Vegetable Oil-Based Printing Inks

S.Z. Erhan*, M.O. Bagby and H.W. Cunningham[1]
Oil Chemical Research, National Center for Agricultural Utilization Research, Agricultural Research Center, U.S. Department of Agriculture[2], Peoria, IL 61604

Nearly 75 black and 25 colored inks consisting of 100% vegetable oil-based vehicles were formulated. The physical properties of these inks met or exceeded the industry standards for lithographic and letterpress newsprint applications. In addition, elimination of petroleum-based resin and reduced pigment usage, due to the light vehicle color, provided a competitively priced alternative to petroleum-based inks.

KEY WORDS: Letterpress, lithography, news ink, pigments, print density, rub-off, tack, vegetable oil, vehicle, viscosity.

In the printing industry, the processes in current use are lithography (52%), gravure (18%), flexography (19%), letterpress (5%) and screen printing and other miscellaneous processes (6%) (Bassemir, R.W., private communication).

Lithography and letterpress processes require paste inks. Printing inks that are conventionally used in these applications are multi-component systems comprising a pigment, a hydrocarbon and/or alkyd resin, a hydrocarbon solvent and optional additives. For example, a typical petroleum-based, black litho-news ink would be comprised of 15–20% carbon black as the pigment, 15–25% hydrocarbon or alkyd resin and 50–70% mineral oil solvent. Nearly 500 million pounds of ink for these applications are produced domestically each year (1). This volume of production represents substantial consumption of a petroleum-based fraction. The petroleum oil shortage in the 1970's stimulated research on vegetable oil-based inks that do not require petroleum products.

Inks containing vegetable oils have been formulated for various specialized applications (2–5). 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 (6–8). The cost and availability of tall oil and the difficulty of equipment clean-up caused by the "gilsonite" has limited the acceptance of these inks by the industry. A later approach by ANPA to produce a vegetable oil-based ink vehicle resulted in a lithographic news ink comprising alkali-refined soybean oil, a hydrocarbon resin and carbon black pigment (9). This black ink prints as well as the mineral oil-based commercial inks, but it costs 30–50% more. The color inks, formulated similarly, print well but they cost about 5% more than the petroleum-based commercial inks. Both the black and color inks contain 20–25% hydrocarbon resin. Thus, the industry has continued to seek vegetable oil-based nonpetroleum ink. We describe here soy and other vegetable oil ink formulations that meet or exceed industry standards in regard to rub-off resistance, viscosity and tackiness and are cost competitive with petroleum-based inks.

[1]Present address: ANPA, The Newspaper Center, 11600 Sunrise Valley Drive, Reston, VA 22091.
[2]The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

EXPERIMENTAL PROCEDURES

Materials. 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).

Vegetable oil-based vehicles were prepared by heat polymerization of the oils (10). Black printing inks were formulated from these vehicles by heating the vehicle to 65–70°C and then blending with 1.0% butylated hydroxytoluene (BHT) and 6–20% carbon black (Elftex 8). The elevated temperature was needed to dissolve the BHT. The pigment was dispersed with a Shar High Speed Disperser, Model D-10P (Shar Inc., Fort Wayne, IN), operated at 2500–3000 rpm over a period of 5–7 hr.

Color pigments, vehicles and additives were premixed with a Shar High Speed Disperser, Model D-10P, at 2500 rpm for 20–30 min. Dispersions of the pigments were completed in an Eiger Mini Mill (Eiger Machinery Inc., Bensenville, IL), loaded with 2-mm chrome steel balls, and operated at 3500 rpm for 10 min. Proper dispersion and milling were assured by checking each formulation with a NPIRI Production Grindometer (Precision Gage and Tool Company, Dayton, OH) by following ASTM 1316-87. Yellow inks were formulated with vehicles of various viscosities and yellow pigment. In some examples, a thickening agent (Bentone 128) was added in an amount of 0.5–2.0% as an optional agent to adjust the viscosity. Red inks were prepared by using magenta pigment with the same procedure as for the yellow inks. Blue inks were formulated as above with cyan pigment. In some examples, 2.0–5.0% thickening agent (Bentone 128) was added to adjust the viscosity, and up to 20% Hydrite R was employed as an optical brightener.

Viscosities of the inks were measured with a Laray Falling Rod Viscometer, Model MV.01 (Testing Machines Inc., Amityville, NY). The apparent viscosity at 2500 S^{-1} was calculated by the Power Log method of ASTM D4040-81. The tack values of the inks were measured with an Electronic Inkometer, Model 101 (Thwing-Albert Instrument Company, Philadelphia, PA). The ASTM D4361-84 method 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 commercial Hamilton Beach mixer was used for the water tolerance test. Ink (50 g) was mixed with 50 g deionized water at 90.0 rpm, for exactly 5 min. Water up-take of 10–18 g is an acceptable range for lithographic inks (11).

A Little Joe Offset Proof Press (Little Joe Color Swatcher, Somerville, NJ), Model HD, was used to obtain letterpress prints. To get the proper film thickness of ink, 0.6 cc of ink (3 notches on an IPI Volumeter) was used to roll up an inking area of 108 square inches. A Quick Peek color proofing kit (Thwing-Albert Instrument Company) was used to evaluate matching of color inks. Ab-

TABLE 1

Ink Formulations with Soybean Oil

Experiment number	Vehicle viscosity[a]	Pigment (% w/w)[b]	Ink tack (g-m)[c]	Ink viscosity (poises)[d]
1[e]	G-H	19.8	2.3–2.4	7.33
2	I-J	19.8	2.8–2.9	10.08
3	M-N	19.8	—	—
4	M-N	15.0	2.8	7.40
5	M-N	12.0	2.7–2.8	6.30
6	M-N	10.0	2.5	5.26
7	T-U	19.8	4.1–4.2	16.58
8	T-U	12.0	3.4–3.5	10.36
9	T-U	10.0	2.9–3.0	7.27
10	T-U	8.0	2.9	7.06
11	T-U	6.0	2.9	6.88
12	U-V	19.8	4.5–4.6	19.04
13	U-V	9.0	3.4	11.23
14	U-V	6.0	3.0	9.79
15	V	19.8	5.0	23.38
16	V	18.0	4.8–4.9	23.71
17	V	17.0	4.6	20.95
18	V	15.0	4.2	15.55
19	V	10.0	3.5	12.37
20	V	8.0	3.5	11.77
21	W	19.8	5.3–5.4	27.65
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
28	X-Y	19.8	7.0–7.1	41.30
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
32[f]	W-X	12.0	4.5	19.56
33	X-Y	10.0	5.0	25.01
34[g]	U-V	12.0	4.2	24.28
35	W-X	12.0	4.9	19.96
36[h]	M-N	19.8	3.1–3.2	12.24
37	M-N	19.8	2.7–2.8	13.14
38	M-N	19.8	3.0	14.09
39	M-N	19.8	—	46.17
40	W-X	12.0	4.5	22.06
41	W-X	12.0	—	—
42	M-N	12.0	2.6	6.22
43	T-U	10.0	2.9	7.44
44	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 1[i]	M-N	19.8	3.6	16.45
ANPA soy ink 2[j]	M-N	12.5	2.6–2.7	6.10

[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 1 to 32 were prepared by Procedure 1 (ref. 10).
[f]Vehicles in experiment 32 and 33 were prepared by Procedure 2 (ref. 10).
[g]Vehicles in experiment 34 and 35 were prepared by Procedure 4 (ref. 10).
[h]Vehicles in experiment 36 to 42 were prepared by Procedure 5 (ref. 10).
[i]Vehicles in experiment 42 and up were prepared by Procedure 3 (ref. 10).
[j]Reference 6.

TABLE 2

Ink Formulations with Vegetable Oil

Oil used in vehicles	Vehicle viscosity[a]	Pigment (% w/w)[b]	Ink tack (g-m)[c]	Ink viscosity (poises)[d]
Cottonseed[e]	W	15.0	4.7	21.22
Cottonseed[e]	W-X	12.0	4.6–4.7	23.95
Cottonseed[e]	X-Y	10.0	4.9	22.43
Cottonseed[f]	X-Y	10.0	4.7–4.8	25.72
Cottonseed[g]	W-X	12.0	4.7	19.72
Canola[e]	W	15.0	4.7–4.8	20.39
Canola[e]	W-X	12.0	4.5–4.6	19.30
Canola[e]	X-Y	10.0	4.9	20.77
Canola[f]	W-X	12.0	4.5–4.6	19.32
Canola[g]	W-X	12.0	4.7	21.53
Safflower[e]	W	15.0	4.9	20.77
Safflower[e]	W-X	12.0	4.5–4.6	19.70
Safflower[e]	X-Y	10.0	4.9–5.0	24.67
Safflower[f]	W	15.0	4.9	20.15
Safflower[g]	W-X	12.0	4.5	19.11
Sunflower[e]	W	15.0	4.9–5.0	23.13
Sunflower[e]	W-X	12.0	4.5–4.6	18.43
Sunflower[e]	X-Y	10.0	5.0	23.93
Sunflower[f]	W	15.0	4.7–4.8	20.52
Sunflower[f]	W-X	12.0	4.5	18.72
Sunflower[g]	W-X	12.0	4.5–4.6	20.68

[a]Gardner-Holdt Viscosity Scale.
[b]Carbon black (Elftex 8).
[c]Measured by Electronic Inkometer.
[d]Measured by Laray Falling Rod Viscometer.
[e]Vehicles were prepared by Procedure 1 (ref. 10).
[f]Vehicles were prepared by Procedure 2 (ref. 10).
[g]Vehicles were prepared by Procedure 3 (ref. 10).

solute print densities were measured with an X-Rite 428 Computerized Color Reflection Densitometer (X-Rite, Incorporated, Grandville, MI). Several formulations, considered to be candidates for offset lithography, were scaled up and evaluated on ANPA's commercial/pilot offset web press.

Rub-off resistance of these prints were evaluated by the ANPA-NAPIM Rub-off Standard Test Procedure. The amount of rub-off 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 (Applied Color, Princeton, NJ) and calculated from the following:

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

where % R is 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 rub-off resistance.

RESULTS AND DISCUSSION

We have succeeded in formulating vegetable oil-based printing inks and have completely eliminated petroleum-based resins. Consequently, these ink formulations cost even less than petroleum oil-based ink formulations. A broad range of viscosity and tack values are possible. Thus, formulations can be prepared that are suitable for both lithographic and letterpress applications. In this study, inks are prepared from the vegetable oil-based vehicles (10) by formulation with pigment and miscellaneous additives as required for the prospective application. These vegetable oil vehicles are compatible with the pigments for producing the four colors commonly used in the newspaper printing industry, *e.g.*, black, cyan (blue), magenta (red) and yellow. The pigment is blended into the vehicle until a uniform dispersion is obtained. Additives that may be formulated into the inks include driers, lubricants, antioxidants and the like. The thickening effect of the pigment on the base vehicle was considered in preselecting a vehicle viscosity. Formulated inks also were evaluated for rub-off resistance. Rub-off is defined as the unwanted transfer of ink from the printed page to another surface. The acceptable water take-up for lithographic ink performance also was tested.

Properties of inks formulated with soybean oil are sum-

TABLE 3

Ink Rub-off Resistance Evaluation

Experiment number	Rub-off values as percent blackness		Improvement (%)
	Initial	After 2 hr	
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 6.

TABLE 4

Letterpress Inks with Soybean Oil

Experiment number	Print density (absolute)[a]	
	One impression[b] print	Two impressions[b] print
4	1.28	1.46
42	1.20	1.44
6	1.15	1.38
8	1.19	1.44
9	1.13	1.37
10	1.03	1.27
11	0.88	1.13
13	1.06	1.32
14	0.91	1.12
19	1.11	1.38
20	1.05	1.25
5	1.20	1.41
43	1.11	1.35
ANPA soy ink 2[c]	1.21	1.41

[a]X-Rite 428 Computerized Color Reflection Densitometer was used to obtain absolute print density.

[b]Prints are obtained by Little Joe Offset Proof Press.

[c]Reference 6.

marized in Table 1. Ink formulations with cottonseed, canola, safflower and sunflower oils are shown in Table 2. These inks are characterized by viscosities in the range of about 5–46 poises and by tack values of about 2–7 gram-meter (g-m). The typical viscosity for a black lithographic news ink is in the range of about 13–24 poises, and about 5–12 poises for a black letterpress new ink. 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. Because of the vehicle system we use (10), 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.

In water tolerance tests, the above lithographic inks demonstrated an acceptable range of 20–30% water take-up, well within the acceptable range of 20–36% (11). Inks with these properties also were characterized by acceptable or superior rub-off values. Rub-off values as percent blackness are shown in Table 3. These 17 samples were chosen to cover a wide range of viscosity and tack properties. The majority showed percent blackness of less than 6% after 2 hr, thus demonstrating good rub resistance. The percent improvement is less important than having the minimal percent blackness after 2 hr of printing. Formulations 25 and 44 in Table 1 were tested for long-term stability, and they both performed exceptionally well. Long-term stability is the ability of an ink to main-

TABLE 5

Yellow Inks with Soybean Oil

Vehicle[a] viscosity	Thickening agent	Pigment % (w/w)	Print density	Ink tack (g-m)	Ink viscosity (poises)
V	+	20	1.14	4.7	23.46
W	+	17	1.09	4.7	21.88
W-X	+	15	1.08	4.6	21.78
X-Y	+	12	1.08	5.0	27.77
X-Y	–	12	1.07	4.2	19.08
X-Y	–	10	1.06	4.1	15.09
$Z\text{-}Z_1$	–	12	1.08	4.9	31.24
M-N[b]	+	25.9	1.07	3.3	17.37

[a]Vehicles prepared by Procedure 1 (ref. 10). Gardner-Holdt Viscosity Scale.
[b]ANPA soybean oil vehicle contains 22–27% Picco Resin (ref. 6).

TABLE 6

Blue Inks with Soybean Oil

Vehicle[a] viscosity	Thickening agent (% w/w)	Optical brightener (% w/w)	Pigment (% w/w)	Print density	Ink tack (g-m)	Ink viscosity (poises)
V	5.0	18.3	9.1	1.25	4.3	25.92
V	5.0	—	9.1	1.31	4.4	23.10
V	5.0	10.0	9.1	1.29	4.4	21.28
X-Y	2.0	20.0	7.0	1.20	4.6	29.38
$Z\text{-}Z_1$	—	10.0	5.0	1.09	4.2	21.05
$Z_1\text{-}Z_2$	—	10.0	5.0	1.16	6.1	38.87
$Z_1\text{-}Z_2$	—	20.0	5.0	1.10	7.0	55.62
U-V[b]	5.0	18.3	9.1	1.19	4.1–4.2	27.26
U-V[b]	5.0	—	9.1	1.21	4.1–4.2	22.47

[a]Vehicles prepared by Procedure 1 (ref. 10). Gardner-Holdt Viscosity Scale.
[b]ANPA soybean oil vehicle contains 22–27% Picco Resin (ref. 6).

TABLE 7

Red Inks with Soybean Oil

Vehicle[a] viscosity	Thickening agent	Pigment % (w/w)	Print density	Ink tack (g-m)	Ink viscosity (poises)
V	–	20.75	1.31	4.2	18.47
W	–	16.75	1.25	4.0	16.07
W-X	–	14.75	1.21	4.3	19.94
X-Y	+	12.75	1.22	4.6	22.44
X-Y	+	10.25	1.21	4.8	23.13
X-Y	–	12.75	1.20	4.2	18.76
$Z\text{-}Z_1$	–	10.25	1.19	5.1	27.17
R-S[b]	+	27.10	1.32	4.6–4.7	28.45

[a]Vehicles prepared by Procedure 1 (ref. 10). Gardner-holdt Viscosity Scale.
[b]ANPA soybean oil vehicle contains 22–27% Picco Resin (ref. 6).

tain its rheological properties and water tolerance for more than 50,000 copies. Many ink formulations that are promising during short production cycles (10,000 copies or less) fail to maintain their printing characteristics thereafter, because of solvent evaporation or long-term emulsion problems. Also, these formulations showed minimum accumulation on the rollers. The residues were soft and easy to clean. Except for #23, all formulations tested had rub-off values lower than that of ANPA's soy oil ink. Print density of letterpress inks with typical viscosity and tack values are tabulated in Table 4.

Properties of yellow, blue and red inks are reported in Tables 5, 6 and 7, respectively. These data show that the addition of up to 5% thickening agent is an option, but not a necessity, for our color ink formulations. Also, the exceptionally light color of our vehicle permitted us to use 20–30% less pigment to obtain desired print density. This fact, alone, translates to substantial savings in the cost of color inks. Elimination of the expensive hydrocarbon resin from the vehicle and 25–30% reduction of pigment results in significant savings. Preliminary cost estimates based on material and vehicle preparation cost (Archer

Daniels Midland Co., Decatur, IL, private communication), show that our black ink should cost 50–55 cents/pound *vs.* 63 cents/pound for petroleum-based ink or 91 cents/pound for ANPA soy oil ink. In 1987, 550 million pounds of letterpress and lithographic news ink was produced according to a census of manufacturers (12). If total conversion to soy-oil ink occurs, about 2.5 billion pounds of soybeans or 500 million pounds of soy oil will be used to supply the news ink market.

REFERENCES

1. *White Paper*, prepared for American Soybean Association, St. Louis, Missouri, 1988.
2. Ono, T., and K. Otake, Japanese Patent no. 123681 (1961).
3. Kuzuwata, M., Japanese Patent no. 227287 (1963).
4. Gupta, P.K., J. Rai, H. Singh, Indian Patent no. 154760 (1984).
5. Kobayaski, S., and K. Nozaki, Japanese Patent no. 17716 (1978).
6. *Manufacturing Directions for Soybean Oil-based ANPA-INK*, Reston, Virginia, 1988.
7. Moynihan, J.T., U.S. Patent no. 4419132 (1983).
8. Moynihan, J.T., U.S. Patent no. 4519841 (1985).
9. Moynihan, J.T., U.S. Patent no. 4554019 (1985).
10. Erhan, S.Z., and M.O. Bagby, *J. Am. Oil Chem. Soc. 68*:635 (1991).
11. Surland, A., *A. Laboratory Test Method for Prediction of Lithographic Ink Performance*, Sun Chemical Corporation, 1980, p. 5.
12. *Product and Product Classes, 1987 Census of Manufacturer Industry Series, Miscellaneous Chemical Products*, U.S. Department of Commerce, Bureau of the Census, 1987.

[Received May 24, 1991; accepted December 30, 1991]