Preparation of Glycol Derivatives of Partially Hydrogenated Soybean Oil Fatty Acids and Their Potential as Lubricants[1]

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Glycol diesters and mixtures of mono- and diesters have been prepared from methyl esters of partially hydrogenated soybean oil fatty acids and diethylene, dipropylene, neopentyl and triethylene glycols. The catalyst used in these reactions was a mixture of calcium acetate/barium acetate (3:1, w/w). The reactions were carried out under nitrogen with 0.5% catalyst at temperatures in the range of 190–275°C. Borated esters of mixed mono- and diesters were prepared with 0.33 equivalent of boric acid per 1.0 equivalent hydroxyl group on the ester. Refractive indices, viscosities, and flash and fire points were determined for diesters, mixed mono- and diesters, and mixed diesters and borated esters. The viscosities, flash points and fire points indicate that these esters can be used as a component of lubricating oils. Wear-prevention characteristics of mixed diesters and borated esters indicated that they can be used as antifriction additives in lubricating oils.

KEY WORDS: **Borated esters, fatty acid methyl esters, glycol esters, lubricants, partially hydrogenated soybean oil, viscosity.**

Environmental factors and dwindling petroleum resources, coupled with the enactment of the Endangered Species Act of 1969 prohibiting the use of sperm oil and its derivatives as industrial lubricants, have made renewable agricultural resources a vital supplement to petroleum products. Unfortunately, economic factors have played a major role in hindering the technical development and progress of vegetable oil use in the lubrication industry, even though the triglycerides have excellent lubricity.

To date, only a few vegetable oils, such as rapeseed and high-oleic sunflower, are used as base fluids for environmentally safe lubricants (1). Soybean oil, because of its abundance and comparatively lower price, has also been considered. Refined soybean oil contains polyunsaturated fatty acids, such as linoleic (55%) and linolenic (8%) acids, making the oil highly susceptible to oxidative and thermal degradation and, therefore, unacceptable for the lubrication industry without chemical modification.

Studies have been carried out to partially hydrogenate soybean oils to varying degrees of saturation and to liberate the fatty acids for use in further modification reactions. Synthetic wax ester and sulfurized wax ester lubricants have been prepared from partially hydrogenated soybean and linseed oil fatty acids as possible replacements for sperm whale oil (2).

It is known (3) that glycerides revert to glycerine, which eventually polymerizes and forms gummy materials at relatively high temperatures and pressures. Attempts have been made to replace the glycerine part of glyceridic oils with polyhydroxy alcohols and diols to enhance the thermal and oxidative stability of the derivatives, making them more desirable as lubricants. These derivatives provide not only flash and fire points comparable to that of partially hydrogenated soybean oil, but also exhibit viscosities of at least 100 SUS at 100°F, which makes them useful as lubricants in the continuous casting of steel and other metalworking (4). Bell (5) has also found that the sulfurized derivatives of alcohol esters of fatty acids can be used as extreme-pressure lubricant additives.

There are numerous (6–9) publications regarding the use of glycol esters as sperm oil substitutes and as centrifugal refrigerant compressor lubricants. Current work aims to expand the utilization of diols and partially hydrogenated soybean fatty acids into the markets for environmentally safe lubricants. This paper reports on the preparation of several glycol esters, their derivatives and their specific physicochemical properties, which may be attributable for their use as components in lubrication oil formulations.

EXPERIMENTAL PROCEDURES

Partially hydrogenated soybean oils were supplied by Archer Daniels Midland Company (Decatur, IL). The methyl esters were prepared in the laboratory with anhydrous methanol and potassium hydroxide, following the procedure described elsewhere (10) with minor modifications, and were purified by distillation. The glycols and catalyst compounds were purchased from Aldrich Chemical Company (Milwaukee, WI) and Fluka Chemie AG (Buchs, Switzerland). These materials were 99% pure and were used without further purification.

Fatty acid methyl esters were analyzed on a Hewlett-Packard HP 5880 gas chromatograph with flame-ionization detector (Hewlett-Packard Company, Palo Alto, CA). The column was an SP-2340 (60 m, 0.25 mm i.d., 0.2 μm film thickness; Supelco, Bellefonte, PA). Infrared spectra were recorded with a PE-710 Infrared Spectrophotometer (Perkin-Elmer, Norwalk, CT) and a 510P FT-IR Spectrometer (Nicolet, Madison, WI).

Viscosities were determined with calibrated Cannon-Fenske viscometers and a Brookfield Digital Viscometer Model DV-II with UL adapter (Brookfield Engineering Laboratories, Stoughton, MA). The viscosity indices were calculated from viscosities at 100 and 210°F by American Society for Testing and Materials (ASTM) Method D2270-91 (11). The kinematic viscosity was converted to Saybolt Universal viscosity in Saybolt Universal Seconds (SUS) according to ASTM Method D2161-87 (12). The viscosity temperature coefficients (VTI) were calculated according to the procedure described elsewhere (13). Smoke, flash and fire points were measured by the Cleveland Open Cup, ASTM Method D92-90 (14) and American Oil Chemists' Society (AOCS) Official Method Cc 9A-48 (15). Hydroxyl and iodine values were determined by AOCS Official Methods Cd 13-60 and Cd 1-25, respectively (16).

Wear-preventative characteristics were determined by Falex Corporation (Aurora, IL) in a four-ball wear machine (Model 19) by following ASTM Method D4172 (17). The

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test parameters were: speed (rpm), 1200 (±50); temperature (°C), 75 (±1.7); load (kg), 40 (±0.2); duration (min), 60 (±1.0); ball material, AISI-52100; hardness (HRc), 64–66; grade, 25 extra polish.

Esterification of diethylene, triethylene, dipropylene and neopentyl glycols. Each glycol (0.3 mol) was reacted with fatty acid methyl esters (0.9 mol) in a three-necked flask equipped with magnetic stirrer, thermometer, nitrogen bubbling tube and a distilling receiver with water condenser. Reactions were carried out in the presence of 0.5% catalyst, which consisted of a mixture of calcium acetate/barium acetate (3:1, w/w). For diethylene glycol, the total reaction time was 5 h (4 h at 212°C and 1 h at 218°C). For triethylene glycol, the total reaction time was 6 h (4 h at 255°C and 2 h at 275°C). The reaction times were substantially longer for the remaining two glycols, and an additional 0.5% catalyst was added upon increasing the temperature during each reaction. For dipropylene glycol, the total reaction time was 24 h (12 h at 217–220°C and 12 h at 245–250°C). For neopentyl glycol, the total reaction time was 20 h (12 h at 195°C and 8 h at 235°C).

The reactions were monitored by thin-layer chromatography (TLC) with two solvent systems: (i) petroleum ether (35–60°C)/ether/acetic acid (90:10:1, vol/vol/vol), and (ii) chloroform/acetone (99.9:0.1, vol/vol). Plates were developed by charring with a 50% sulfuric acid spray. On completion of each reaction, the products were cooled under nitrogen and extracted with petroleum ether (35–60°C). The extract was washed thrice with water and dried over Drierite for a period of 12 h. After removal of the solvent, the material was subjected to vacuum distillation to remove unreacted methyl esters. Undesirable products were removed by filtering with filter aid (Hyflosupercel). In each case, both TLC and infrared analysis confirmed the absence of hydroxyl groups in the diester products.

A typical example is illustrated by the reaction of dipropylene glycol and partially hydrogenated soybean oil fatty acid methyl esters (Scheme 1), where R may be C15:0, C17:0, C17:1, C17:2, C17:3, C19:0.

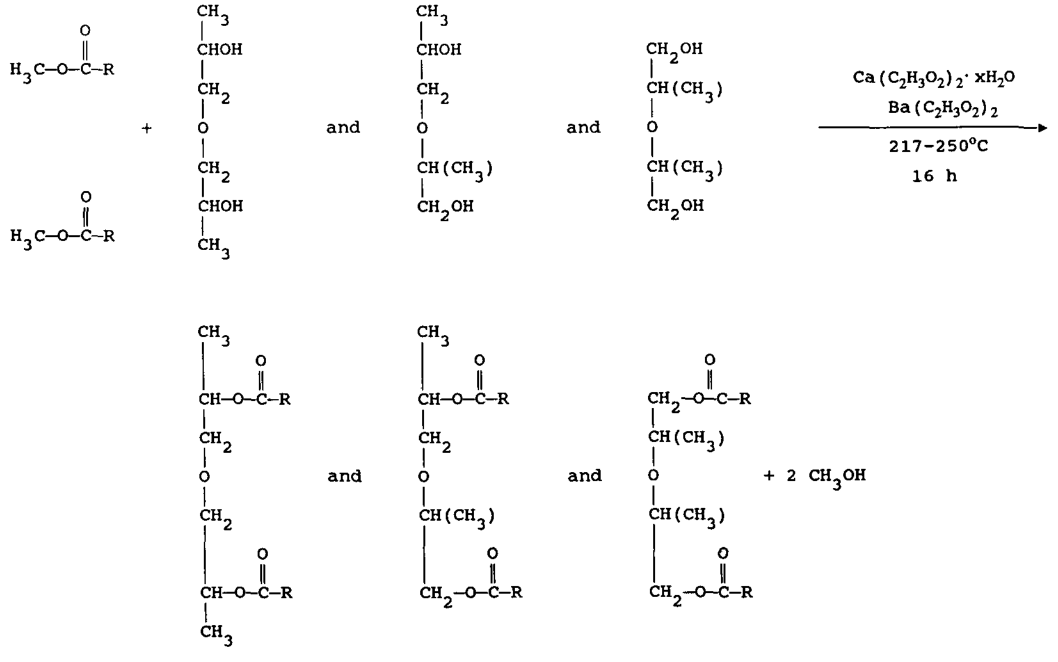
Preparation of mono- and diesters of dipropylene, neopentyl and triethylene glycol. Each glycol (1.0 mol) was reacted with fatty acid methyl esters in a three-necked flask equipped with a magnetic stirrer, thermometer, nitrogen bubbling tube and a distilling receiver with water condenser. The mole ratios of fatty acid methyl esters to glycol for dipropylene, neopentyl and triethylene glycols were 1.50, 1.33 and 1.54 mol, respectively. The reactions were carried out in the presence of 0.5% of the catalyst described above. For neopentyl glycol, the total reaction time was 10 h (at 200–245°C). For neopentyl glycol, the total reaction time was 16 h (12 h at 190–200°C and 4 h at 235°C). For triethylene glycol, the total reaction time was 12 h (at 235°C).

The reactions were monitored by TLC as described above. On completion of each reaction, the products were filtered to remove the catalyst and subjected to vacuum distillation to remove unreacted materials. The residual mixture was then filtered with Hyflosupercel at 80°C (or 100°C for the triethylene glycol esters).

Borated glycol esters. The glycol esters were reacted with boric acid at a temperature of 120–130°C under 19 mm Hg for a period of 3 h. The amount of boric acid used in each case was 0.33 equivalents per 1.0 equivalent hydroxyl group on the glycol ester. The products were recovered without any further purification.

RESULTS AND DISCUSSION

The diol esters have lower smoke, flash and fire points than the original partially hydrogenated oils from which the fatty acids were derived (Table 1). Table 2 shows that



SCHEME 1

TABLE 1

Physicochemical Characteristics of Partially Hydrogenated Soybean Oil Feedstocks

	Refactive index at 40°C	Free fatty acid (%)	Smoke point (°F)	Flash point (°F)	Fire point (°F)	*Trans* isomer		Fatty acid methyl ester analysis by gas chromatography (%)					
						C18:1	C18:2	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0
Feedstock IV[a] 106.3	1.4641	0.04	435	630	675	4.2	1.4	11.2	4.9	45.0	36.0	2.4	0.5
Feedstock IV 83.5	1.4615	0.03	480	640	690	30.3	1.5	10.3	5.2	69.2	14.0	0.5	0.5

[a] IV, iodine value.

TABLE 2

Properties of Glycol Diesters

	Refractive index at 40°C	Iodine value (IV)	Smoke point (°F)	Flash point (°F)	Fire point (°F)	Viscosity at °F				Viscosity index	Viscosity temperature coefficient
						70 (Cp)	80 (Cp)	100 (SUS)[a]	210 (SUS)[a]		
Feedstock IV 106.3											
Diethylene glycol diesters	1.4588	100.6	280	470	520	30.0	22.9	100.2	44.8	241	0.725
Triethylene glycol diesters	1.4599	90.0	330	560	630	40.0	33.8	127.5	49.6	251	0.733
Dipropylene glycol diesters	1.4575	95.4	—	554	572	—	—	109.4	44.9	211	0.750
Feedstock IV 83.5											
Diethylene glycol diesters	1.4551	78.5	345	440	485	—	—	106.6	44.7	225	0.744
Triethylene glycol diesters	1.4576	71.3	320	505	585	—	—	135.9	49.3	227	0.754
Neopentyl glycol diesters	1.4565	75.8	—	536	583	—	—	127.2	46.3	190	0.770
Dipropylene glycol[b] diesters	1.4513	72.0	295	440	495	—	—	95.8	40.7	139	0.775

[a] SUS, Saybolt Universal Seconds.
[b] The hydroxyl number was 21.

TABLE 3

Properties of Glycol Mono- and Diester Mixtures

	Refractive index at 40°C	Iodine value	Hydroxyl value	Smoke point (°F)	Flash point (°F)	Viscosity at 100°F (SUS)[a]	Viscosity at 210°F (SUS)[a]	Viscosity index	Viscosity temperature coefficient
Dipropylene glycol esters	1.4528	66.9	43.0	491	522	154.4	44.4	105	0.712
Neopentyl glycol esters	1.4522	71.6	69.5	428	491	136.6	45.4	151	0.668
Triethylene glycol esters	1.4569	65.6	46.9	509	543	145.1	47.3	169	0.791

[a] See Table 2 for abbreviation.

the viscosity indices of the diesters are within the range of 211–241, except for neopentyl glycol diesters, which was 190. The viscosity index of dipropylene glycol esters was 139 because of the presence of some monoesters. It is evident (Table 3) that a mixture of mono- and diesters has a lower viscosity index than pure diesters, which translates to lower pour points for the mixtures. Thus, it is possible to modify properties of these lubricants (e.g., viscosity, flash and fire points) by varying the ratio of reactants to yield different proportions of mono- and diesters in the product.

The presence of unsaturation in the fatty acid moieties and the presence of hydroxyl groups in the mixture of mono- and diester mixtures introduce a number of options for modification of these glycol esters. The introduction of sulfur in the fatty acid moieties (from these types of esters) produces lubricants that can be used under extreme pressures, such as those found in certain gear elements in automotive vehicles and industrial machinery (18). Several of these compounds have been prepared in our laboratory, and their properties will be reported in a separate communication.

The presence of hydroxyl groups in these lubricants allows use as nonionic emulsifiers; and hence, they are useful in water-based cutting fluids, rust-preventative materials, *etc.* The antimicrobial properties of boric esters

TABLE 4

Properties of Glycol Diester and Borated Ester Mistures

	Refractive index at 40°C	Iodine value	Smoke point (°F)	Flash point (°F)	Viscosity at 100°F (SUS)[a]	Viscosity at 210°F (SUS)[a]	Viscosity index	Viscosity temperature coefficient	Wear scar[b] (mm)
Dipropylene glycol esters	1.4573	69.3	554	536	138.5	48.7	212	0.648	0.624
Neopentyl glycol esters	1.4567	71.0	543	529	171.2	51.9	193	0.697	0.632
Triethylene glycol esters	1.4506[c]	65.3	529	482	138.8	54.1	293	0.710	0.615

[a] See Table 2 for abbreviation.

[b] Base fluid consisted of a mixture of triethylene glycol monomethyl ether/polypropylene glycol (65:30, vol/vol) and produced a 0.855 mm scar in the wear test. Wear tests were run with a mixture of sample/base fluid (6:94, w/w).

[c] Refractive index taken at 60°C.

of various alcohols involving numerous long-chain fatty acid derivatives have been studied (19). Mixed diesters of aliphatic diols also show antimicrobial properties (20). It is possible that mixtures of diesters with boric acid derivatives of monoesters have commercial potential as biostatic additives in the use of water-based cutting fluids.

Borate esters and succinimide complexes of borated fatty esters of glycerol are useful as friction-reducing additives in crankcase lubricants (21,22). It is evident from data within Table 4 that the presence of borated glycol esters instills antiwear properties. In each case, the wear scar of the base fluid with 6% ester added was less than the wear scar of the base fluid itself.

The above results suggest that the glycol esters of partially hydrogenated soybean oil fatty acids and their derivatives can be used as components of lubricating oil, water-based cutting fluids and as antifriction additives.

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