Plasticizers, Paints, and Biodiesel Expand Markets for Fats and Oils

About 15 percent of the plasticizers produced in the United States are derived from plant matter, mostly vegetable oils, and the market is growing 3 to 5 percent a year. The market for epoxidized soybean oil may expand tremendously if it can be incorporated into paints and coatings to replace volatile solvents. U.S. Environmental Protection Agency regulations issued in the last few years require diesel fuel to meet reduced sulfur standards and engine-emission requirements, which may open niche markets for biodiesel.

Use of Plant-Based Plasticizers Is Small but Growing

Plasticizers are organic compounds added to plastics to improve workability during fabrication and to extend or modify the natural properties of the original resin. Plasticizers make molding and shaping plastic resins into consumer end products, such as bottles and plastic bags, easier. Plasticizers also impart flexibility and other desired properties to the finished product.

Plastics contain about 2 to 5 percent plasticizers, 1 to 2 percent other additives, and 10 percent or more builders to control properties and cost. One of the most important uses of plasticizers is molding polyvinyl chloride (PVC), a plastic widely used in construction, electrical, consumer, packaging, transportation, and medical applications. PVC resin is very brittle and cannot be molded without plasticizers.

Of the 1.6 billion pounds of plasticizers produced in the United States in 1990, 230 million pounds, or 15 percent, were derived from plant matter. Most of these plant-based materials are from vegetable oil feedstocks (table 3). Epoxidized soybean oil (ESO) accounted for 100 million pounds, while acrylic esters, which are derived from a variety of plant sources (including wood extractives and coconut oil), accounted for 74 million pounds. Over a dozen companies produce ESO. The market for plant-derived plasticizers is growing 3 to 5 percent a year.

ESO and mercaptoethyl oleate, a vegetable-oil-based compound, are proven plasticizer/stabilizers for PVC. Metallic stearates, made from vegetable oils such as coconut and palm oils, are currently used in polystyrene, polypropylene, and acrylonitrile-butadiene-styrene copolymers. Sebacate and azelate esters, both vegetable-oil derived, impart low-temperature flexibility to thermoplastics.

The price of plant-based plasticizers has come down in the past 10 years, and generally ranges from 50 cents to $3 per pound. These plasticizers have properties similar to higher quality, property-specific petrochemical plasticizers and compete at the upper end of the price scale. Research into new processes promises to reduce the price of plant--based plasticizers in the future. For example, improvements in esterification, a process used by the chemical industry to make surfactants and other fat- and oil-based intermediate chemicals, has the potential to produce plant-based plasticizers more cheaply.

Table 3--U.S. production of plasticizers from vegetable oil and petrochemical feedstocks, 1990

Category	Production
	Million pounds
Epoxidized soybean oil	100
Epoxidized linseed oil	6
Other epoxidized esters	14
Oleic acid esters	12
Stearic acid esters	8
Palmitic acid esters	6
Sebacic acid esters	6
Isopropylmyristate	4
Other acrylic acid esters	74
Total	230
Petrochemical-based plasticizers	1,324
Total plasticizers	1,554

Source: Irshad Ahmed, Institute for Local Self-Reliance, Washington, DC, May 1994.

Another example of increased commercial activity in plant-matter-based plasticizers is the development of acrylates. Plant-based acrylates were developed by Battelle Memorial Institute's Pacific Northwest Laboratory (Richland, WA). Battelle derives its acrylates from blackstrap molasses, a byproduct of sugarcane production, in a process that uses bacterial and chemical means to convert the residue sugars into acrylates. Battelle currently sells its acrylates, which are used as plasticizers in plastics and as a plasticizer-resin in acrylic paints, for 70 to 75 cents a pound.

Epoxidized Soybean Oil May Substitute for Volatile Solvents in Paints and Coatings

The market for ESO could expand tremendously if it is incorporated into paints and coatings to replace volatile solvents. The Clean Air Act Amendments of 1990 (CAAA) require paint manufacturers to reduce volatile organic compounds (VOC's) in their formulations. Petroleum-based toluene, xylene, methyl ethyl ketone, and methyl isobutyl ketone must be eliminated entirely. Chlorinated solvents must be removed from formulations because of their ozone-damaging potential. Manufacturers must also make efforts to reduce emissions of several other pollutants. The actual limits on VOC content depend upon where the coating is used and the particular category. Regulations issued by the U.S. Environmental Protection Agency (EPA) list over 50 different paint categories, each with its own VOC limit. However, implementation of the EPA rules is left to the states. Consequently, current VOC limits vary by location, but there is an effort underway to settle on a national standard. National rules could be in place as early as January 1996.

Given these and anticipated future regulations, researchers and paint formulators are looking at ESO derivatives as reactive diluents. In paints and coatings, the diluent (solvent) evaporates, leaving the solid covering. While they can substitute at least partially for organic solvents, ESO derivatives react chemically to become part of the finish, hence less evaporation and reduced VOC's. EPA regulations now in effect require reducing VOC evaporations from 500 grams per liter of finish to less than 200 grams. Some ESO-based, reactive-diluent finishes have evaporation rates of less than 100 grams per liter.

To be successful, ESO reactive diluents must be able to produce an effective, solid covering when manufactured in commercial quantities, as they appear to do when tested under laboratory conditions. Each new formulation will be tested for VOC emissions by the American Society for Testing and Materials (ASTM) under EPA-designated procedures. However, ESO diluents will drive up the cost of paints and coatings. How much has not yet been determined, but ESO-based products should have better coverage (i.e., cover more area per gallon) than conventional paints, countering at least some of the higher cost. It remains to be seen whether coverings that include ESO reactive diluents can meet performance objectives and also be price competitive.

Typical paints are about 70 percent solvent and 30 percent solids. The redesigned paints containing reactive diluents would be about 50 percent solvent and 50 percent solids. Of the 50 percent solids, up to 10 percent could be ESO. By the end of the year, Ecotek Corporation is planning scale-up tests in California with finishes containing as much as 10 percent ESO.

The market for ESO diluents could reach 250 to 300 million pounds a year, more than doubling the size of the current ESO market. This estimate is based on the assumption that, of the combined 3-billion-pound-per-year market for epoxy and alkyd binders, ESO could replace as much as 10 percent of these binders in some coatings and less in others, depending on the kind of finish required and the durability expected. This is probably an upper bound, given current and expected regulations and present technology, which limits the proportion of ESO in the formulation.

One of the current problems with a higher ESO content in coatings is the so-called rubber-toughening effect. High levels of ESO would impart a more "rubbery" quality to the finish, which is undesirable in some applications. For example, it gives paints a flat appearance rather than a glossy one. However, a rubber-toughened coating would be useful when chip resistance is important, such as in automobile undercoatings, or where some flexibility is desirable, such as in bridge paints where the coating should accommodate the movement of the structure.

The rubber-toughening effect could be useful in other applications as well. The effect comes as ESO forms globules that arrest the cracking propensity of some resins. The result is a strong, light material with flexibility and resistance to fracturing. Rubber-toughened materials also could be used in manufacturing plastic composites. The major application would be as a substitute for metal parts, such as engine mountings and frames, in automobiles, appliances, and other manufactured goods where strength and weight are important considerations.

Changes in Diesel Regulations
May Create Niche for Biodiesel

New EPA regulations issued in the last few years make diesel fuel subject to quality standards and engine-emission requirements, which may open niche markets for biodiesel. Before 1993, the only specification for diesel fuel was the D 975 Standard Specification for Diesel Fuel Oils issued by ASTM. In addition, refinery operations were primarily geared toward gasoline quality and output, which meant that diesel quality would vary depending on gasoline demand. (Producing more gasoline from a barrel of crude oil changes the characteristics of the diesel fuel made from that same barrel.)

According to the EPA regulations, beginning October 1, 1993, diesel fuel for on-highway uses must (1) contain no more than 0.05 percent sulfur by weight, and (2) have a cetane index of at least 40 or not more than 35 percent aromatic hydrocarbons by volume. Previously, diesel fuel averaged approximately 0.25 percent sulfur. The cetane value is a measure of the fuel's ability to self-ignite. Diesel engines perform better with straight-chain molecules that increase the cetane index. Gasoline engines, on the other hand, perform better with branched molecules, like iso-octane.

Any vehicle with a diesel engine that is designed to transport persons or property on streets and highways is subject to these regulations. High-sulfur diesel fuel may still be sold, but it must be dyed blue and can only be used in off-road applications, including railroad, marine, construction, and agricultural uses.

In addition to adopting the federal regulations on sulfur, the California Air Resources Board and the California State Government implemented a stricter set of regulations that limit the aromatics in diesel fuel to 10 percent by volume, or to the use of alternative formulations that produce emissions equal to that standard. Small refiners, however, are allowed to meet a 20-percent aromatics standard.

As part of the CAAA, on-road diesel engines (1993 model year and later) must meet emission limits on particulate matter, carbon monoxide, hydrocarbons, and nitrogen oxides (table 4). Smoke (opacity) is limited to 20 percent in acceleration mode, 15 percent in lug mode, and 50 percent at peak. Research and testing continues to evaluate how biodiesel and biodiesel/petroleum-diesel blends may be used to meet these new Clean Air Act requirements.

Table 4--Emission standards for on-road diesel engines 1/

Engine type and pollutant	Emission standard
	Grams per brake horsepower hour
On-road diesel engines	
Particulate matter	0.25
Carbon monoxide	15.5
Hydrocarbons	1.3
Nitrogen oxides	5.0
Buses	
Particulate matter	
1993	0.10
1994	0.07
1996	2/ 0.05
Carbon monoxide	15.5
Hydrocarbons	1.3
Nitrogen oxides	5.0
All heavy-duty diesel engines, including buses	
Nitrogen oxides	
1998	4.0

1/ 1993 model year and later. Some standards become stricter in later years. 2/ 0.05 grams per brake horsepower hour for certification and 0.07 grams per brake horsepower hour for in-use testing.

Source: Federal Register, Vol. 58, No. 55, Wednesday, March 24, 1993, pp. 15781-802.

Low-Sulfur Diesel May Create Lubricity Problems

The recent change to low-sulfur diesel fuel for on-road vehicles has raised questions about the lubricating properties of the reformulated fuel and its reaction with elastomers in fuel injection equipment. The lubricating properties of diesel fuel are important, especially for users of rotary-type fuel pumps, which are common on trucks, tractors, light-duty vans, school buses, and other diesel-powered vehicles with less than 190 horsepower. Rotary fuel pumps depend on the fuel itself for lubrication. Therefore, problems with low-sulfur diesel could include premature rotary pump wear, plugged injector nozzles, and low power. After the mandated change to low-sulfur diesel fuel, many reports of o-ring failure and other potential injector problems surfaced. The concerns are being attributed to the refining process used to remove sulfur, called hydrotreating, which apparently leaches out some of diesel's lubricating components.

A representative of the American Association of Diesel Specialists reports that there seem to be serious problems with lubricity in California, where the seizing of fuel pumps has increased dramatically. This problem seems to be concentrated in that state, which has more stringent aromatic standards than the rest of the country. Reports from the California Diesel Fuel Task Force indicate that problems have occurred in all types of light-, medium-, and heavy-duty engines (1).

Given these concerns, the International Standards Organization formed a Diesel Fuel Lubricity Committee to determine a standard, analytical-test method for the measurement of lubricity. The committee's intent is to eventually set a lubricity standard for diesel fuel. Currently, there are no specifications or requirements for diesel fuel lubricity.

Preliminary results are available from a biodiesel lubricity study funded by soybean checkoff funds and managed by MARC-IV, a biodiesel consulting firm in Bucyrus, KS. Test results from the scuffing-ball-on-cylinder-lubricity-evaluator (BOCLE) machine indicate a 20-percent biodiesel blend significantly improved lubricity with both low-sulfur/high-aromatic and low-sulfur/low-aromatic diesel fuel. Ten-percent biodiesel mixed with low-sulfur/high-aromatic petroleum diesel also showed significant improvement in lubricating quality. Results from the testing with low-sulfur/low-aromatic diesel, although improved, were close to the analytical variation of the test (table 5).

A field test in St. Louis, MO, has been planned to examine the lubricity qualities of biodiesel over an 18-month period in conjunction with Stanadyne Automotive Corporation and Robert Bosch Gmbh, the leading manufacturers of rotary fuel pumps. Three school buses with 7.3 Navistar diesel engines equipped with Stanadyne fuel pumps will be tested with a 20-percent biodiesel/80-

percent diesel blend, and three will serve as controls. A field test with Bosch pumps will be initiated in the near future.

Biodiesel Is Nontoxic and Biodegradable

Biodiesel is considered nontoxic and biodegradable. Procter & Gamble, Inc., and Midwest Biofuels, Inc., a subsidiary of Interchem Environmental, Inc., (Overland Park, KS) have released data quantifying the safety of soybean-oil-based biodiesel (methyl soyate) (table 6). Due to these nontoxic characteristics and its biodegradability, biodiesel is being considered as a fuel source in geographic areas that are environmentally sensitive, such as rivers, bays, parks, and forests.

In addition to research conducted in Europe, USDA's Cooperative State Research Service and the U.S. Department of Defense are funding biodegradability research on biodiesel. Respirometry experiments at the U.S. Army Natick Research, Development, and Engineering Center (Natick, MA) were conducted to determine the biodegradability of methyl soyate in an aqueous medium. The results, which are reported on the basis of carbon dioxide evolution, show that after 8 days the conversion was 55 percent, with degradation continuing. Similar research at the University of Idaho indicates that the degradability of biodiesel (rapeseed methyl esters and rapeseed ethyl esters) is comparable to that of sucrose. The degradability of No. 2 diesel was considerably lower. [Lewrene Glaser (202) 219-0085, Alan Weber (314) 882-4512, Roger Hoskin (202) 219-0840, and Irshad Ahmed (202) 232-4108]

Reference

1. *Report of the Diesel Fuel Task Force*, presented to Pete Wilson, Governor of California, February 18, 1994.

Table 5--Lubricity qualities of petroleum diesel, petroleum diesel/biodiesel blends, and biodiesel on a scuffing-ball-on-cylinder-lubricity-evaluator (BOCLE) machine 1/

Low-sulfur/high-aromatic petroleum diesel 2/		Low-sulfur/low-aromatic petroleum diesel 3/	
Percent biodiesel added	BOCLE results 4/	Percent biodiesel added	BOCLE results 4/
	Grams		Grams
0.0	4,200	0.0	3,500
0.2	3,900	0.2	3,300
2.0	4,400	2.0	3,500
5.0	4,500	5.0	3,600
10.0	5,200	10.0	3,800
20.0	5,200	20.0	4,100
100.0	6,100	100.0	6,100

1/ Test performed by the Southwest Research Institute. These results are not an endorsement of biodiesel by the Institute. 2/ Contains less than 35 percent aromatics by volume. 3/ Contains less than 10 percent aromatics by volume. 4/ Test bias +/- 200 grams. A diesel fuel with good lubricity qualities will give BOCLE results in the 4,500- to 5,000-gram range and a bad lubricity diesel will give results in the 1,500-gram range.

Table 6. SoyDiesel (methyl soyate) toxicity data

Test	Subject	Result
Acute oral toxicity	Rats	The acute oral LD_{50} (the lethal dose for 50 percent of the rats in the test) was greater than 17.4 grams per kilogram of body weight. By comparison, table salt has an LD_{50} of 1.75 grams per kilogram.
Eye irritation	Rabbits	Application of undiluted material to the eye produced only mild transient irritation, meaning the eye returned to normal in one day or less.
Skin irritation	Humans	A 24-hour patch test indicated that undiluted methyl soyate produced very mild irritation. The irritation was less than that resulting from a 4-percent aqueous soap solution.
Aquatic toxicity	Bluegills	The 96-hour LC_{50} (lethal concentration) was greater than 1,000 milligrams per liter. This level is in the "insignificant" classification, according to the Registry of the Toxic Effects of Chemical Substances published by the National Institute for Occupational Safety and Health.

Source: Biodiesel Alert, November 1993.