# Lithographic and Letterpress Ink Vehicles from Vegetable Oils

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**Our objectives for this study were to produce vegetable oil-based printing ink vehicles that did not require any petroleum components, which meet or exceed industry standards for rub-off resistance, viscosity and tackiness for a variety of printing applications. These objectives were satisfactorily met. Vehicles were completely compatible with carbon black, making them suitable for black ink formulations. In addition, the resulting vehicles had exceptionally light colors, and permitted formulations of colored inks that had substantially reduced pigment levels compared to industry standards.**

KEY WORDS: Gel, heat-bodied, ink, soybean, vegetable oils, vehicle.

The petroleum shortage in the mid 1970s stimulated research to find alternatives to mineral oil and other petroleum products in ink formulations.

In the early 1980s blends of "gilsonite" and tall oil fatty acids were investigated by the American Newspaper Publishers Association, Reston, Virginia, as a nonpetroleum-based vehicle for news inks (1–3). Acceptance of these inks by the industry has been limited due to the cost, availability of tall oil and the difficulty of equipment clean-up caused by the "gilsonite."

Later in 1985 research efforts resulted in a vegetable oil-based vehicle comprising alkali-refined soybean oil and hydrocarbon resin to produce a lithographic news ink by using the four news ink pigments in the formulations (American Newspaper Publishers Association, private communication). While the colored inks have become commercial, widespread acceptance of black ink has been inhibited by cost, which exceeds the traditional petroleum-based black inks by 50–70%.

The industry has continued to seek a nonpetroleum-based printing ink. In late 1987 the American Newspaper Publishers Association asked the Agricultural Research Service, Peoria, IL, to develop a vehicle and ink that would: i) be cost competitive with petroleum-based inks; ii) not require petroleum-derived components; iii) resist rub-off on hands and clothing; and iv) enable formulation over a wide range of viscosities as required by various printing applications.

Because of its general availability, soybean oil was emphasized in our studies. However, other vegetable oils of various iodine values were evaluated to determine the influence of unsaturation on properties of the vehicles. For our studies, we selected alkali-refined soybean, cottonseed, canola, safflower and sunflower oils. Alkali refining removes not only the gums and waxes, which may interfere with the properties of the vehicles and the ultimate ink formulations, but also removes free fatty acids. The latter tend to reduce hydrophobicity properties desired in certain ink formulations.

Discussed here are the results of successful development of vehicles for ink formulations that meet the major criteria stated above.

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## EXPERIMENTAL PROCEDURES

*Materials.* Alkali-refined soybean oils were obtained from Riceland Foods, Stuttgart, AR, and Archer Daniels Midland, Decatur, IL. Alkali-refined canola oil and cottonseed oil were purchased from Bunge Foods, Bradley, IL. Alkali-refined sunflower oil was obtained from Archer Daniels Midland. Alkali-refined safflower oil was obtained from Pacific Anchor Chemical Co., Cumberland, RI.

*Polymerization.* Procedure 1: Alkali-refined vegetable oil (300–1600 mL) was placed in a 0.5–2 liter four-necked reaction flask equipped with a "Jiffy-Mixer" agitator. The oil was heated to 330 ± 3°C and agitated under nitrogen atmosphere to attain the desired viscosity. Procedure 2: Procedure 1 was repeated in a four-necked reaction flask equipped with either a Dean-Stark trap or a reflux condenser to recover any oil that might be entrained with the nitrogen gas flow. Procedure 3: Procedure 1 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 agitator. Procedure 4: Procedure 1 was repeated at 300 ± 3°C with 5% by weight of anthraquinone catalyst (4). Heating was terminated when the desired viscosity was reached. The catalyst shortened the heating time by about 10–20%. The heat-bodied oil was allowed to cool to room temperature and then filtered to remove the precipitated catalyst.

*Vehicle.* Procedure 5: Some polymers prepared as described in Procedure 1 were used directly as vehicles; others, having Gardner-Holdt viscosities as high as $Z_8$–$Z_9$, were admixed with low-viscosity polymers/vehicles and/or unmodified, alkali-refined vegetable oil at 65–75°C in a reaction flask equipped with a "Jiffy-Mixer" mechanical stirrer.

In a four-necked reaction flask equipped with a "Jiffy-Mixer" agitator, the gel from Procedure 3 was blended in various ratios with unmodified alkali-refined vegetable oil at 330 ± 3°C under a nitrogen atmosphere. The heating softened the gel and promoted blending. Agitation was continued until a smooth vehicle was obtained. Dissolution of the gel in the oil under these conditions tends to be complete, obviating the need for filtration. The proportions of the gel and unmodified oil determine the resultant vehicle viscosities.

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

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

Rub-off values of inks formulated with these vehicles were evaluated by the American Newspaper Publishers Association (ANPA)-National Association of Printing Ink Manufacturers (NAPIM) Rub-off Standard Test Procedure. The amount of rub-off is monitored by the percent blackness of a stain that results by drawing a tissue under a given pressure over the surface of a printed sheet. Dark black stains indicate the potential transfer of the ink pigment to the hands of the reader. Light gray stains indicate low rub potential of the ink. The percent improvement determines the rate of pigment fixation on the newsprint by either penetration into the sheet or vehicle hardening. A percent blackness of less than 6% after 2 hr is considered characteristic of an ink with good rub-off resistance.

## RESULTS AND DISCUSSION

The vehicles prepared by Procedures 1, 2 and 4 typically had Gardner-Holdt viscosities in the range of G-Y or about 1.6–18 poises (5). These viscosities correspond to molecular weights of about 2600–8900 (6) (S.Z. Erhan and M.O. Bagby, submitted for publication).

Presumably, the molecular weight and viscosity increases are due to the triglycerides undergoing Diels-Alder reaction (6). At the temperature of heat bodying, the double bonds migrate and conjugated dienes are formed (7). In Procedure 4, the catalyst increases the polymerization rate by enhancing the isomerization of the polyunsaturated fatty acids to the necessary conjugated configuration before the polymerization reaction takes place (4). Conjugated unsaturated oils heat-body much more rapidly than nonconjugated oils. Characteristics and composition of oils that are 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. The triglyceride structure of the oils, consisting of three fatty acids at which addition may occur, introduces the possibility of forming complex structures and very large molecules. The complexity increases if all three acyl groups in the triglyceride are reactive. Gelling times for safflower, soybean, sunflower, cottonseed and canola oil were 110, 255, 265, 390 and 540 min, respectively. Iodine values of the oils given in Table 1 were consistent with these gelling times. Although iodine values of cottonseed and canola oil were similar, canola oil, with its high oleic acid and low polyunsaturate content, requires a longer time to gel.

It is possible to blend such heat-bodied oils of different viscosities to produce a desired vehicle viscosity. The component properties and viscosities of six vehicles prepared by Procedure 5 are set forth in Table 2.

The viscosities of vehicles prepared by Procedure 3 were varied by blending different proportions of the gel and unmodified oil. The gel-to-oil proportion for a vehicle having a viscosity of M–N ranged from about 21.5:78.5 to about 22.5:77.5; whereas for a viscosity of X–Y, the proportion ranged from about 51:49 to about 53:47 (Table 3).

The principal advantage of these vehicles is that the gel can be prepared and stored as a stock material for subse-

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 (X–Y)[d] | 75 (G–H) | 0 | M–N |
| 15 (X–Y) | 85 (I–J) | 0 | M–N |
| 50 (X–Y) | 0 | 50 | M–N |
| 34 ($Z_8$–$Z_9$) | 26.6 (U–V) | 39.4 | M–N |
| 70 ($Z_3$–$Z_4$) | 0 | 30 | W–X |
| 32.5 ($Z_8$–$Z_9$) | 0 | 67.5 | W–X |

[a]Heat-bodied oils were prepared by using either soybean, sunflower, safflower, cottonseed or 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 viscosity[b] |
|---|---|---|
| Gel | Oil | |
| 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 or canola oil.

[b]Gardner-Holdt Viscosity Scale.

TABLE 4

**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.

TABLE 5

**Rub-Off Resistance of Ink Formulations**

| Ink | Rub-off values as percent blackness | |
|---|---|---|
| | Initial | After 2 hr |
| 1[a] | 6.0 | 5.5 |
| 2[b] | 6.6 | 5.2 |
| ANPA soy ink[c] | 14.1 | 8.4 |

[a]Vehicle prepared by Procedure 1.

[b]Vehicle prepared by Procedure 3.

[c]Vehicle consists of 22–27% Picco Resin and 53–58% soybean oil (Reference 8).

quent custom blending of vehicles over a broad viscosity range.

All of our vehicles were characterized by exceedingly light coloration, with values on the Gardner Color Scale of about 6 or less, typically in the range of about 2–4 (Table 4). This property permits a substantial reduction in the amount of pigment required for colored inks as compared to the pigment levels required by commercial vehicles with Gardner Color Scale values of about 13–14.

Inks formulated with our vehicles showed superior rub-off characteristics, initially and 2 hr after printing (Table 5). When values differ more than 1.4 units between two formulations, the lower valued ink is judged to be significantly superior.

We have now succeeded in making vegetable oil-based printing ink vehicles that have all of the desired characteristics. These vehicles are prepared by thermal transformation of the vegetable oil starting material.

In general, the oil is heated under nitrogen, with mixing, to a suitable temperature to promote an increase in the viscosity of the oil. Heat bodying promotes polymerization of the vegetable oils via conjugation of conjugatable double bonds. Inter- and intra-molecularly crosslinked polymers are formed by virtue of cyclization involving conjugated double bonds of one fatty acyl moiety and a point of unsaturation on another moiety.

The process can be easily tailored to give products with a range of properties (*e.g.* viscosity, tackiness, etc.), enabling use for formulating inks with a variety of end-use applications. The exceptionally light colors of the resulting vehicles permit formulation of colored inks with substantially reduced levels of pigment as compared to industry standards. The vehicles are also completely compatible with carbon black and are useful in formulating black inks.

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## REFERENCES

1. Moynihan, J.T., and American Newspaper Publishers Association, U.S. Patent 4419132 (1983).
2. Moynihan, J.T., and American Newspaper Publishers Association, U.S. Patent 4519841 (1985).
3. Moynihan, J.T., and American Newspaper Publishers Association,

U.S. Patent 4554019 (1985).
4. Falkenburg, L.B., W. DeJong, D.P. Handke and S. Radlove, *J. Am. Oil Chem. Soc. 25*:237 (1948).
5. Mattil, K.F., F.A. Norris, A.J. Stirton and D. Swern, *Bailey's Ind. Oil Fat Prod.*, 513 (1964).
6. House, H.O., *Modern Synthetic Reactions*, 2nd edn., 817 (1971).
7. Powers, P.O., *J. Am. Oil Chem. Soc. 27*:468 (1950).
8. American Newspaper Publishers Association, *Manufacturing Directions for Soybean Oil-Based ANPA Ink*, Reston, Virginia, 1988.

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