Symposium

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Trends in Industrial Usage for Vegetable Oils
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Trends in Industrial Usage for Vegetable Oils – Symposium Overview

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ABSTRACT

Vegetable oils are firmly established components of many industrial products and contribute a small but important share to the oleochemical and chemical industries–about 2% of total organic chemicals produced. The oleochemical industry is a mature one with low profit margins and in need of novel products and product applications, the development of which will require both basic and applied research. Several symposium participants identify areas that could add significantly to existing markets for unmodified vegetable oils, such as a diluent or enhancing agent in the application of pesticides and as an energy or heat source. Others show that considerable potential exists for new chemicals and modified vegetable oils and unique chemicals derived therefrom in value-added products such as coatings, polymers, lubricant additives or food additives, sometimes involving unique oils other than the traditional commodity mix. Without doubt, this is a time for the oleochemicals industry to invest in the future with nontraditional approaches to research and development. The oleochemical industry can and should expand its horizons, but with the realization that vegetable oils will have a lesser role compared to that of other renewable resources, such as wood and agricultural residues.

INTRODUCTION

Common sense dictates conservation of our fossil resources used for fuel and chemicals and, further, suggests that renewable resources be given closer attention. In fact, wood and agricultural residues have received considerable attention, while commercial vegetable oils, although already contributing substantially to socio-economic needs, have received comparatively less attention. Fats and oils as a whole now contribute perhaps 2% to the total of U.S. organic chemical production and probably could contribute substantially more, with limitations imposed by land availability and marketability of coproducts.

This symposium examines some current industrial uses for vegetable oils and attempts to assess potential for future growth.

Sulfurized Lubricant Additives

Kammann and Phillips (1) show that satisfactory lubricant additives can be made from vegetable oils sulfurized in the presence of methyl lardate. Vegetable oils, such as rapeseed and *Limnanthes*, having favorable contents of monounsaturation and long-chain fatty acids, give the best performances. The former is used extensively in Europe and the latter is undergoing trial plantings in Oregon but is not yet available on a significant scale.

Application of Pesticides

Tremendous potential exists for using vegetable oils in the application of crop pesticides. As Kapusta (2) explains, soybean oil performs adequately as a carrier (to replace water) in ultra-low volume applications of pesticides or as an enhancing agent for the pesticide (to replace petroleum-based oils).

Coatings

The coatings industry now uses perhaps a few hundred million pounds of seed oils as film-forming pigment binders, but this will not be a good growth area, as explained by Fulmer (3). Fortunately, oil-based alkyd resins will continue to be used in latex paints, because of improved adhesion and early water resistance, to maintain consumption at about present levels.

Soybean Oil Uses

In his review of nonfood uses of soybean oil, Sonntag (4) predicts an increase from 8-10% to up to 12% of the total U.S. consumption of soybean oil over the next five years. While this may be optimistic, he, too, suggests large potential volume use in pesticide and dust suppressant applications associated with crop production. He also looks at oil-refining byproducts and mono- and diglycerides as food additives.

Epoxidized Oils

Demand for epoxidized vegetable oils and esters is tied closely to their value as plasticizer-stabilizers for polyvinyl chloride resins. Market growth for this group of chemicals, beyond that shown by epoxidized soybean oil (5% annually over 20 years), will require new and unique products and applications. Carlson and Chang (5) suggest that the natural epoxidized oil from *Vernonia galamensis* could be used in these and other markets, especially when further epoxidized (chemically) to an oxirane content (8.2%) intermediate between that of epoxidized soybean and linseed oils.

Thermochemical Applications

Lipinsky et al. (6) report preliminary data on some novel thermochemical applications for vegetable oils, e.g., as alternative fuels for stationary engines in steam and electric power generation, and possibly as a fuel for space heaters. Application for the first-time of steam cracking to stearic, oleic and linoleic acids produced primarily methane and ethylene.

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Sulfurized Vegetable Oil Products as Lubricant Additives

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ABSTRACT

Sulfurized products based on hog fat and its derivatives have extensive commercial use as additives for metalworking and industrial oils, but only relatively small quantities of vegetable oils find such application in North America. Products were made by sulfurization of soybean, sunflower, cottonseed, high erucic rapeseed, canola, *Limnanthes* (meadowfoam) and prime lard oils. Unlike products from the wax ester jojoba oil, the sulfurized vegetable triglycerides alone had physical properties generally undesirable for lubricant additives. When the oils were sulfurized in the presence of methyl lardate, however, the products had potential practical application. High-sulfur (active) products were made using a 50:50 ratio of triglyceride to methyl lardate, and low-sulfur (inactive) products were made using a 70:30 ratio. Compared to the other sulfurized vegetable triglyceride products, *Limnanthes* products showed the best solubility in high viscosity-index paraffinic oil. For solutions, measurements of extreme pressure, friction and wear were compared. Whereas products from jojoba were best, of the triglyceride group the *Limnanthes*-containing products generally gave the best performance. Although this oil had much promise, it is only in its early stage of commercial development. The other vegetable oils also have potential depending on cost and applications. However, overall competition with the well-established, usually lower-cost products from hog fat or greases would appear to be difficult.

TRENDS IN SULFURIZED PRODUCTS

Commercial Products

Most of the sulfurized fatty materials made and sold in the U.S. are based on animal fats. Although often considered together and generically called "lard oils," there actually is a wide variety of raw materials available, including several relatively low cost versions which often can be utilized as effectively as lard oil itself. Examples, with typical Acid Value (AV) and Iodine Value (IV) range, include: choice white grease, AV 6, IV 55-70; rendered pork fat or No. 1 pigskin grease, AV 2, IV 55-65; No. 1 lard oil, AV 30, IV 60-75; prime lard oil, AV 3, IV 65-75, and yellow grease, AV 20, IV 55-65 and higher. Yellow grease often contains cooking oil reclaimed from restaurants, which is usually of vegetable origin. "Methyl lardate," AV 1, IV 55-75 also is used. The latter is made by methanol transesterification of triglycerides and is sold for metalworking applications both as is and in the sulfurized form.

Some typical sulfurized products from hog-derived fats or methyl esters are listed in Table I. In addition, there are a variety of products made by cosulfurization of triglyceride and methyl ester.

The formulation of lubricants with sulfurized products remains an art. However, industrial lubricants may be categorized broadly as follows. Lubricants for metalworking operations, such as cutting, threading, broaching, drawing and stamping, require active sulfur more often than inactive, and the presence of free fatty acid often is preferred or at least acceptable. These formulations usually are made with lower viscosity base oils, in recent years involving the increasing use of paraffinic oils, in which solubility of additives is sometimes a problem. Large quantities of sulfurized hydrocarbons and sulfurchlorinated hydrocarbons and fatty materials also are used, especially for cutting operations. Gear oils and machine lubes, previously formulated using sulfurized sperm oil, generally incorporate inactive sulfur, low free fatty acid and higher alkyl ester "synthetic sperm oil" additives along with higher viscosity base oils. They also contain several other components with which the sulfurized material must be compatible. Automotive crankcase oils sometimes contain friction modifying additives with inactive sulfur and low acid values.

Sulfurized fatty products should, of course, have good oxidation and thermal stability. By providing films at the metal surface under the conditions of boundary lubrication they should be able to give wear reduction at extreme pressure (EP) loads, and to possibly provide friction reduction at lesser loads. There are several papers and discussions available on the role and mechanism of fatty materials in lubrication, including sulfurized products (1-3).

Economic Importance

The U.S. International Trade Commission's figure for the

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TABLE I

Typical Sulfurized Products From Hog Fats or Methyl Ester

Main component	Product acid value	% Sulfur total	Copper corr.[a]	Viscosity, cSt, 40 C	Viscosity, cSt, 100 C	Specific gravity 25 C	Pour point, °C
Triglyceride	6	10	1b	1160	92	0.99	23
Triglyceride	25	10	1b	1100	80	0.98	18
Triglyceride	26	17	4b	6440	270	1.00	29
Ester	5	9	1b	20	4	9.94	10
Ester	7	17	4a	40	9	0.98	10

[a]ASTM D-130, 10% in oil.