Chapter 9

Printing Inks

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Introduction

Printing inks are applied to substrates by printing presses of various designs and are divided into five categories according to the type of printing press. Major printing processes used by the industry are lithography (offset), letterpress, flexography, gravure, and screen printing (1). Letterpress and lithographic inks are viscous and paste-like. Flexographic and gravure inks are extremely fluid and they are generally called liquid inks. On the other hand, screen inks are intermediate in viscosity between the liquid flexographic and gravure inks, and the paste-like lithographic inks.

Vegetable oils are mainly used in paste inks; therefore, the role of vegetable oils in paste ink formulations will be described.

Lithographic Inks

Lithographic inks, the leading type of ink both in volume and dollar shipments, accounted for an estimated 1,230 lbs, valued at $1,770 million in 2001 (2). They represent about 41% of all ink shipments as measured in dollars. Publication and commercial printing represents an estimated 80% of consumption. Of this, newspapers account for 40% of the total. In approximate order, the balance is: advertising printing; magazines and periodicals; catalogs and directories; financial and legal printing; labels and wrappers; and other commercial printing, including packaging. The petroleum shortage in the 1970s stimulated research into vegetable-oil based inks as a substitute for petroleum-based products.

Inks containing vegetable oils have been formulated for various specialized applications (3–6). In the early 1980s, the American Newspaper Publishers Association (ANPA) (later changed to the Newspaper Association of America/NAA) developed a series of ink formulations comprising a blend of "gilsonite" and tall-oil fatty acids with carbon black pigment (7–9). The cost and availability of tall oil and the difficulty of equipment cleanup created 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, a hydrocarbon resin, and carbon black pigment (10). This black ink prints as well as the mineral oil-based commercial ink, but costs 30 to 50% more. The color inks are formulated similarly, with a good print quality, but cost about 5 to 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 a 100% vegetable oil-based ink to replace the petroleum-based inks.

Ink Vehicles

Printing ink consists of two components: the colorant (pigment) and the vehicle. The ink vehicle is the liquid or fluid portion of the ink which (i) functions as the carrier and transport system for the pigment, and (ii) upon reaching the substrate, must be converted to a solid and anchor the pigment to the substrate.

Important properties of the vehicle as a pigment carrier and transport system include (i) pigment wetting and dispersion; (ii) ink rheology (ink transfer, ink misting, and press stability); and (iii) ink/water balance for lithography. Ink rheology relates to both viscosity and body or structure of the vehicle (or ink). For example, misting indicates that the vehicle has to have more rheology, or more body.

The lithographic (offset) printer plate consists of two distinct areas. One area has been rendered hydrophobic (image area) while the non-image area is hydrophilic. Thus, the offset printing process involves a two-phase system consisting of an oil phase (the ink) and aqueous phase (the 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 (11).

Important properties of the vehicle as the pigment binder or anchor to the substrate area (12) include (i) ink setting; (ii) ink drying; and (iii) gloss and rub-resistance of dried ink.

Setting and Drying. Setting has to occur very quickly. Slow setting results in undesirable smearing. Drying occurs after the ink was set and ink is considered dry when its viscosity reaches one million centipoises (10,000 ps). Substrate plays an important role during the setting and drying process. Setting and drying mechanisms include one or more of the following (13): (i) solvent/oil penetration; (ii) solvent evaporation; (iii) oxidation polymerization; (iv) catalytic polymerization; (v) resin precipitation.

Drying Oils

Drying oils are mixtures of fatty acid triglycerides. Fatty acids can exist alone as free fatty acids or in a combined form of esters. A majority of the combined forms are esters with glycerol (propane 1,2,3-triol) (14). They are called triacylglycerols or triglycerides. Upon hydrolysis, each triglyceride molecule can release three fatty acids and one glycerol (Fig. 9.1). Types of fatty acids in common drying oils are tabulated in Table 9.1.

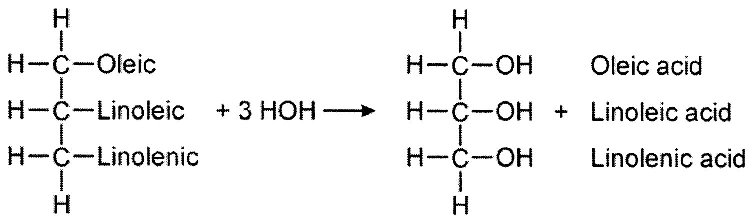

Fig. 9.1. Triglyceride and hydrolyzed components.

In order to dry by oxidation polymerization, the predominant fatty acid component of the vegetable oil must have at least two unsaturated groups. Oxidation occurs across the double bonds and it involves absorption of oxygen from air. It causes those double bonds to open up and form peroxides, which are unstable, break down, and are crosslinked. One fatty acid chain gets attached to the next one and they form a more rigid structure which essentially gives dry ink.

For example, in oleic acid, there is one double bond, which is not enough to oxidize properly. On the other hand, linoleic acid has two double bonds but they are not conjugated. A conjugated structure is very important to the oxidation process. Therefore the linoleic acid is a slower oxidizer than linolenic or eleostearic acid. The double bonds in eleostearic acid are conjugated. In the case of linolenic acid, there are three double bonds and more opportunity for oxidation to occur, but anything that changes the non-conjugated double bonds to conjugated double bonds will enhance the drying process.

The drying index indicates how well or how poorly certain drying oils will oxidize. The drying index of drying oil, semi-drying oil, and non-drying oil is >70, 50–70, and <50, respectively. If a particular drying oil has a blend of two and three double bond fatty acids, the percentages of the fatty acids should be included in the determination of the drying index. For example, linseed oil has 52% linolenic and

TABLE 9.1
Fatty Acid Composition of Common Drying Oils

Common name	Chemical name	Soybean (%)	Safflower (%)	Linseed (%)	Tung (%)
Myristic	Tetradecanoic	Tr–0.5	Tr	—	—
Palmitic	Hexadecanoic	7–11	3–6	4–7	3–5
Stearic	Octadecanoic	2–6	1–4	2–5	Tr–1
Arachidic	Eicosanoic	0.3–3	Tr–0.2	0.3–1	—
Oleic	9-Octadecaenoic	15–33	13–21	12–34	4–9
Linoleic	9,12-Octadecadienoic	43–56	73–79	17–24	8–10
Linolenic	9,12,15-Octadecatrienoic	5–11	Tr	35–60	2–3
Eleostearic	9,11,13-Octadecatrienoic	—	—	—	77–86

15% linoleic acid, therefore the drying index of linseed oil is: (52 × 2) + 16 = 120. Similarly, the drying index of tung oil (Chinawood oil), soybean oil, and safflower oil is calculated as 170, 69, and 77, respectively.

Alkali refined vegetable oils are used in ink formulation. Alkali refining removes the gums, waxes, free fatty acids and gives the oil greater clarity and lighter color. The presence of any one of these materials will interfere with the desirable hydrophobic characteristics of the vehicle and the ultimate ink formulation (15).

The most frequent use of drying oils in ink vehicles is as the oil component in liquid resins (alkyds). Alkyds are oil modified polyesters with well defined chemistry (16). Modified oil can be used as an ink vehicle without the need of resin in the formulation.

The vehicles can be prepared from vegetable oils by two methods (17–18). In one method, vegetable oils are heat-polymerized at a 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.

To further characterize the gels and ink vehicles prepared from vegetable oils, the viscosities and apparent molecular weights of these vehicles are determined by gel permeation chromatography.

The prepared vehicles typically had viscosities in the range of G–Y on the Gardner-Holdt viscometer scale, or about 1.6–18 P (19–20). These viscosities corresponded to apparent average molecular weights of 2600–8900.

For all oils studied, the viscosity (from crosslinking 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, 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 content required a longer reaction time.

During heat-bodying, conjugated dienes are formed by bond migration in polyunsaturated fatty acids. These can form six-membered rings by intra- or intermolecular reaction with the double bonds of other fatty acids. If these reactants come from different triglycerides, the molecular weight 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. Viscosity increases are directly proportional to increases in apparent molecular weight and the degree of polymerization. Apparent molecular weight at the same viscosity of different oils may be due to differences in lin-

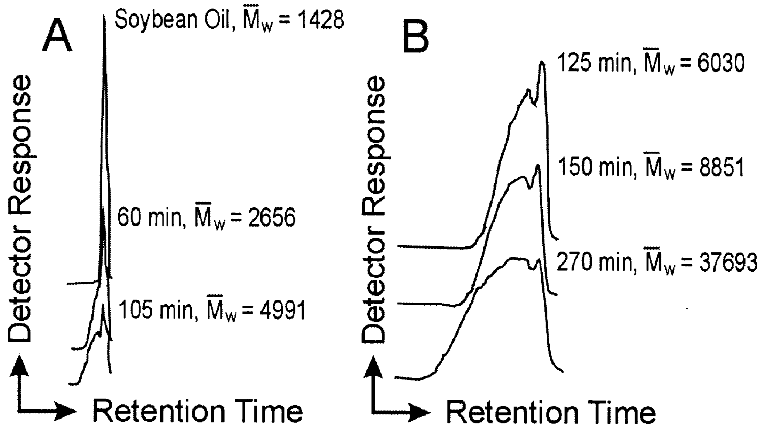

Fig. 9.2. (A) Gel permeation chromatograms of alkali refined, 60 and 105 minute heat-bodied soybean oil. (B) Gel permeation chromatograms of 125, 150, and 270 minute heat-bodied soybean oil.

earity of the bodied oils. As heat-bodying time was increased, the ratio of polymerized oil to unpolymerized oil increased. These behaviors are readily seen by the plots in Figure 9.2. At the heat-bodying time of zero, the peak shows the unmodified soybean oil. When heat-bodying time of the oil increases to 60 minutes, a shoulder appears, resulting from formation of the polymer, and this shoulder becomes dominant as the heating time increases from 60 to 270 minutes.

Such heat-bodied oils of different viscosities can be blended to produce viscosities of any desirable value. Also, blending different proportions of the gel and unmodified oil gave different vehicle viscosities.

Additives which may be formulated into the inks include driers, lubricants and antioxidants. The thickening effect of the pigment on the base vehicle should be considered in preselecting a vehicle viscosity (21–23).

Biodegradation

Biodegradation plays an important role in the transformation of many organic compounds in the environment. Several articles speculate that vegetable oil (soybean oil) should biodegrade more readily than mineral oil (24–25). Cavagnaro and Kaszubowski (26) have reviewed the biodegradation of food oils and greases. Erhan *et al.* studied and reported the biodegradation of soybean oil and the ink vehicles by using the microorganisms that are commonly found in soil (27–28). Also, biodegradation of printing inks was tested by using the "Modified Sturm Test" by Erhan *et al.* (29). Rosinski (30) reported the results of a de-inking study conducted at Western Michigan University, Kalamazoo, Michigan.

Conclusion

Technology is available for manufacturing vegetable oil-based printing ink vehicles with the desired commercial characteristics. This technology allows manufacturers to increase the vegetable oil content of the ink formulations and in turn improve environmental properties by increasing the biodegradability, lowering the volatile organic compound content, and improving the de-inking properties.

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