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2,787,644

**PROCESS FOR THE PREPARATION OF SYNTHETIC LUBRICANTS**

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8 Claims. (Cl. 260—615)

This invention relates to compositions of matter and to a new process for their preparation. Particularly the invention relates to a process for the conversion of the acetals derived from the action of carbon monoxide, hydrogen and olefins in the Oxo process to formals, with a recovery of the corresponding Oxo aldehydes from the 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 preignition 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

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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.

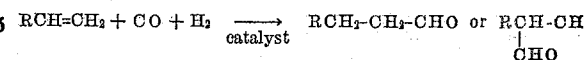
In general it has been found that the above listed properties are a function both of molecular structure and of molecular weight. This fact makes it possible, within certain limits, to prepare compositions having similar low and high temperature properties in a variety of ways, and also enables the manufacturer 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 from an acetal having a great degree of branching that is obtained from the Oxo process by treatment of said acetal with formaldehyde.

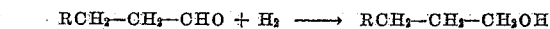
It has been known to the art that oxygenated organic compounds may be made by reacting together carbon monoxide, hydrogen, and a monoolefinic hydrocarbon to form an intermediate product which may be subsequently reduced to an alcohol having one carbon atom more than the starting hydrocarbon. This reaction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

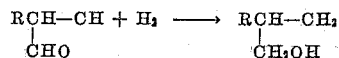
First Stage:



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 or diolefin known to the art. Such olefins as ethylene, propylene, butylenes, pentenes, hexenes, butadiene, pentadienes, 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<sub>3</sub> and C<sub>4</sub> monoolefins. These monoolefins are readily available in petroleum refinery streams and processes for their conversion to liquid copolymers have been de-

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scribed by the art. One such process, known as U. O. P. polymerization, 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 phosphoric acid catalyst of the U. O. P. type are temperatures of 300° 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 feedstock 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° 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.

In the second, or hydrogenation stage, any catalyst such as nickel, copper, tungsten sulfide, nickel sulfide, or sulfides of groups VI and VII 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 Oxo process described above, that the instant invention is concerned. It has been found, and forms the object of this invention, that excellent synthetic lubricants

may be formed by reacting the acetals of the Oxo stage with formaldehyde to recover a formal synthetic lubricant and an Oxo aldehyde which may subsequently be used to form an alcohol, or converted to alcohol and reacted with additional formaldehyde to increase the yield of the synthetic lubricant formed.

As was pointed out above, the primary products of the first stage of the Oxo process are the aldehydes and acetals of the corresponding olefins, containing, however, an added carbon atom. The mixture of products formed by the oxonation, or carbonylation, of a C<sub>7</sub> olefin polymer of mixed propylenes and butylenes has the following approximate compositions:

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

The first step of the instant process is the recovery from this mixture of products the acetal component which involves the following procedure:

*Step 1.—Removal of unreacted olefin*

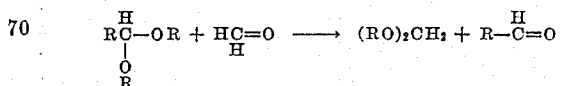
The olefinic constituent of the mixture of products of the Oxo stage are preferably, but not necessarily, removed by topping in a distillation step.

It may be desirable to recover the acetal component of the mixture by a fractional distillation step at pressures up to about 100 mm. Hg. It may also be desirable to convert the aldehydes and alcohols in the mixture of products to acetals by an acetalization reaction, to increase the yield of acetals from the Oxo stage product. This acetalization may be accomplished by the following procedure:

The Oxo stage product, having been topped to remove unreacted olefins, is admixed with sufficient catalyst of an acidic nature, such as sulfuric acid, toluene sulfonic acid, sodium acid sulfate, etc., with the former being preferred, to make the mixture acidic. To prevent hydrolysis of the acetals, water is removed from the reaction as formed. This mixture is then heated to about 175° to 300° F. for about 0.5 to 6 hours. During this time the aldehydes present react with the alcohols present to form acetals. It may be desirable, depending upon the constituents of the mixture of Oxo stage products, to add sufficient alcohol or aldehyde to make up a material balance, thus insuring complete utilization of all the available material. The acetals formed, plus the acetal component of the product, are then removed from the product by a distillation step, ordinarily carried out at pressures up to about 100 mm. Hg. Steam distillation under alkaline or slightly alkaline conditions may be used to separate the unchanged alcohol and aldehyde from the acetal, the alcohol and aldehyde going overhead while the acetal is largely left behind.

The acetals recovered as described above represent a wide range of molecular distribution depending upon the starting olefin used, and the alcohol or aldehyde added to the mixture. This mixture of acetals are then subjected to the following process.

Formaldehyde, or a formaldehyde donor, such as paraformaldehyde, hexamethylenetetramine, etc., is reacted with the acetal mixture at a temperature of about 150° to about 300° F. for from 0.5 to 6 hours. During this reaction time, the formal of the acetal mixture is formed in accordance with the following equation:



The aldehyde generated as a by-product of the reaction may be converted to the alcohol by hydrogenation in accordance with the procedure described above, or it may

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be reacted with additional alcohol to form another molecule of acetal which is then formalized in accordance with the above to increase the yield of the desired product.

The invention will be more clearly explained by reference to the following illustrative example.

100 g. of an acetal of a C<sub>10</sub> Oxo alcohol and a C<sub>3</sub> Oxo aldehyde which had a boiling point at .3 mm./Hg of 150° to 158° C. were treated with an equal molar proportion of paraformaldehyde in the presence of one gram of paratoluene sulfonic acid. The reaction was maintained at a temperature of from 90° C. to 130° C. for six hours. The yield of the C<sub>10</sub> Oxo formal was 70 mol percent and the product boiled at 130° to 140° C. at .6 mm./Hg.

The C<sub>10</sub> Oxo formal has the following inspections:

ASTM pour point	-----° F.	75
ASTM flash point	-----° F.	345
Viscosity (SUS):		
At 210° F.	-----	32.8
At 100° F.	-----	47.2

Instead of the catalyst used above, other acidic catalysts, such as hydrogen chloride gas, concentrated hydrochloric acid, sulfuric acid, sodium acid sulfate, boron fluoride, and the like may be used. If the reactants are used in the vapor state, solid catalysts, such as aluminum oxide, silica gel, and the like may also be used. Operable temperature range would be from room temperature to about 500° F., with 190–300° F. being preferred. Although the reaction time used above was 6 hours, from 1 to 10 hours may be used, with from 1 to 6 hours being preferred.

It is to be recognized that the reactants are not limited to the materials described above, but that any acetal may be used with any formaldehyde donor. In general, the acetal chosen will be dependent upon the qualities desired in the final product, formals having from about 20 to 130 carbon atoms per molecule in branched chain configuration being generally desirable for use as synthetic lubricants.

Although the primary and most important use of the compositions prepared in accordance with the instant invention is for synthetic lubricants, these materials have a wide industrial application generally. They are suitable, for instance, as 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 as raw materials for many other industrial compositions. Although the invention is particularly described with reference to the acetals derived from the oxonation of olefins in the Oxo process, it will readily be understood that any acetal may be used in the new process.

The materials in the lubricating oil range that are prepared in accordance with the inventive concept are readily compatible with the various additive materials known to the art. For instance, such additives may be blended with the instant products to enhance special characteristics as oxidation inhibitors, viscosity index improvers, pour point depressants, and the like. Although these new synthetic materials are very useful as lubricants alone, they may also be blended with other lubricants, either naturally occurring mineral oils, or other synthetic lubricants such as other formals, silicone polymers, esters, ether esters, glycol ethers, alkylene oxide-alcohol condensation products, and the like. The new materials of the invention may also be converted to solid and semi-solid lubricants by the incorporation of any of the well-known thickening agents such as the grease forming soaps of metals and fatty acids.

Although the materials of invention may be purified by the methods described above, other methods may also be used, such as filtration through or contacting with alumina, fuller's earth, charcoal, and the like.

To summarize briefly, the instant invention relates to a new process for the preparation of compositions of matter. These materials have been found to be new synthetic lubricants and have outstanding properties of

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viscosity and viscosity-temperature relationship. The novel process comprises the steps of reacting acetals obtained on oxonation of olefins with carbon monoxide and hydrogen at high temperatures and pressures in the presence of a cobalt catalyst with formaldehyde to obtain a formal and an aldehyde. The formalization reaction is carried out at temperatures between room temperature to 500° F. for from 15 minutes to 10 hours, with temperatures of 190° to 300° F. and times of from 1 to 6 hours being especially preferred.

What is claimed is:

1. A new process for the preparation of compositions of matter in the lubricating oil range which comprises the steps of reacting an olefin polymer with carbon monoxide and hydrogen in the presence of a cobalt catalyst at temperatures in the range of from 200° to 400° F. and at pressures within the range of from 100 to 300 atmospheres to obtain a mixture of products, acidifying said mixture of products, raising the temperature of said acidified mixture to about 175° to about 300° F. for from one half to about 6 hours, distilling said heated mixture to recover therefrom the acetal component thereof, reacting said acetal component with formaldehyde at a temperature of about room temperature to about 500° F. for from 15 minutes to 10 hours, and separating and purifying the formal thus obtained.

2. A process according to claim 1 wherein there is added to the said mixture of products prior to acidification sufficient alcohol or aldehyde to make up a material balance.

3. A new process for the preparation of compositions of matter having ASTM pour points below about 35° F., flash points in excess of about 300° F., and kinematic viscosities at 210° F. between about 2 and about 60 centistokes, which comprises the steps of reacting a C<sub>2</sub>-C<sub>18</sub> olefin with carbon monoxide and hydrogen in the presence of the cobalt catalyst at temperatures in the range of from 200° to 400° F. and at pressures within the range of from 100 to 300 atmospheres to obtain a mixture of products, acidifying said mixture of products, raising the temperature of said acidified mixture to about 175° to about 300° F. for from ½ to about 6 hours, distilling said heated mixture to recover therefrom the acetal component thereof, reacting said acetal component with formaldehyde at a temperature of from about room temperature to about 500° F. for from 15 minutes to 10 hours in the presence of a catalyst and separating and purifying the desired composition of matter thus obtained.

4. A new process for the preparation of compositions of matter having ASTM pour points below about 35° F., flash points in excess of about 300° F., and kinematic viscosities at 210° F. between about 2 and about 60 centistokes, which comprises the steps of reacting a C<sub>2</sub>-C<sub>18</sub> olefin with carbon monoxide and hydrogen in the presence of the cobalt catalyst at temperatures in the range of from 200° to 400° F. and at pressures within the range of from 100 to 300 atmospheres to obtain a mixture of products, adding to said mixture of products a material of the class consisting of aliphatic alcohols and aliphatic aldehydes to obtain a material balance, acidifying the resulting mixture, raising the temperature of said acidified mixture to about 175° to about 300° F. for from ½ to about 6 hours, distilling said heated mixture to recover therefrom the acetal component thereof, reacting said acetal component with formaldehyde at a temperature of from about room temperature to about 500° F. for from 15 minutes to 10 hours in the presence of a catalyst and separating and purifying the desired composition of matter thus obtained.

5. A new process for the preparation of compositions of matter having ASTM pour points below about 35° F., flash points in excess of about 300° F., and kinematic viscosities at 210° F. between about 2 and about 60 centistokes, which comprises the steps of reacting a

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C<sub>2</sub>-C<sub>18</sub> olefin with carbon monoxide and hydrogen in the presence of the cobalt catalyst at temperatures in the range of from 200° to 400° F. and at pressures within the range of from 100 to 300 atmospheres to obtain a mixture of products, acidifying said mixture of products, raising the temperature of said acidified mixture to about 175° to about 300° F. or from ½ to about 6 hours, distilling said heated mixture to recover therefrom the acetal component thereof, reacting said acetal component with formaldehyde at a temperature of from about 190° to about 300° F. for from 1 to 6 hours in the presence of toluene sulfonic acid as a catalyst and separating and purifying a composition of matter having from about 20 to about 130 carbon atoms per molecule.

6. A process according to claim 5 wherein said olefin 15

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contains from about 6 to about 18 carbon atoms per molecule.

7. A process according to claim 5 wherein said olefin is an olefin copolymer of propylene and butylene having 7 carbon atoms.

8. A process according to claim 3 wherein said olefin is a polymer of propylene and contains 9 carbon atoms.

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