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SYNTHETIC LUBRICATING COMPOSITION

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This invention relates to new and improved synthetic lubricating compositions. Particularly the invention relates to new and improved synthetic lubricants which comprise derivatives of the mixture of products obtained from the Oxo process and to the process for their preparation. More particularly the invention relates to formals, ethers and esters prepared from the mixture of products derived from 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 6 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

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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 contemplated 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.

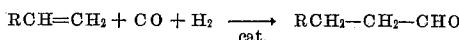
In general it has been found that the above listed properties are a function both of molecular structure and of molecular weight. This fact makes it possible within certain limits, to prepare compositions having similar low and high temperature properties in a variety of ways, and also enables the manufacturer to "tailor" a composition to fit a certain specific set of specifications, within rather general limits. In general, molecules having from about 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 formalizing, etherifying or esterifying the mixture of products obtained from the Oxo process.

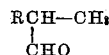
It has been known to the art that oxygenated organic compounds may be made by reacting together carbon monoxide, hydrogen and a monoolefinic hydrocarbon to form an intermediate product which may be subsequently reduced to an alcohol having one carbon atom more than the starting hydrocarbon. This reaction 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:



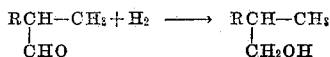
or



Second stage:



or



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 C₃ and C₄ 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 normal 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. Of particular interest, and contemplated in the preferred embodiment of this invention, is an olefin feed known generally as the C₁₂+ cut of a phosphoric acid polymerization using propylene or propylene-butylene mixtures as a feed stream. This cut is the residual components of the polymer after the gasoline components have been removed by fractionation. This material is almost completely olefinic and contains mostly the highly branched tertiary olefins. This cut has the following approximate composition:

	Vol. percent
C ₁₂ (350-420° F.)	55-75
C ₁₃ -C ₁₄ (420-475° F.)	15-20
C ₁₅ (475-508° F.)	5-10
C ₁₅ +	<10

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 Oxo stage is generally carried out at pressures ranging from about 1500 to 5000 pounds per square inch (p. s. i.) 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 tempera-

tures in the presence of a gas, vapor or liquid, to decompose the cobalt catalyst and to free the aldehyde of dissolved cobalt compounds.

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° F. to 750° F., while the pressures generally employed are in the range of about 1500 to 5000 p. s. i.

The process of the instant invention may be more clearly described by reference to the following:

1. PREPARATION OF THE OLEFIN FEED

A mono-olefinic feed stream comprising less than 5% isobutylene was passed over a phosphoric acid impregnated kieselguhr catalyst at a temperature of from 300° to 500° F. and at a pressure of about 1000 p. s. i. g. The resulting crude olefinic polymer was separated into a gasoline fraction (350° F. end point) and a C₁₂(+) fraction.

Inspection data of the olefin polymer C₁₂+ fraction were as follows:

25	Gravity, ° API	-----	48.8
	Bromine No.	-----	117
	Refractive index	-----	1.4423
	Specific dispersion	-----	111.6
	ASTM distillation (percent off at ° F.):		
	Initial boiling point	-----	358
	5	-----	366
	10	-----	367
	20	-----	370
	30	-----	372
35	40	-----	376
	50	-----	379
	60	-----	383
	70	-----	390
	80	-----	400
40	90	-----	424
	95	-----	454

2. OXONATION OF C₁₂+ OLEFIN FEED

The olefinic material as prepared in (1) above was oxonated as follows:

A volume of 1500 cc. (1173 grams) of the C₁₂+ olefin fraction and 10 grams of solid cobalt acetate (tetrahydrate) were charged to a 3-liter shaker autoclave. The system was purged with synthesis gas having an H₂/CO ratio of about 1.1/1. With a synthesis gas pressure of about 200 pounds the contents of the autoclave were heated to 325° F. and the synthesis gas pressure was increased to 2700-3000 pounds. The pressure was allowed to drop to about 2000 pounds and then repressured to 2700-3000 pounds. The reaction was allowed to proceed for about three hours at which time gas absorption was essentially complete.

Decobalting was carried out at 350° F. for two hours at 500 pounds' hydrogen pressure after having depressured the system of synthesis gas and purged three times with hydrogen.

After decobalting was complete the autoclave was cooled and depressured and 75 cc. of water and 200 grams of a nickel-kieselguhr catalyst added. The mixture was then hydrogenated for 6 hours at 350° F. and 2700-3000 pounds hydrogen pressure.

3. CONVERSION TO FORMAL

1174 gms. of the crude alcohol mixture obtained as described in 2 above was admixed with 45 gms. of paraformaldehyde and 1.7 grams of sodium bisulfate in the presence of 210 grams of hexane as a water entrainer.

The mixture was heated at temperatures of 175-205° F. for about 3 hours but no appreciable amount of water was separated. After cooling and adding 150 cc. of hexane

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a vigorous reflux was maintained and in 2½ hours about 14 cc. of water was separated. The mixture was cooled and 30 grams paraformaldehyde and 200 cc. of hexane added. After 3 hours under reflux conditions about 4.5 cc. of water was separated.

The crude formal mixture was washed at 130-150° F. with distilled water, 10% sodium carbonate solution, and twice with distilled water.

The hexane diluent was distilled off at atmospheric pressure and the product was then stripped under vacuum (9-10 mm.) to a vapor temperature of 437° F. The mixture of formals amounted to 816 grams or a yield of about 70 wt. percent based on the crude alcohol.

The resulting product was compared with a formal prepared using the C₁₃ alcohol obtained by the oxonation and hydrogenation of that portion of the polymeric olefin containing only the C₁₂ olefin, which represents approximately 55-75% of the total olefinic polymer. Data are set out in Table I below:

Table I
ASTM INSPECTION DATA ON LUBRICANTS

Lubricant.....	Formal of C ₁₃ Oxo Alcohol		Formal of In- vention	
Yield, (Percent on Total Olefin Feed to Process).....	30%		70%	
Wt. Percent Polybutene, 14,000- 16,000 M. Wt. Staudinger.....	0	2.5	0	2.9
Flash Point (°F.).....	397	375	420	425
Pour Point (°F.).....	-75		-60	-35
Viscosity, SUS:				
100° F.....	78.2	163.6	103	244
210° F.....	37.5	49.1	39.5	56.2
Viscosity Index.....	96	147.5	94	141

These data indicate that the yield of the final lubricant is more than doubled in comparison with the conventional method of preparing the tridecyl formal. It is also significant that the process of this invention uses as the primary starting material the mixture of olefins which cannot be used for blending in premium quality fuels. The quality of the product, both with and without the addition of polybutene viscosity index improver surpasses the conventional formal in both flash and viscosity properties. Also at least two major processing steps are eliminated by using the mixture of olefins rather than a single purified olefin.

The formals in accordance with the instant invention may also be prepared by using any formaldehyde source such as, for example, paraformaldehyde, hexa-methylene-tetra-amine and the like. If desired, acidic materials, such as hydrochloric acid, sulphuric acid, benzene sulfonic acid, p-toluene sulfonic acid, sodium acid sulfate, phosphoric acid ion exchange resins or any inorganic acidic substance may be used as a catalyst. Entraining liquids, such as hexane, heptane, heptane fractions, benzene and the like may be used in order to remove the water of reaction although good yields are readily obtainable without the use of a water entrainer.

It may also be desirable to prepare the formal derivatives by means of the chloro methyl ether reaction. In this procedure the chloro methyl ether may be prepared by addition of formaldehyde, formalin, etc., to the crude alcohol and then adding to the mixture hydrogen chloride, either as an aqueous solution or by passing the gaseous hydrogen chloride through the mixture. This chloro methyl ether reaction is ordinarily less desirable, however, since excellent yields are obtained directly with the formaldehyde.

It is also within the concept of this invention to first react the mixture of products obtained by oxonation of the C₁₂+ olefin with an alkylene oxide such as ethylene oxide, propylene oxide, butylene oxide, etc., at temperatures of about 50 to 400° F. in the presence of condensation catalysts.

The resulting alkylene oxide treated product may then be treated with formaldehyde as above to give a formaldehyde product containing ether oxygen. From 2 to 10 moles, for example, of ethylene oxide may be reacted with the Oxo product mixture.

It is also within the concept of this invention to treat the Oxo product mixture obtained with acidic materials to form esters thereof. For example, the Oxo product mixture may be reacted with monobasic acids such as those monocarboxylic acids containing from 4 to 18 carbon atoms. If desired, dibasic acids such as adipic, suberic, azelaic, sebacic and the like may be used to form diesters. It may also be desirable to first react the Oxo product mixture with alkylene oxides as described above and then esterify with monobasic or dibasic acids. These esterification reactions are accomplished by well-known prior art procedures.

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 incorporation 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 preventives, 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 formalizing, etherifying or esterifying a mixture of alcohols prepared by the action of carbon monoxide and hydrogen on an olefinic polymer containing mostly C₁₂-C₁₈ olefins 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 carbonylation catalyst.

The materials according to the instant invention may be simple formals prepared by reacting the Oxo product with formaldehyde or a dichloro methyl ether. They may be esters formed by reacting the products with an excess of a dibasic acid or an excess of a monobasic acid. The product may also be reacted with an alkylene oxide and then either formalized or esterified in accordance with known procedures. 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. A process for the preparation of formal lubricating compositions which comprises reacting (1) a crude alcohol mixture obtained by the reaction of a mixture of substantially C₁₂ to C₁₈ olefins with carbon monoxide and hydrogen, thereby obtaining a mixture of products which is then further hydrogenated to form said crude alcohol mixture, and (2) a formaldehyde donor selected

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from the group consisting of formaldehyde, paraformaldehyde, formalin and hexa-methylene-tetra-amine; at a temperature of about 150-300° F. in the presence of an acidic catalyst and stripping the mixture of products thus obtained to vapor temperatures equivalent to about 650 to 750° F.

2. The process according to claim 1 wherein said mixture of olefins contains approximately 55-75 vol. percent of a C₁₂ olefin, 15-20% of C₁₃-C₁₄ olefin, 5-10% of C₁₅ olefin and less than 10% of a C₁₅+ olefin.

3. A process for the preparation of formal lubricating compositions having A. S. T. M. pour points below about -15° F., flash points above about 375° F. and viscosities at 210° F. within the range of from 2.6 to 13 centistokes, which comprises reacting (1) a crude alcohol mixture obtained by the reaction of a mixture of C₁₂ to C₁₈ highly branched-chain olefins with carbon monoxide and hydrogen to obtain a mixture of products which are then further hydrogenated to form said crude alcohol mixture, with (2) an excess of a formaldehyde donor

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selected from the class consisting of formaldehyde, paraformaldehyde, formalin, and hexa-methylene-tetra-amine, at a temperature of about 175-205° F. in the presence of an acidic catalyst and a water entrainer selected from the class consisting of hexane, heptane, heptane fractions and benzene and stripping the reaction product thus obtained to vapor pressures equivalent to about 650-750° F.

4. A process according to claim 3 wherein said formaldehyde donor is paraformaldehyde.

5. A process according to claim 3 wherein said vapor temperature is about 437° F. at about 10 mm. (Hg) absolute pressure.

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