil ink. Two of the formulations (25 and 44) were tested for long-term stability, and they both performed exceptionally well. This test assessed the ability of the inks to maintain their rheological properties and water tolerance for more than 50,000 copies. Many ink formulations which are promising during short production cycles (10,000 copies or less) fail to maintain their printing characteristics because of solvent evaporation or long-term emulsion problems. Also, these formulations showed minimum cumulations on the rollers, and the residues were soft and easy to clean.

Properties of yellow, blue and red inks are meeting the industrial standards. The addition of up to 5% thickening agent and/or optical brightner is an option but not a necessity for our color ink formulations. Elimination of the hydrocarbon resin from the vehicle results in significant savings for both black and colored inks. In addition, some reduction of pigment for colored inks due to the light coloring of vehicle lowers the price of the ink further. Thus, we have succeeded in making vegetable oil-based printing inks having all of the aforementioned characteristics. In 1987, 550 million pounds of letterpress and lithographic newsink were produced according to Census of Manufacturer (Brant, 1987). If a total conversion to our soy-oil ink occurs, about 2.5 billion pounds of soybean or 500 million pounds of soy oil will be used to supply the newsink market.

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