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DIESTERS OF OXO GLYCOLS

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5 Claims. (Cl. 260—488)

This invention relates to novel synthetic lubricating compositions and to their method of preparation. Particularly the invention relates to ester type synthetic lubricants which are prepared by reacting together acids with glycols that are derived from the aldol condensation of Oxo aldehydes. Still more particularly the invention relates to new and useful synthetic lubricating compositions having ASTM pour points below about −15° F., flash points in excess of about 375° F., and viscosities within the range of 2.0 to 13 centistokes at 210° F. which comprise the esters of glycols prepared by the aldol condensation and reduction or hydrogenation of aldehydes resulting from the action of carbon monoxide and hydrogen on olefins in the Oxo process.

In recent efforts to obtain superior lubricating compositions which have unusual and specific properties, there have been developed entirely new synthetic materials that have lubricating properties. In general, these new synthetic lubricants are characterized by viscosity properties that are outstanding at both high and low temperatures, especially when compared to mineral oils. These outstanding low and high temperature properties are especially desirable for use in equipment designed to operate over a great temperature differential, such as jet engines for aircraft use, combustion engines for aircraft, and the like. It has been found that mineral lubricating oils are generally undesirable for the lubrication of these engines because of their high and low temperature viscosity limitations.

It has also been found that synthetic lubricants may be desirable for the lubrication of standard automotive engines. In addition to the versatility of their viscosities, the use of some types of the synthetic lubricants investigated have been found to result in very low rates of combustion chamber deposit formation, particularly when used for long periods of time. Low rates of formation of combustion chamber deposits result in increased power factor from fuel, less increase in the octane requirement of the engine, less pre-ignition tendency, and a general overall improvement in engine operation. Also these lubricants may serve to reduce or remove combustion chamber deposits from an engine already heavily loaded with such deposits.

For use in reciprocating engines particularly as a lubricant for automotive engines, a lubricating composition must meet several requirements. In order to form an effective lubricating film and to maintain that film at low and high temperatures, it must have certain viscosity characteristics. At low temperatures the lubricant must be sufficiently labile to flow through the circulatory system of the equipment and allow movement of lubricated surfaces without an undue power requirement. A lubricant having an ASTM pour point of below about 35° F. has sufficient low temperature lability to make it satisfactory in these respects. At high temperatures a lubricant must have sufficient "body" or "thickness" to furnish and maintain a satisfactory lubricating film. It has been

found that a lubricant that is satisfactory in this respect will have a viscosity at 210° F. of between about 2 and 60 centistokes, or 32.8 and 280 Saybolt Seconds Universal. To prevent lubricant loss, due to volatility and general molecular disintegration, and to insure against explosion hazards at high temperatures sometimes encountered, a lubricating composition should have a flash point in excess of about 300° F. These requirements are all inherent in the term "lubricating composition," as used in this specification, and the materials of the invention are limited to those within these operable ranges. In general, the preferred materials as comtemplated herein, and as described in the preferred embodiment hereof, will have an ASTM pour point below about −15° F., a flash point above about 375° F., and will have a viscosity within the range of 2.6 to 13 centistokes, or 35 to 70 Saybolt Seconds Universal at 210° F.

In general it has been found that the above listed properties are a function both of molecular structure and of molecular weight. This fact makes it possible within certain limits, to prepare compositions having similar low and high temperature properties in a variety of ways, and also enables the manufacturer to "tailor" a composition to fit a certain specific set of specifications, within rather general limits. In general, molecules having from 20 to 130 carbon atoms meet the desired viscosity standards with those molecules having from 25 to 100 carbon atoms being preferred.

It has been found, and forms the object of this invention, that materials having the desirable properties listed above, may be prepared by esterifying a glycol having a great degree of branching that is obtained from the Oxo process.

It has been known to the art that oxygenated organic compounds may be made by reacting together carbon monoxide, hydrogen and a monoolefinic hydrocarbon to form an intermediate product which may be subsequently reduced to an alcohol having one carbon atom more than the starting hydrocarbon. This reaction is carried out in the presence of a cobalt-containing catalyst, or an equivalent catalyst, in a two-stage operation, the product formed in the first stage being predominantly aldehydic with a minor portion of alcohols. In the second stage, the product of the first stage is hydrogenated, or reduced, to the corresponding alcohol containing an additional carbon atom.

These reactions may be simply represented for a monoolefinic feed as follows, it being understood that other reactions may take place to a minor extent.

First stage:

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[\text{cat.}]{} RCH_2{-}CH_2{-}CHO$$

or

$$\begin{array}{l} RCH{-}CH_3 \\ \quad | \\ \quad CHO \end{array}$$

Second stage:

$$RCH_2{-}CH_2{-}CHO + H_2 \longrightarrow RCH_2{-}CH_2{-}CH_2OH$$

or

$$\begin{array}{l} RCH{-}CH_3 \\ \quad | \\ \quad CHO \end{array} + H_2 \longrightarrow \begin{array}{l} RCH{-}CH_3 \\ \quad | \\ \quad CH_2OH \end{array}$$

It is evident from the above equations that a primary alcohol containing one more carbon atom than the starting monoolefin will result and that the position in the molecule of the added group will depend on the position of the double bond in the original olefin, or the position to which the double bond may shift by isomerization under the reaction conditions used.

The olefin feed for the above reactions may be any olefin known to the art. Such olefins as ethylene, propylene,

butylenes, pentenes, hexenes, olefin polymers, such as diisobutylene, triisobutylene, polypropylenes, and olefinic fractions from the hydrocarbon synthesis process, thermal or catalytic cracking operations, and from other sources may be used as starting materials.

Of particular interest are the polymers and copolymers of C_3 and C_4 monoolefins. These monoolefins are readily available in petroleum refinery streams, and processes for their conversion to liquid copolymers have been described by the art. One such process consists of passing the olefin-containing stream in liquid phase in contact with an acid catalyst comprising phosphoric acid impregnated on kieselguhr. Other acidic catalysts, such as phosphoric acid or copper phosphate impregnated on silica gel, sulfuric acid, Friedel-Crafts catalysts, activated clays, silica-alumina, copper pyrophosphate, etc., may be used. Suitable conditions when employing catalyst of the phosphoric acid type are temperatures of 300° F. to 500° F., pressures of from 250 to 5,000 p. s. i. and feed stocks comprising refinery streams containing propylene and mixed butylenes. Suitable feed stocks, for example, may contain from 15 to 60 mol. percent propylene, from 0.5 to 15 mol. percent butylenes, and from 0.1 to 10 mol. percent isobutylene, the remaining being saturated hydrocarbons. Other suitable feed stocks are the dimer and trimer of isobutylene.

The carbon monoxide and hydrogen may be manufactured by conventional methods from many materials, such as coke, coal, lignite, or hydrocarbon gases, such as natural gas or methane. The solid materials may be converted by known methods into carbon monoxide and hydrogen by treatment with steam and/or carbon dioxide. The ratio of carbon monoxide to hydrogen may be varied by varying the amount of steam used to react with the solid material so that a part of the carbon monoxide may react with the steam to form carbon dioxide and hydrogen, thus increasing the molar ratio of hydrogen to carbon monoxide. The carbon dioxide may be removed by scrubbing the gaseous mixture with aqueous ethanolamine or other basic substance. The hydrocarbon gases may be converted to hydrogen and carbon monoxide in a number of ways, such as treatment with oxygen, carbon dioxide, or steam, or a combination of steam and carbon dioxide, catalytically, in accordance with known procedures.

In the first stage of the reaction, or the aldehyde synthesis stage, hereinafter referred to as the "Oxo stage," the ratio of hydrogen to carbon monoxide employed may vary appreciably. Ratios of 0.5 volume to 2.0 volumes of hydrogen per volume of carbon monoxide may be employed. The preferred ratios comprise about 1.0 volume of hydrogen per volume of carbon monoxide. The quantities of olefins employed per volume of carbon monoxide and hydrogen likewise may vary considerably, as may the composition of the olefin feed stream. The olefin feed, as mentioned above, may comprise pure olefins or may comprise olefins containing paraffinic and other hydrocarbons. In general, it is preferred that the olefin feed stock comprise olefins having from 2 to 18 carbon atoms per molecule. Particularly desirable olefins comprise those having from about 6 to about 18 carbon atoms per molecule.

The Oxo stage is generally carried out at pressures ranging from about 100 to 300 atmospheres and at a temperature in the range of about 200° F. to about 400° F. The quantity of hydrogen plus carbon monoxide with respect to olefin utilized may vary considerably, as for example, from 1000 to 45,000 standard condition cubic feet of carbon monoxide and hydrogen per barrel of liquid olefin feed. In general, however, approximately 2500 to 15,000 cubic feet of carbon monoxide-hydrogen gas per barrel of olefin feed is used.

Following the Oxo stage, the aldehyde product, containing considerable amounts of dissolved catalyst is generally decobalted; i. e., treated at elevated temperatures in the presence of a gas, vapor, or liquid, to decompose the cobalt catalyst and to free the aldehyde of dissolved metal.

In the second, or hydrogenation stage, any catalyst such as nickel, copper, tungsten sulfide, nickel sulfide, or sulfides of groups VI and VIII metals of the periodic table or mixtures of them may be used. The hydrogenation temperatures are generally in the range of from about 150° to 750° F., while the pressures generally employed are in the range of about 100 to 300 atmospheres.

It is with the products of the first, or Oxo, stage of the process described above, that the instant invention is concerned. The primary products of the first stage of the Oxo process are the aldehydes of the corresponding olefins, containing, however, an added carbonyl group. For instance, the product obtained by the oxonation, or carbonylation, of a C_7 olefin polymer of mixed propylene and butylene has the following approximate composition:

	Percent
Unreacted olefin	20
Aldehydes	35
Esters	10
Alcohols	10
Acetals	15
Higher alcohols, glycols, ethers, etc.	10

The glycols prepared from the aldehydes present in the mixture above have a high degree of branching and contribute very desirable properties to the materials formed by their esterification with acids.

In processes known to the art, generally by distillation under reduced pressures, the aldehydic constituent of the mixture of products as illustrated above is separated and purified. The aldehydes so separated are treated to a process of aldol condensation and then reduced to the glycol in accordance with the following steps:

STEP 1.—SEPARATION OF ALDEHYDES FROM PRODUCT OF THE OXO STAGE

Example I

Laboratory distillation of the decobalted product from the Oxo stage was accomplished in a 30 plate Oldershaw column at 200 mm. Hg. using a 5/1 reflux ratio. The data shown below constitute an example of such a distillation of C_8 Oxo product for the recovery of isooctyl aldehyde. Purity of the C_8 aldehyde as established by carbonyl number was better than 97+%.

	Grams
Total charge	6566.2
Recovered	6565.7

Constituent	Distillation Range	Weight Percent
Forecut (chiefly hydrocarbons)	Initial—215° F.	18.0
C_8 Aldehyde	215—255° F.	24.5
Bottoms (largely C_8 alcohol)	255° F—plus.	57.0

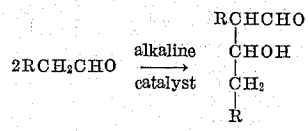
Example II

Distillation of decobalted Oxo product was accomplished in a continuous still (1.6 B./D. capacity) under the following conditions. Feed to the still contained about 60% C_8 aldehyde. The 1.6 B./D. still was operated under continuous conditions at 4.0 gal./hr. feed rate, 2.0 gal./hr. overhead take off and 22 inches of mercury vacuum. Inspection of the product indicated aldehyde purities of about 97%.

STEP 2.—ALDOLIZATION OF THE ALDEHYDE

At a temperature of about 30° F. to about 200° F. in the presence of an alkaline catalyst, such as sodium alcoholate, sodium carbonate, sodium hydroxide, and the like, aldehydes possessing a methylene group adjacent to the carbonyl group readily condense to the beta-hy-

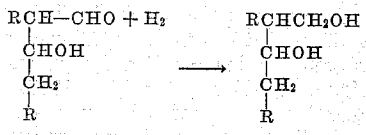
droxy aldehyde. This material may be said to be prepared in accordance with the following:



It is preferred that the molecular ratio of the catalyst to aldehyde in this reaction be about 1 to 20 or more, preferably from 1 to about 10.

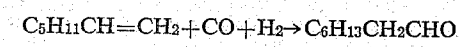
STEP 3.—REDUCTION OF ALDEHYDE TO GLYCOL

Conversion of the beta-hydroxy aldehyde as above to the corresponding di-hydric material, or glycol, may be accomplished by catalytic hydrogenation in the presence of catalysts such as platinum, Raney nickel, and the like. Hydrogenation conditions such as in the second stage of the Oxo process as described above are preferably used, e. g., catalysts such as nickel, copper, tungsten sulfide, nickel sulfide, or sulfides of groups VI and VIII metals of the periodic table, temperatures of about 150° to 750° F. and pressures in the range of about 100 to 300 atmospheres. This reduction, or hydrogenation, to the corresponding glycols proceeds as follows:

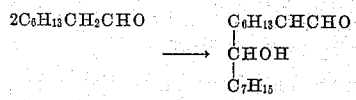


Starting with a C_7 polymer of mixed butylene and propylene, the reactions outlined above are as follows. It is understood that the reactions are exemplary only, and that the inventive process is not limited to the materials shown.

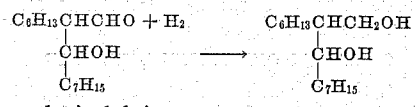
I. Carbonylation
- A. Conditions:
  - (1) Catalyst—cobalt oleate
  - (2) Temperature—200° F. to 400° F.
  - (3) Pressure—100 to 300 atmospheres
- B. Reaction:



II. Aldolization
- A. Conditions:
  - (1) Catalyst—alkaline (sodium hydroxide)
  - (2) Temperature—30° F. to 200° F.
- B. Reaction:



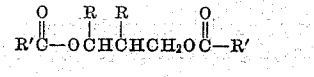
III. Reduction or hydrogenation
- A. Conditions:
  - (1) Catalyst—nickel sulfide
  - (2) Temperature—150° F. to 750° F.
  - (3) Pressure—100 to 300 atmospheres
- B. Reaction:



The synthetic lubricants contemplated by the instant invention are formed by the esterification of the Oxo glycol as prepared above, and are of the following types:

TYPE I.—SIMPLE DIESTERS

Diesters formed by reacting two moles of a monobasic acid, preferably of a branched chain configuration with the glycol to form a compound of the following formula:



wherein R represents the alkyl radicals of the starting glycol and wherein R′ represents the alkyl radicals of the monobasic acid used. R′ preferably contains from 3 to 19 carbon atoms of branched chain configuration, i. e., the acids used preferably contain from about 4 to about 30 carbon atoms.

The value of R will depend upon the olefin used as a starting material, and one R radical will contain one more methylene group than the other. For example, if the starting olefin contains 7 carbon atoms, one R group will be the radical $C_7H_{15}-$ and the other will be $C_6H_{13}-$. If a C_{12} olefin is used, one R group will be $C_{12}H_{25}-$ and the other $C_{11}H_{23}$. In general, when a C_nH_{2n+1} olefin is the olefin to be oxonated one R group will be C_nH_{2n+1} and the other will be $C_{n-1}H_{2(n-1)+1}-$. Generally it is preferred that the R groups contain from 4 to 18 carbon atoms each with from 6 to 12 being especially preferred.

The esterification reaction between the glycol and the acid chosen may be straightforward and is preferably carried out using the acid chloride. A detailed example is set out below.

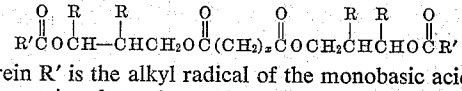
Operable acids include the following:

n-Butyric acid
Isobutyric acid
n-Valeric acid
Isovaleric acid
Caproic acid
2-ethyl butyric acid
n-Heptylic acid
Caprylic acid
Pelargonic acid
Capric acid
Stearic acid
The various Fischer-Tropsch synthesis acids containing from 4 to 20 carbon atoms

Especially preferred, and contemplated in the preferred embodiment of the instant invention, are the various Oxo acids containing from 4 to 20 carbon atoms and prepared by the oxidation of the corresponding aldehydes from the first, or Oxo, stage of the Oxo synthesis as described in detail above.

TYPE II.—DIBASIC ACID CENTERED COMPLEX ESTERS

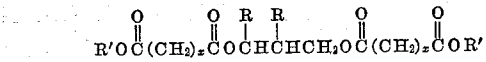
These dibasic acid centered complex esters are formed by reacting the Oxo glycol with an equimolar proportion of a monobasic acid to form the half ester and reacting two moles of the half ester so formed with one mole of a dibasic acid. This complex ester has the following general formula:



wherein R′ is the alkyl radical of the monobasic acid used and contains from 3 to 19 carbon atoms and wherein x is an integer of from 2 to 8 and designates the length of the body portion of the dibasic acid used. R is the alkyl portion of the glycol and is as described above. The body of the dibasic acid used may contain oxygen or sulfur in the form of ether or thioether linkages. Operable dibasic acids may include succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, glycolic, diglycolic, beta,beta-oxydipropionic, beta,beta-thiodipropionic acid, and the like. Operable monobasic acids used to form the half ester include those listed above as being operable in preparing the ester of Type I.

TYPE III.—GLYCOL-CENTERED COMPLEX ESTERS

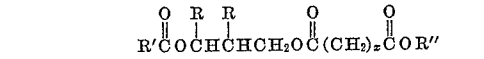
To prepare the ester of Type III, the glycol is preferably reacted with a double molar proportion of a half ester of an alcohol and a dibasic acid. This half ester is prepared by reacting a dibasic acid with a half molar proportion of an alcohol. The ester of Type III has the following general formula:



In this formula R has the values as in Types I and II, and R' is the alkyl radical of the monohydric alcohol used to form the half ester with the dibasic acid. Operable alcohols include those having from 2 to 12 carbon atoms of either branched or straight chain configuration. Alcohols such as ethyl, propyl, butyl, isobutyl, amyl, hexyl, octyl, capryl, decyl, lauryl, 2-ethyl hexyl, any of the various Oxo alcohols, Fischer-Tropsch alcohols, butoxyethyl alcohol, butoxyethoxyethyl alcohol, C8 Oxoxyethyl, isopropoxyisopropyl alcohol, etc., may be used to form the half ester. The value of the *x* grouping again may be from 2 to 8 and designates the body of the dibasic acid used. Operable acids are set out in connection with Type II above.

TYPE IV.—COMPLEX MIXED ESTERS

The esters of this type are prepared by reacting the glycol with one-half molar proportion of a monobasic acid to give a half ester. This half ester is reacted with equimolar proportions of a half ester formed by reacting a one-half molar proportion of an alcohol with one mole of a dibasic acid. This complex mixed ester has the following formula:



In this equation the value of R and of *x* is as described above. R' is the alkyl radical of the monobasic acid used and is as described in the Type I ester. R'' is the alkyl radical of the alcohol used and is as described in connection with the Type III ester above.

As was stated above, the esters of Type I above are the preferred esters of the invention and are contemplated in the preferred embodiment. Particularly desired are the esters of the Oxo glycols with branched chain acids derived from the oxonation of olefins in the Oxo process.

The invention will be more clearly defined with reference to the following examples, which are to be considered as exemplary only, and not as restrictive of the concept of the instant invention.

EXAMPLE I

A. *Preparation of a* C_{16} *glycol*

A C_7 olefin prepared by the U. O. P. polymerization of mixed butylenes and propylenes was subjected to the action of carbon monoxide and hydrogen at a temperature of about 350° F. and at a pressure of about 200 atmospheres in the presence of a cobalt oleate catalyst. The mixture of products had the following approximate composition:

	Percent
Unreacted olefins	20
Aldehydes	35
Esters	10
Alcohols	10
Acetals	15
Higher alcohols, glycols, ethers, etc	10

The aldehyde portion of this mixture was separated from the remainder of the product by distillation at 215°–255° F. vapor temperature and under a pressure of 200 mm. Hg. The product was substantially a C_8 Oxo aldehyde.

B. *Aldolization of aldehyde and reduction to a* C_{16} *glycol*

The aldehydes recovered as described above were aldolized into a beta-hydroxy aldehyde and reduced to the corresponding glycol by treating as follows:

1. ALDOLIZATION PROCEDURE

Two liters (1650 grams) of 95% isooctyl aldehyde prepared as above, were placed in a 3 liter rb. flask

equipped with a reflux condenser, stirrer and thermometer. Eighty grams (5 wt. percent) of potassium hydroxide were dissolved in 50 ml. of water and 450 ml. of 95% ethanol. The alcoholic caustic was added slowly to the aldehyde and after the initial heat has subsided the temperature is maintained for 2 hours at 180–190° F. The reaction mixture is allowed to cool down under a blanket of nitrogen.

The reaction product was washed with 1 liter of water and the alkaline water layer separated from the organic portion. The water layer was then extracted with 1000 ml. of petroleum ether and the ether extract combined with the organic portion. The combined product was then washed successively with two 1 liter quantities of 2% sulfuric acid followed by two water washings. The washed product was then ready for hydrogenation.

2. HYDROGENATION

The aldol product was hydrogenated in an autoclave operation under the following conditions: 6 hours at 350° F., methanized hydrogen at 3000 p. s. i. g., reduced nickel as catalyst.

3. DISTILLATION

The hydro product was filtered and distilled in a 30 plate Oldershaw column. Hydrocarbons and petroleum ether were removed by an atmospheric distillation initial to 265° F. The distillation was continued at reduced pressure (20 mm.) using a 5/1 reflux ratio. The C_{16} glycol fraction was collected at 385–405° F. and on an acid free basis the wt. percent yield was approximately 16 percent. Purity as estimated from hydroxy number was 98%.

C. *Preparation of* C_8 *Oxo acids*

The C_8 Oxo aldehyde product as prepared above may be converted into a crude composite of C_8 Oxo acid by treatment as follows:

1. BATCH OXIDATION WITH AIR AND CAUSTIC

The batch oxidations were carried out in the small glass reactor (16"×100 mm. ID) which is equipped at the bottom with a coarse fritted glass plate for air inlet and with internal and external means of temperature control. A charge of 167 grams of the aldehyde feed and 500 ccs. of 5–10% caustic were charged to the reactor and oxidized for 3–5 hours at 110–115° F. with air rate of 50–100 liters of air/hour/100 grams of feed. The exit gases from the reaction were conducted in series through cold water and Dry Ice traps, activated charcoal absorber and wet test meter. The total product including those from the traps were separated into non-soap and C_8 acid constituents by methods involving

(1) Extraction with isopentane solvent to recover the main bulk of non-soap and unreacted aldehyde feed.
(2) Steam distillation of extracted soap solution to recover final traces of non-soap solution.
(3) Acidification of residual soap solution with 10% HCl and extraction of crude fatty acids with isopentane solvent.
(4) Distillation of the isopentane extracts to recover the respective crude non-soap and fatty acids products.

2. BATCH OXIDATION WITH AIR

A few batch oxidations were also carried out in the small oxidation tube employing the same volume of aldehyde feed, temperature and air to feed ratio. The crude products were worked up by saponification with dilute caustic (5–10 wt. percent) for 2–3 hours, followed by extraction of the non-soap with light hydrocarbon solvent such as isopentane. The crude acids and non-soap products were recovered in the usual manner.

3. CONTINUOUS OXIDATION WITH AIR AND CAUSTIC

A number of continuous oxidations were conducted in the large packed glass reactor (30"×100 mm. ID) fitted

with a 190 min. coarse fritted glass plate for an inlet, stainless steel bellows type pumps for aldehyde and caustic feed lines, stainless steel pump for recycling and withdrawal of feed and recycle stream through a glass tube situated directly below the air inlet plate and exit gas recovery system essentially the same as in the case of the batch oxidation equipment.

In the case of the both batch runs with air and an air caustic, conversion of 82–85% of the inlet aldehyde and selectivity of 95–96% to crude C_8 acids were obtained. Results on the continuous runs were not as good: conversions were 46–53% and selectivities were 85–86%.

Distillation of the crude acids composited from the products obtained in all three types of oxidation operations was carried out in the 25 mm. Podbielniak column at 1 mm. Hg pressure absolute. Net yields of 89% of C_8 acid, boiling at 146–155° F. at 1 mm. Hg and 10% of heavy acid cut (C_{16} acid) were obtained. The distilled C_8 cut had the following properties:

Acid No.	378
Sap. No.	380
Engler Distillation Range, ° F.	430–456

140 grams of thionyl chloride was next distilled in a Claisen flask to obtain a purified distillate cut boiling in the range of 167°–169° F. To a 500 cc. 3-necked flask equipped with a stirrer, dropping funnel and reflux condenser was added 1 mole (144 gms.) of the distilled C_8 acid cut. To the flask heated to 200° F. was added over an hour period a slight excess of the thionyl chloride (134 gms.). Reaction was completed by heating for an additional hour. The crude C_8 acid chloride was fractionated to recover 140 grams of distillate acid chloride product boiling in the range of 356°–380° F.

D. *Preparation of the C_{32} Ester*

64 grams (0.25 mol) of the C_{16} glycol product prepared as in (B) above (B. P. 360°–540° F. (Pot) at 20 mm. Hg) was dissolved in 150 cc. of redistilled pyridine and charged to a 500 cc. 3-necked flask which was equipped with reflux condenser, calcium chloride drier, stirrer and separatory funnel. A solution of 94 grams (0.5 mol) of the distilled isooctonyl chloride prepared as in C above in 300 cc. of pyridine was added gradually over a period of one hour to the glycol solution. The mixture was refluxed for an additional hour and cooled. The resulting ester product was transferred to a separatory funnel and diluted with 500 cc. of ethyl ether. The mixture was extracted with dilute sodium carbonate solution and sodium sulfate solution to remove the pyridine salt and most of the pyridine. The washed extract was dried and fractionated in the 25 mm. Podbielniak column. A wet recovery of 100 grams of light colored ester product as bottoms was obtained. Inspection data indicated that the product was essentially pure diester (infra red and saponification number) and possessed good viscosity index and pour properties. The yield corresponds to 95% of the theoretical.

ASTM inspection on the C_{32} Oxo ester as detailed above was as follows:

Saponification No.	214
Acid No.	3
Gravity, °API	26.6
Viscosity at 100° F.	119 SUS
Viscosity at 210° F.	41 SUS
Viscosity Index	101
Flash point	386° F.
Pour point	−60° F.

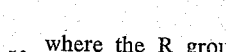
The ester was blended with various percentages of a polymerized isobutylene of a molecular weight of about 15,000 Staudinger and this commercially available viscosity index improver gave the following results:

Weight Percent Improver	0	0.37	0.7	3.2
Vis./100° F. (SUS)	119	143.7	146.5	225
Vis./210° F. (SUS)	41	43.34	43.57	51.9
Viscosity Index	101	112.5	113	131

As is detailed above, the materials of the instant invention are readily compatible with viscosity index improvers and with other additives of the art. Such materials for enhancing special characteristics of the lubricants as oxidation inhibitors, detergents, corrosion inhibitors, pour point depressants, and the like, may be blended with them. Although these synthetic lubricants may be used as lubricants per se, they may also be blended with other lubricants, either naturally occurring mineral oils or with other synthetic lubricants such as formals, silicone polymers, ethers, ether-esters, glycol-ethers, oxylene ethers, and the like. The synthetic lubricants of the instant invention may also be converted to solid and semi-solid lubricants by the incorportion of thickening agents, such as the commonly known grease forming soaps, such as the metallic soaps of fatty acids.

Although the materials of the instant invention are of interest primarily as synthetic lubricants, they may also be used in a wide variety of industrial applications. For instance, they may be used per se, or as starting materials for plasticizers, solubilizers, heat transfer agents, insecticides, weed killers, rust preventatives, solvents, such as for gum in gasoline, dewaxing aids, detergents, oiliness agents as in penetrating oils, and for many other purposes as those familiar with the art will appreciate.

To summarize briefly, the instant invention relates to synthetic lubricating compositions having ASTM pour points below about −15° F., flash points in excess of about 375° F., and viscosities at 210° F. of between about 2.6 and 13 centistokes, i. e., 35 to 70 Saybolt Seconds Universal. The compositions of the instant invention are derived by esterifying a glycol that is prepared by the aldolization and reduction of an Oxo aldehyde, that is to say by the aldolization and hydrogenation of an aldehyde formed by the action of carbon monoxide and hydrogen on an olefin at temperatures in the range of about 200° F. to 400° F. and pressures of about 100 to 300 atmospheres in the presence of a cobalt carbonyl catalyst. Although the exact composition of the glycol is not definitely known, it is believed to have the formula



where the R groups are alkyl radicals that correspond to the olefinic starting material, one R group having one less methylene group than the other. When the starting olefin has the formula C_nH_{2n}, one R group has the formula C_nH_{2n+1} and the other $C_{n-1}H_{2(n-1)+1}$. The materials according to the instant invention may be simple esters formed by reacting the Oxo glycol with two mols of a monobasic acid, in which case it is preferred that the monobasic acid is derived from an Oxo aldehyde. They may be complex esters formed by reacting the glycol with two mols of the half ester formed by reacting one mole of an alcohol with one mole of a dibasic acid, or by reacting one mole of the Oxo glycol with one mol of a monobasic acid and reacting that half ester with a mole of a half ester of a dibasic acid and an alcohol. The molecules should have from about 20 to 130 carbon atoms per molecule, preferably from 25 to 100, and preferably in branched chain configuration.

What is claimed is:

1. As a new composition of matter, a compound having the formula



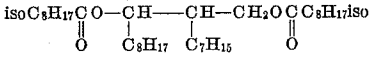
wherein the R's are alkyl radicals of monobasic acids containing from 3 to 19 carbon atoms each and wherein R and R″ are alkyl radicals, R containing from 6 to 18

carbon atoms and R'' containing one less carbon atom than R.

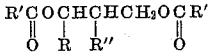
2. A compound according to claim 1 wherein the R's are alkyl radicals each containing 8 carbon atoms.

3. A compound according to claim 1 wherein R and R'' contain 8 and 7 carbon atoms respectively.

4. As a new composition matter, a compound of the formula



5. As a new composition of matter, a compound having the formula



wherein the R's are alkyl radicals of monobasic acids containing from 3 to 19 carbon atoms each and wherein R and R'' are alkyl radicals, R containing from 6 to 12 carbon atoms and R'' containing one less carbon atom than R.

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