Potential Lubricants for Continuous Casting of Steel: Polyol Esters of Partially Hydrogenated Soybean Acids[1]

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ABSTRACT

In the past decade continuous casting of steel into billets and slabs without going through the ingot stage has drawn widespread attention in the steel industry. Mold lubrication is vital to continuous casting to prevent sticking. Approximately 50% of this operation uses a vegetable oil lubricant, primarily rapeseed oil. Trimethylolethane, trimethylolpropane, trimethylolbutane and pentaerythritol esters of partially hydrogenated soybean fatty acids, derived from commercially hydrogenated soybean oils, have been readily prepared in good yields. Preliminary measurements of viscosities, smoke, flash and fire points of these polyol esters indicate that they are possible candidates for use as lubricants in the continuous casting of steel.

INTRODUCTION

The continuous casting of steel is considered one of the major technological advances in the steel industry in recent years (1,2). In conventional steelmaking, up to 30% of the steel poured is lost in ingot trimming and mill scale; continuous casting cuts these losses down to 10% or less (3). Continuous casting produces billets and slabs with no ingot pouring and reheating before rolling–processes required in the handling of blooms. Because of economic advantages there has been a continuous growth in this new steelmaking method. The projected capacity for continuous casting of steel in this country is 40 million tons by 1973. Domestic steelmakers express the belief that eventually about half their production will roll off a continuous line (2). Based on the use of 4-6 oz. of lubricant per ton, a substantial market for lubricants for continuous casting of steel is developing.

The most important function of a mold lubricant is to prevent sticking. Without continuous and reliable lubrication of the mold walls, the steelmaking process slows down or stops (4,5). The most widely used lubricants to date have been rapeseed oil high in erucic acid and a blend of rapeseed oil with a more viscous mineral oil. Blown rapeseed is selected primarily because it does not penetrate into the surface of the steel. It is of medium viscosity, 150-200 cP at 100 F, and has a flash point of 450 F. Crambe, another high erucic oil, is an excellent mold lubricant and has great potential of becoming a new crop. In plant scale tests by the steel industry, crambe oil proved superior to rapeseed oil in continuous casting of steel. Other oils tried as lubricants are silicone, fish and mineral, as well as paraffin wax, inorganic salts and mixtures of fatty acids and graphite (4,6).

Because a reduction in the erucic acid content of rapeseed oil is anticipated (6) and because continuous steel production is on the rise, a survey of new potential lubricants has been made. This paper describes the preparation and physical properties of polyol esters from commercial soybean oil. Fatty acids from these partially hydrogenated oils were esterified with trimethylolethane and trimethylolpropane. The oils were transesterified with trimethylolbutane and pentaerythritol. Preliminary measurements of viscosities, smoke, flash and fire points of these polyol esters indicate that they are possible lubricants in the continuous casting of steel.

EXPERIMENTAL PROCEDURES

Instrumentation

Gas liquid chromatographic (GLC) analyses were made on an F&M Model 5750 gas chromatograph equipped with a hydrogen flame detector and a 6 ft x 1/4 in. OD stainless steel column packed with 10% EGSS-X on Gas Chrom P, 100-120 mesh (organosilicon polyester packing Applied Science Laboratories, Inc., State College, Pa.). The column was held at 170 C with a helium flow of 35 ml/min.

IR spectra were recorded with a Beckman IR 8 spectrophotometer both for thin films of 100% material and for carbon disulfide solutions of compounds. UV spectra were obtained on a Beckman DB spectrophotometer.

Viscosities were determined with Brookfield and Cannon-Fenske-Ostwald viscometers.

Smoke, flash and fire points were measured by the Cleveland open flash cup.

Starting Materials

Soybean fatty acids: Partially hydrogenated soybean oils were specially prepared by Anderson Clayton and Co., Dallas, Tex. GLC analyses of these oils are given in Table I.

TABLE I

Partially Hydrogenated Soybean Oils

HSBO[a]	GLC analysis[b]						Viscosities, cP at F[d]					Points, F		
no.	Palmitic	Stearic	Oleic	Linoleic	IV	N.E.[c]	73	50	40	34	0	Smoke	Flash	Fire
1	9.2	4.6	46.9	39.3	104.3	271.9	69.5	142	367	1370	Semisolid	446	644	790[e]
2	12.6	7.3	65.2	14.9	82.9	276	2205	Solid	—	—	—	437	626	788[e]
3	10.4	7.9	75.8	5.9	71.8	279.9	Solid	—	—	—	—	446	608	842
4	10.7	18.0	71.8	Trace	60.9	279	Solid	—	—	—	—	401	653	797

[a] HSBO, partially hydrogenated soybean oil.

[b] Analysis of methyl esters by gas liquid chromatography.

[c] Neutral equivalent of free fatty acids.

[d] Determined with Brookfield viscometer.

[e] Not fire point; sample boiled over side of cup.

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[2] N. Market. Nutr. Res. Div., ARS, USDA.

TABLE II

Polyol Esters of Partially Hydrogenated Soybean Oil

Polyol[a] HSBO no.	IV	Viscosity, cP at F						Points, F			Viscosity, SUS, F		Viscosity index	N_D30
		73	50	40	34	0	-20	Smoke	Flash	Fire	100	210		
TME/1	97.1	108	186	650[b]	1565[b]	6900[c]	Plastic	401	635	851[d]	270	62.4	195	1.4697
TME/2	78.3	95	172[b]	629[b]	1085	Semisolid	—	342	535	825[e]	239	58.7	191	1.4651
TME/3	69.3	2895[b]	Semisolid	—	—	—	—	320	518	788[e]	263	58.5	169	1.4631
TME/4	59.3	638[b]	Semisolid	—	—	—	—	365	572	831[e]	281	64.0	197	1.4630
TMP/1	98.4	90	170	219	270	846	42,000[b]	464	644	806[e]	251	59.9	192	1.4695
TMP/2	80.0	144	280	1223	805	Plastic	—	437	608	806[e]	297	62.9	176	1.4670
TMP/3	67.2	117	2985	Plastic	Semisolid	—	—	437	653	842[e]	295	62.5	179	1.4657
TMP/4	58.6	119[c]	Semisolid	—	—	—	—	455	635	842[e]	307	64.7	184	1.4648
TMB/1	90.8	117	214	310	400[b]	Semisolid	—	370	620	842[d]	286	60.9	146	1.4699
TMB/2	79.2	117	210[b]	Semisolid	—	—	—	374	599	820[e]	283	58.6	246	1.4666
TMB/3	67.7	157[b]	Semisolid	—	—	—	—	378	590	810[e]	297	65.0	191	1.4649
TMB/4	58.5	142[c]	Semisolid	—	—	—	—	374	608	851[e]	333	63.1	158	1.4640
PE/1	106.4	125	214	578	3780[c]	Plastic	—	401	662	797[d]	297	63.0	171	1.4709
PE/2	80.0	157	1425[c]	Semisolid	—	—	—	392	545	815[d]	371	76.6	204	1.4689
PE/3	70.2	193[b]	Semisolid	—	—	—	—	374	572	824[d]	435	72.1	252	1.4676
PE/4	61.8	Semisolid	—	—	—	—	—	399	622	810[e]	369	67.5	163	1.4657
Crambe oil	94	mp 43 F						518	680	815[d]	246	61.6	240	1.4716[f]
Rapeseed oil	109.5	mp 28-14 F						489	689	806[d]	216	57.1	204	1.4655[f]

[a] TME, trimethylolethane; TMP, trimethylolpropane; TMB, trimethylolbutane; PE, pentaerythritol.

[b] Crystals settled out.

[c] Slurry of crystals and oil.

[d] Not fire point; sample boiled over side of cup.

[e] Not fire point; sample decomposed with charring.

[f] Refractive index at 40 C.

Partially hydrogenated soybean fatty acids were obtained by saponification of the desired oil.

Other reagents: Trimethylolethane and trimethylolbutane were provided by Trojan Powder Company, Division of Commercial Solvents Corp., Alltentown, Pa. Trimethylolpropane and pentaerythritol were provided by Celanese Chemical Co., Division of Celanese Corp., New York, N.Y.

Reagents with 96-98% hydroxyl content were used without further purification.

Preparation of Esters

Generally, trimethylolethane and trimethylolpropane esters were prepared by refluxing the desired partially hydrogenated soybean fatty acids and polyol in a molar ratio of 3.1:1 in the presence of 0.5% of a catalyst consisting of three parts by weight of calcium acetate and one part of barium acetate with xylene (50% by volume, based on acids). Theoretical amounts of water of esterification were removed by a Dean-Stark trap. After the reaction mixture was washed with water, dried and stripped of solvent, the excess fatty acids were removed by high vacuum distillation. IR analysis of esters showed no hydroxyl present. Esters had acid values less than 2.3.

Trimethylolbutane and pentaerytiritol esters were prepared by transesterification of an equivalent amount of the appropriate partially hydrogenated soybean oil in the presence of 0.5% of a catalyst consisting of three parts by weight of calcium acetate and one part of barium acetate and by simultaneous removal of glycerol under reduced pressure. Reactions were carried out at 220-250 C at 20-45 mm Hg pressures until collection of distillate stopped. The theoretical amount of glycerol was obtained from each reaction. The product was taken up in petroleum ether, washed with water, dried and stripped of solvent. IR analysis of esters showed no hydroxyl present, and since acid values were less than 2.8, esterification was essentially complete.

Measurement of Viscosities

Viscosities of the oils and esters were determined with a Brookfield viscometer. Graduated 600 ml low form Griffin beakers were charged with 450 ml samples and covered with watch glasses. Beakers were placed in moisture proof plastic bags, flushed with nitrogen and stored from 50-168 hr in 73, 50, 40, 34, 0 and -20 F constant temperature rooms. At given temperatures, measurements were made at different shear rates. When crystals were present, viscosities of the esters changed with a change in the rate of shear. Because of this non-Newtonian behavior of the esters, the viscosities given in Tables I and II should be considered relative and not absolute values.

Viscosities of the esters at 100 and 210 F were determined in Cannon-Fenske-Ostwald viscometers. The viscosity indexes were obtained from viscosities at 100 and 210 F by ASTM Method D 2270 (7). The kinematic viscosity was converted to Saybolt Universal viscosity (SUS) according to ASTM Method D 2161 (7).

Determination of Smoke, Flash and Fire Points

Smoke, flash and fire points for all materials were determined by the Cleveland open flash cup, ASTM D 92-33 (8) and AOCS Official Method Cc 9a-48 (8). Fire points were determined in a laboratory hood with ventilation cover removed and hood fan operating because of the dense smoke.

DISCUSSION

Physical properties of the four commercially supplied, partially hydrogenated soybean oils and their polyol esters were studied and compared with crambe and rapeseed oils now used as steel lubricants. IR analysis of these nickel-hydrogenated oils showed 14-48% *trans* isolated double bonds. UV analysis indicated only traces of conjugated double bonds.

Physical properties of crambe and rapeseed oils are included in Table II for comparison. Commercial, crude, crambe oil from Ashland Oil Co., Mapleton, Ill., was washed with alkali to give an acid value of 0.67. The rapeseed oil, a Swedish variety, was processed with phosphoric acid treatment, neutralization, addition of citric acid, bleaching and deodorization.

Replacing glycerol with polyols having three or four primary hydroxyl groups gave esters having different distributions of hydrogenated acid moieties and therefore different physical properties. Viscosity data showed that the polyol ester had a lower pour point than the corresponding hydrogenated soybean oils. The esters listed as semisolids had a pumpable consistency at 0 F. Many of the polyol esters had pour points lower than melting points reported for crambe and rapeseed oils.

With the exception of the esters of oil no. 3, Tables I and II show that the polyol esters had fire points higher than the corresponding hydrogenated soybean oil and equal to or higher than that of rapeseed oil. As indicated in Tables I and II, the fire points given are not true fire points but temperatures either at which the materials boiled over into the flame of the burner or at which the thermometer could not be observed visually because of the dense smoke. These temperatures are reported for consideration because fire point relates thermal and oxidative stability to spontaneous ignition temperature. Under the temperature and heating conditions of the test, esters sometimes decompose to give flammable products which then burn. Flash points of the polyol esters were lower than those of either rapeseed or crambe oil. With the exception of the trimethylolpropane esters, the polyol esters had lower smoke points than the corresponding hydrogenated soybean oil. The trimethylolpropane esters had the lowest acid values, less than 0.5. It should be possible to raise the smoke points of other esters by neutralization.

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