Vegetable-oil-based printing ink formulation and degradation

Sevim Z. Erhan *, Marvin O. Bagby

Oil Chemical Research, National Center for Agricultural Utilization Research, Agricultural Research Center, U.S. Department of Agriculture [1], Peoria, IL 61604, USA

Abstract

Printing ink vehicles that did not require petroleum components were prepared from modified vegetable oil. The apparent average molecular weight ($\overline{M}_w$) of 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 $\overline{M}_w$ of these vehicles was established. Physical properties of the formulated inks meet or exceed the industry standards for lithographic and letterpress newsprint applications. Elimination of petroleum-based resin and reduced pigment requirements, due to the light vehicle color, should provide a competitively priced alternative to petroleum-based inks.

These ink vehicles along with the commercial ones were subjected to biodegradation. Results show that the vegetable-oil vehicles degrade faster and more completely than commercial soy- or mineral-oil-based vehicles. Fermentations were allowed to proceed for 5, 12 and 25 days. Both mono- and mixed cultures of microorganisms, which are commonly found in soil, were used. Greater increase in biodegradation with time was observed for our vehicles than the commercial vehicles. In 25 days, commercial mineral-oil-based vehicles degrade 17–27%, while commercial partial soy-oil-based vehicles degrade 58–68% and our 100% soy-oil-based vehicles degrade 82–92%.

Keywords: Soybean oil; News ink; Biodegradation

1. Introduction

In the printing industry, the processes in current use are lithography (47%), gravure (18%), flexography (18%), letterpress (8%) and screen printing (3%), and electronic desktop publishing (6%) (R.W. Bassemir, pers. commun., 1990).

Lithography and letterpress processes require paste inks. Conventional printing inks used in these applications are multi-component systems comprising: a hydrocarbon and/or alkyd resin; a hydrocarbon solvent; a pigment; and optional additives. For example, a typical petroleum-based, black litho-news ink composition is 15–25% hydrocarbon or alkyd resin and 50–70% mineral oil solvent combined as the vehicle, and 15–20% carbon black as the pigment. Nearly 227 million kilograms of ink for these applications are produced domestically each year (American Soybean Association, 1988). The petroleum shortage in the 1970's stimulated research on vegetable-oil-based inks as substitute for petroleum-based products.

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* Corresponding author. Fax: 309-681-6686.

[1] 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.

Inks containing vegetable oils have been formulated for various specialized applications (Kobayashi and Nozaki, 1978; Gupta et al., 1984; Ono et al., 1986; Kuzuwata and Koho, 1988). 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 with carbon black pigment (Moynihan and ANPA, 1983; Moynihan and ANPA, 1985; ANPA-INK, 1988). The cost and availability of tall oil and the difficulty of equipment clean-up caused by the "gilsonite" limited the acceptance of these inks by the industry. A later approach by ANPA to produce an ink vehicle from renewable materials resulted in a lithographic news ink formulated with a commercial ANPA vehicle consisting of alkali-refined soybean oil and a hydrocarbon resin and carbon black pigment (Moynihan and ANPA, 1985). This black ink prints as well as the mineral-oil-based commercial inks, but costs 30 to 50% more. The color inks are formulated similarly, with good print quality, but cost about 5–10% more than the petroleum-based commercial inks. Both, the black and color inks contain 20 to 25% hydrocarbon resin. Thus, industry has continued to search for 100% vegetable-oil-based ink to replace the petroleum-based inks.

Because of its availability and favorable price, soybean oil is the primary candidate for ink production. However, other vegetable oils are available with their distinct compositions, preparation, and properties. Of special consideration is the effect of unsaturation (iodine value, I.V.) and fatty acid composition of commodity oils available worldwide. Alkali refining removes the gums, waxes and free fatty acids. The presence of any one of these materials can interfere with the hydrophobic property of the vehicle and the ultimate ink formulation.

This hydrophobic characteristic deserves further comment. The lithographic (offset) printer plate or cylinder consists of two distinct areas. The image area is made hydrophobic, whereas the non-image area hydrophilic. Thus, the lithographic printing process involves a two-phase system consisting of an oil phase (ink) and an aqueous phase (fountain solution). During the printing process, these phases must not form stable emulsions or

they will not separate properly on the printer plates. Poorly separated phases lead to smudged or ill-defined print. Understanding of this characteristic directed our attention toward techniques for modifying vegetable oils that would provide relatively non-polar products, i.e., low oxygen content polymers.

The objectives of our study are (a) to prepare news ink based on vegetable-oil sources such as canola, cottonseed, safflower, soybean and sunflower that can meet industry standards in regard to ruboff resistance, viscosity, and tack, and (b) to determine the biodegradability of several types of news ink by soil microorganisms.

The vehicles can be prepared from vegetable oils by two methods (Erhan and Bagby, 1991). In one method, vegetable oils are heat-polymerized at constant temperature in a nitrogen atmosphere to the desired viscosity. In another method, the heat polymerization reaction is permitted to proceed to a gel point, and then the gel is mixed with vegetable oils to obtain the desired viscosity.

Besides the preparation and suitability of vegetable oil-based inks, information on their degradability is needed. Cavagnaro et al. (1988) have reviewed the biodegradation of food oils and greases. Several articles speculate that soy oil should biodegrade more readily than mineral oil (Ticer, 1988); however, published experimental data are limited. Moreover, there are no published data on the biodegradation of news ink vehicles. Knowledge of biodegradation, rates of degradation, and resulting products from ink vehicles are needed, as well as of the influence of the resin on degradation.

In this study, the biodegradation of three major types of news ink vehicles were evaluated. These include: (a) commercial petroleum-based (Flick, 1985), (b) American Newspaper Publishers Association's (ANPA) partial soy-oil-based (ANPA-INK, 1988), and (c) United States Department of Agriculture's (USDA) 100% soy-oil-based (Erhan and Bagby, 1991). For this purpose, we selected three soil microorganisms: *Aspergillus fumigatus*, *Penicillium citrinum* and *Mucor racemosus*.

We describe soy- and other vegetable-oil ink formulations that meet or exceed industry standards in regard to ruboff resistance, viscosity and

tack and are cost-competitive with petroleum-based inks. To study oils with a broad range of I.V. and containing saturated, mono-unsaturated, di-unsaturated and tri-unsaturated acids, we selected alkali-refined canola, cottonseed, safflower, soy and sunflower oils.

2. Materials and methods

Alkali-refined soybean oils were obtained from Riceland Foods, Stuttgart, Arkansas and Archer Daniels Midland Co., Decatur, Illinois. Alkali-refined canola oil and cottonseed oil were purchased from Bunge Foods, Bradley, Illinois. Alkali-refined sunflower oil was obtained from Archer Daniels Midland Co., Decatur, Illinois. Alkali-refined safflower oil was obtained from Pacific Anchor Chemical Co., Cumberland, Rhode Island.

Carbon black ("Elftex 8") was obtained from Cabot Co., Boston, Massachusetts. 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, Ohio.

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

2.1. Polymerization

Product 1: alkali-refined vegetable oil (300–1600 ml) in a 0.5–2 l four-necked reaction flask equipped with a "Jiffy Mixer" agitator was polymerized under a nitrogen atmosphere with heat (330 +3°C) and agitation to obtain the desired viscosity. Samples were taken periodically to determine the viscosity. *Product 2*: the procedure for making product 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. *Product 3*: the procedure used for product 1 was continued until the oil gelled. The reaction was discontinued when clumps of gel began to move up the shaft of the agitator. *Product 4*: product 1

procedure was repeated at 300 ± 3°C with 5% by weight of anthraquinone catalyst (Falkenburg et al., 1948). Heating was terminated when the desired viscosity was reached. The catalyst shortened the heating time by about 25–50%. The heat-bodied oil was allowed to cool to room temperature and then filtered to remove the precipitated catalyst.

2.2. Vehicle

Some of the product 1 polymers were used directly as vehicles. Others with 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°C in a reaction flask equipped with a "Jiffy-Mixer."

The product 3 gel was blended in a four-necked reaction flask equipped with a "Jiffy-Mixer" agitator at various ratios with unmodified alkali-refined vegetable oil at 330 ± 3°C under a nitrogen atmosphere. Heating softened the gel and aided blending. Agitation was continued until a smooth vehicle was obtained. Dissolution of the gel in the oil under these conditions tended to be complete, obviating the need for filtration. The ratio of the gel to unmodified oil controlled the vehicle viscosities.

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

The color of the vehicles was evaluated on the Gardner Color Scale by ASTM D1544-63.

The iodine value (I.V.) was obtained by the AOCS Cd.I.25 Wijs method and the peroxide values were obtained by the AOCS Cd.8.53 tentative method.

2.3. GPC analyses

Polystyrene standards from Polymer Laboratories Ltd. (Amherst, Massachusetts) were used with the following specifications (peak average molecular weight, $\bar{M}_p$, and molecular weight distribution, MWD): 580, 1.14; 1320, 1.09; 3250, 1.04; 9200, 1.03; 28,500, 1.03, 66,000, 1.03; 156,000, 1.03; 435,500, 1.04; 1,030,000, 1.05; 2,250,000, 1.04; 2,880,000, 1.04.

All samples in duplicate were dissolved in tetrahydrofuran (THF) (0.4% w/v), filtered through 0.5 μm Teflon filters, and then injected into the HPLC (Model 8100, Spectra Physics, Freemont, California). Chromatography conditions were: flow 1 ml/min; oven temperature 40°C; column 30 cm, 7.5 mm, PL-Gel 5 μ mix; detector, differential refractive index (Model 6040, Spectra Physics); injection volume 100 μl. Average molecular weights (M_w) were determined from elution volumes compared to the polystyrene standards.

Ink. Black printing inks were formulated by heating the previously prepared 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, Indiana), operated at 2500–3000 rpm for 5–7 h.

Color pigments, vehicles, and additives were premixed with a Shar High Speed Disperser at 2500 rpm for 20–30 min. Dispersion of the pigments was completed with an Eiger Mini Mill (Eiger Machinery Inc., Bensenville, Illinois) using 2 mm chrome steel balls 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, Ohio) using ASTM 1316-87.

Yellow inks were formulated with vehicles of various viscosities and yellow pigment. In some samples, a thickening agent ("Bentone 128") was added at 0.5–2.0 wt% to adjust the viscosity. Red inks were similarly prepared using magenta pigment.

Blue inks were formulated as with cyan pigment, but for some samples, 2.0 to 5.0% thickening agent ("Bentone 128") was added to adjust the viscosity, and up to 20% Hydrite R as an optical brightener.

Viscosities of the inks were measured with a Model VM.01 Laray Falling Rod Viscometer (Testing Machines Inc., Amityville, New York). The apparent viscosity at 2500 S^{-1} was calculated by the power log method using ASTM D4040-81.

The tack values of the inks were measured with a Model 101 Electronic Inkometer (Thwing-Albert Instrument Company, Philadelphia, Pennsylvania). The ASTM D4361-84 method was used to obtain the apparent tack values at 1200 rpm and 32.2 ± 0.05°C. Tack values are 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 rpm for 5 min. Water uptake in the range of 10 to 18 g per 50 g ink is an acceptable range for lithographic inks (Surland, 1980).

A "Little Joe" offset Proof Press Model HD (Little Joe Color Swatcher, Somerville, New Jersey) was used to obtain letterpress prints. To get the proper film thickness of ink, 0.6 ml of ink (3 notches on an IPI Volumeter) was used to roll up an inking area of 6.98 × 10^{-2} m^2. A "Quick Peek" color proofing kit (Thwing-Albert Instrument Company) was used to evaluate color matching of color inks. Absolute print densities were measured with an "X-Rite 428 Computerized Color Reflection Densitometer" (X-Rite, Incorporated, Grandville, Michigan).

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 was evaluated by the ANPA–NAPIM Ruboff Standard Test Procedure. The amount of ruboff, as percent blackness, was determined by pulling a tissue weighted with a 6.89 × 10^3 Pa pressure over the surface of a printed sheet. The extent of ruboff was measured at 10 and 20 min following printing by reflectance with an Applied Color Science Spectrometer, Model 1101 (Princeton, New Jersey). The percent blackness was calculated from the following relation:

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

where $\%R$ = percent reflection at 560 nm. The percent decrease in blackness determines the rate of pigment fixation on the newsprint by either penetration into the sheet or resin hardening. Inks with a blackness of less than 6% after 2 h are considered to have good ruboff resistance.

2.4. Biodegradation

Aspergillus fumigatus (NRRL 163), *Penicillium citrinum* (NRRL 1843) and *Mucor racemosus* (NRRL 5281) were obtained from the USDA, ARS Culture Collection, National Center for Agricultural Utilization Research (NCAUR). A synthetic liquid medium was prepared as described previously (Koritala et al., 1987). The culture medium (1000 ml) was sterilized in a 2800-ml flask by autoclaving at 120°C. A 4-g portion of alkali-refined soybean oil or ink vehicle was added to the flask with the growth medium. The following ink vehicles were evaluated: two USDA soy news-ink vehicles (Gardner–Holdt viscosity of M–N and W–X) (Erhan and Bagby, 1991), a USDA soy news-ink vehicle containing gel (Gardner–Holdt viscosity of W–X) (Erhan and Bagby, 1991), an ANPA soy oil news-ink vehicle (ANPA-INK, 1988) (prepared at NCAUR) and a commercial petroleum news-ink vehicle (Flick, 1985) (prepared at NCAUR). Two, 3-mm diameter, loopsful of microorganisms grown on yeast-malt agar slants were transferred to the medium, and the flask and its contents were shaken (200 rpm) on a rotary shaker at 25°C for 5, 12 and 25 days. Duplicate or triplicate samples were inoculated with either mono- or mixed cultures. The fermentations were terminated by refrigeration at 1.1°C.

The extent of biodegradation of the soybean oil and the ink vehicles was determined by differences in weight between that added to the fermentation and that recovered at termination. The relative rates of degradation were ascertained at intervals of 5, 12 and 25 days.

To determine residual lipid content, the fermentation broth was extracted four times with diethyl ether (200 ml). Validity of extraction protocol efficiency was established in the absence of microorganisms. The combined ether extract was washed with water (800 ml) and then dried with anhydrous sodium sulfate. The ether solution was filtered through silicone-coated filter paper (Whatman Lab Sales, Hillsboro, Oregon) into a tared round-bottomed flask. To assure quantitative transfer, the sodium sulfate was washed four times with ether and the ether removed with a rotary evaporator. The flask with the lipid material was vacuum-desiccated overnight. Lipid recovery was determined gravimetrically.

3. Results and discussion

The prepared vehicles typically had viscosities in the range of G–Y on the Gardner–Holdt viscometer scale or about 1.6–18 P (Surland, 1980). These viscosities corresponded to apparent average molecular weights ($\bar{M}_w$) of 2600–8900 (Mattil et al., 1964).

For all oils studied, the viscosity (from cross-linking and polymerization) increased with time at the heat-bodying temperature of 330 ± 3°C. The reaction time necessary to reach a desired viscosity depends on the mass and the structure of the reactants and the rate of heat transfer and agitation. As expected, oils with higher unsaturation polymerized more rapidly than those with lower unsaturation. 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 the iodine values of cottonseed and canola oil are similar, canola oil with its greater oleic and low linoleic acid contents required a longer reaction time.

During heat-bodying, conjugated dienes are formed by bond migration in polyunsaturated fatty acids. These can form 6-membered rings by intra- or intermolecular reaction with the double bonds of other fatty acids. If these reactants come from different triglycerides, the M_w increases for the system. As heating continues, another conjugated group can add to the previously formed unsaturated ring structure. Triglycerides consisting of three polyunsaturated fatty acids where addition may occur, increase the probability of forming very complex, highly branched structures and very large molecules.

Gardner–Holdt scale viscosities and corresponding apparent $\bar{M}_w$ of soybean, safflower, sunflower, cottonseed, and canola oil-based vehicles are summarized in Table 1. Viscosity increases are directly proportional to increases in apparent $\bar{M}_w$ and the degree of polymerization. Apparent $\bar{M}_w$ at the same viscosity of different oils may be due to differences in linearity of the bodied oils. As

Table 1
Molecular weight and viscosity relation of various vegetable-oil vehicles

Oil used in vehicle	Vehicle viscosity[a]	Apparent $\bar{M}_w$ [b]
Soybean oil	G–H	2656
	M–N	3757
	T–U	4991
	U–V	5133
	V	6030
	W	6193
	W–X	7208
	X–Y	8851
Canola oil	W	5928
	W–X	6656
	X–Y	8196
Cottonseed oil	W	5364
	W–X	7046
	X–Y	7644
Safflower oil	W	7191
	W–X	7215
	X–Y	7445
Sunflower oil	W	6165
	W–X	7345
	X–Y	8827

[a] Gardner–Holdt viscosity scale. Different viscosities were obtained at different heat-bodying times.
[b] Obtained by GPC analysis.

Table 2
Gel molecular weights of various vegetable oils

Gel	Apparent $\bar{M}_w$ [a]
Soybean	60423
Canola	44924
Cottonseed	38266
Safflower	31772
Sunflower	15055

[a] Obtained by GPC analysis.

heat-bodying time was increased, the ratio of polymerized oil to unpolymerized oil increased. These behaviors are readily seen by the plots in Fig. 1. At the heat-bodying time of zero, the peak shows the unmodified soybean oil. When heat-bodying time of the oil increases to 60 min, a shoulder appears resulting from formation of the polymer, and this shoulder becomes dominant as the heating time increases from 60 to 270 min.

Apparent $\bar{M}_w$ values of the vegetable-oil-derived gels are given in Table 2. The differences among oils in apparent $\bar{M}_w$ at the gel point suggest a decrease in the size of the gel particles from soybean oil to sunflower oil (Erhan and Bagby, 1992).
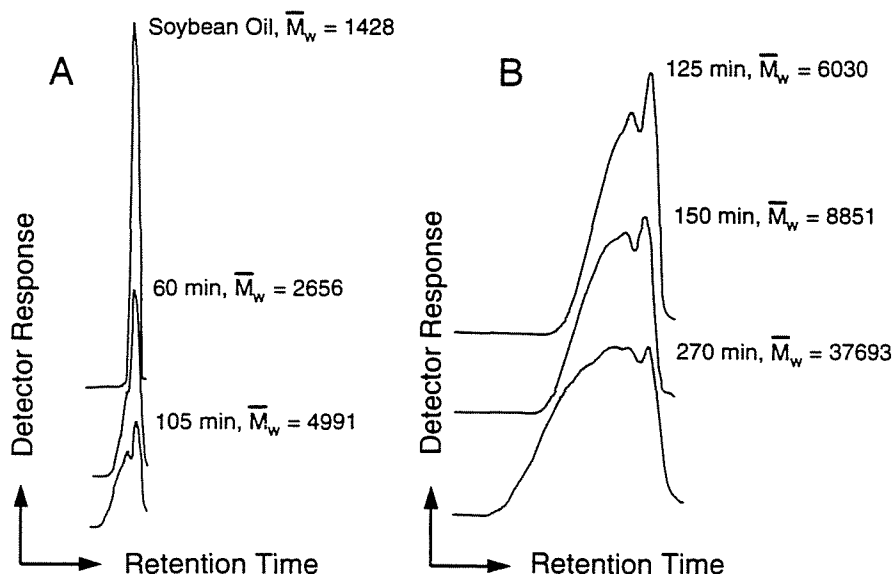

Fig. 1. (A) Gel permeation chromatograms of alkali-refined, 60 and 105 min heat-bodied soybean oil. (B) Gel permeation chromatograms of 125, 150, and 270 min heat-bodied soybean oil.

Table 3
Viscosity of heat-bodied oil blends[a]

Vegetable-oil component (% w/w)			Vehicle viscosity[c]
heat-bodied	heat-bodied	unmodified[b]	
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 (Z₈–Z₉)	26.6 (U–V)	39.4	M–N
70 (Z₃–Z₄)	0	30	W–X
32.5 (Z₈–Z₉)	0	67.5	W–X

[a] Heat-bodied oils were prepared by using either of soybean, sunflower, safflower, cottonseed and canola oils.
[b] Unmodified alkali-refined soybean oil.
[c] Gardner–Holdt viscosity scale.
[d] Letter values in parentheses represent Gardner–Holdt viscosities of heat-bodied oils.

Such heat-bodied oils of different viscosities can be blended to produce viscosities of any desirable value. The component properties and viscosities of six vehicles are shown in Table 3.

Blending different proportions of the gel and unmodified oil gave different vehicle viscosities. 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 4).

Vehicles prepared by these procedures are compatible with pigments for producing the four colors commonly used in the newspaper printing industry, namely, black, cyan, magenta and yellow. These vehicles are lightly colored. Except for canola, they have values on the Gardner color

Table 4
Vehicle viscosity of 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 and canola oil.
[b] Gardner–Holdt viscosity scale.

scale of about 6 or less and typically are in the range of about 2–4 (Erhan and Bagby, 1991). Because of the low degree of coloration, less pigment is needed compared to the darker commercial vehicles.

Inks formulated with the preceding vehicles are characterized by viscosities from 5 to 46 P and tack values from 2 to 7 g-m (gram-meter). Thus, these inks are suitable for both letterpress 5 to 12 P and lithographic 13 to 24 P applications. Tack values for lithographic inks are 3.5 to 4.8 g-m, and 2.6 to 3.4 g-m for letterpress. By using our vehicle technology (Erhan and Bagby, 1991), the desired viscosity and tack values of the formulated inks are easily attained. Additives which may be formulated into the inks include driers, lubricants, and antioxidants. The thickening effect of the pigment on the base vehicle was considered in preselecting a vehicle viscosity.

The preceding lithographic inks based on water tolerance tests had 20–30% water take up, which is within the acceptable range of 20–36% (Surland, 1980). Inks prepared in this study also were characterized by acceptable or superior ruboff values (Erhan et al., 1992). The majority of tested ink samples showed a blackness of less than 6% and as low as 4.2% 2 h after printing; thus they demonstrate good rub resistance.

Properties of yellow, blue and red inks are reported in Tables 5–7. These data show that the addition of up to 5% thickening agent is optional but not necessary for our color ink formulations. Eliminating hydrocarbon resin from the vehicle can significantly reduce the costs of both black and colored inks. In addition, reduction of pigment for colored inks due to the light coloring of vehicle can lower the price of the ink. Thus, we have succeeded in making vegetable-oil-based printing inks that require little thickening agent, less pigment, and no resin. In 1987, 250 million kg of letterpress and lithographic news ink were produced (Brant, 1987). If the news print industry converts completely to our soy-oil ink, about 1.14 billion kg of soybeans or 227 million kg of soy oil will be needed to supply the news ink market.

The *biodegradation* of the three USDA vehicles with *Aspergillus fumigatus* (NRRL 163) was 24,

Table 5
Properties of yellow inks with soybean oil

Vehicle viscosity[a]	Thickening agent (% w/w)	Pigment (% w/w)	Print density	Ink tack (g-m)	Ink viscosity[c] (poises)
V	2.0	20	1.14	4.7	23.46
W	2.0	17	1.09	4.7	21.88
W–X	2.0	15	1.08	4.6	21.78
X–Y	2.0	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–Z$_1$	–	12	1.08	4.9	31.24
M–N[b]	2.1	25.9	1.07	3.3	17.37

[a] Vehicles prepared by procedure 1 (Erhan and Bagby, 1991). Gardner–Holdt viscosity scale.
[b] ANPA soybean-oil vehicle contains 22–27% Picco Resin (ANPA-INK, 1988).
[c] Obtained by the Laray falling rod viscometer.

Table 6
Properties of blue inks with soybean oil

Vehicle viscosity[a]	Thickening agent (% w/w)	Optical brightener (% w/w)	Pigment (% w/w)	Print density	Ink tack (g-m)	Ink viscosity[c] (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–Z$_1$	–	10.0	5.0	1.09	4.2	21.05
Z$_1$–Z$_2$	–	10.0	5.0	1.16	6.1	38.87
Z$_1$–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 (Erhan and Bagby, 1991). Gardner–Holdt viscosity scale.
[b] ANPA soybean oil vehicle contains 22–27% Picco Resin (ANPA-INK, 1988).
[c] Obtained by the Laray falling rod viscometer.

Table 7
Properties of red inks with soybean oil

Vehicle viscosity[a]	Thickening agent (% w/w)	Pigment (% w/w)	Print density	Ink tack (g-m)	Ink viscosity[c] (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	1.25	12.75	1.22	4.6	22.44
X–Y	1.75	10.25	1.21	4.8	23.13
X–Y	–	12.75	1.20	4.2	18.76
Z–Z$_1$	–	10.25	1.19	5.1	27.17
R–S[b]	2.8+	27.1	1.32	4.6–4.7	28.45

[a] Vehicles prepared by procedure 1 (Erhan and Bagby, 1991). Gardner–Holdt viscosity scale.
[b] ANPA soybean-oil vehicle contains 22–27% Picco Resin (ANPA-INK, 1988).
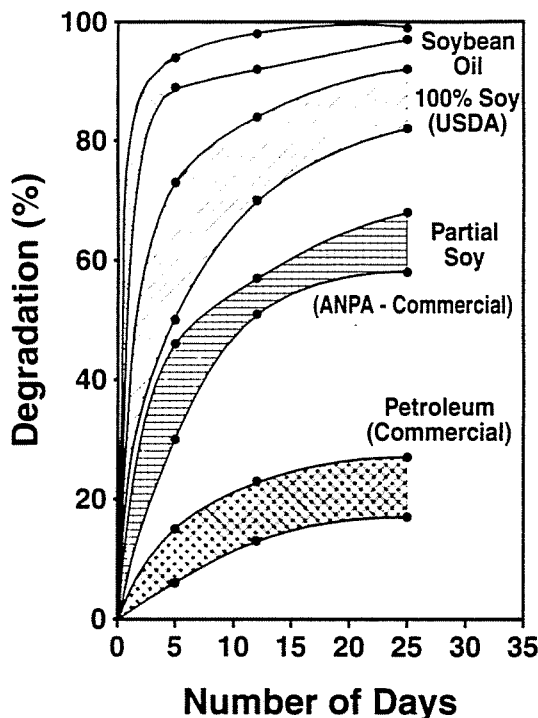[c] Obtained by Laray falling rod viscometer.

Fig. 2. Biodegradation of news ink vehicles.

21, and 29% greater than the commercial ANPA vehicle, and 42, 62, and 68% greater than the commercial petroleum-based vehicle for the three degradation intervals of 5, 12 and 25 days, respectively. For the USDA vehicles with *Penicillium citrinum* (NRRL 1843), the average degradation was 40, 27, and 21% greater than the ANPA vehicle, and 56, 60, and 63% greater than the commercial petroleum-based vehicle for the three degradation intervals, respectively. With *Mucor racemosus* (NRRL 5281), the average degradation of the USDA vehicles was 30, 26, and 23% greater than the ANPA vehicle and 51, 53, and 57% greater than the petroleum-based vehicle at 5, 12, and 25 days, respectively. The degradation rates obtained with mixed cultures were similar to those with monocultures.

Fig. 2 shows the composite percent degradation data of all tested vehicles and soybean oil with mono- and mixed cultures used in the test. Obviously, microorganisms consumed the various substrates at markedly different rates and differ-

ing levels of completeness. After 25 days, soybean oil is nearly completely degraded, whereas for USDA's 100% soy-oil-based vehicles degradation was 82 to 92%, for commercial ANPA 58 to 68%, and for commercial petroleum-based vehicles 17 to 27%.

4. Conclusion

Technology is available for manufacturing vegetable-oil-based printing ink vehicles with the desired commercial characteristics. These vehicles are prepared by thermal polymerization of vegetable oils as the raw materials.

A positive relationship was observed between the apparent $\bar{M}_w$ and their viscosities of heat-bodied oils, and a correlation between the shapes of the GPC peaks and the apparent $\bar{M}_w$ of heat-bodied oils. These relations will provide useful tools to monitor the scaling-up of the process developed to prepare printing ink vehicles from various vegetable oils.

Inks formulated with these vehicles have met or exceeded the industry standards for lithographic and letterpress newsprint applications. In addition, the elimination of petroleum-based resin and the reduced amount of pigment usage, due to the light vehicle color, make the 100% vegetable-oil-based inks a competitively priced alternative to petroleum-based inks.

Aspergillus fumigatus caused slower vehicle degradation than *Penicillium citrinum* and *Mucor racemosus*, at 5 days of fermentation, but they were more compatible at 12 and 25 days.

Most biodegradation occurred during the initial 5 days with all vehicles. As expected, the petroleum-based vehicle showed the least degradation even after a period of 25 days, when only 19–27% had degraded. The commercial ANPA vehicle degraded only 30–36% after 5 days, and from 58 to 66% after 25 days. These results were expected because 30–33% of the vehicle is petroleum-based resin and the remainder is soybean oil. Thus, the USDA vehicles offer both environmental and printing ink properties superior to commercial petroleum-based inks previously described, i.e., no petroleum, less ruboff, and lower cost.

Acknowledgements

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