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PROCESS FOR PREPARATION OF COMPLEX FORMAL SYNTHETIC LUBRICANTS BY A FORMAL INTERCHANGE

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This invention relates to synthetic lubricating oil compositions. Particularly, the invention relates to synthetic lubricating compositions of the complex formal type and to an improved process for their preparation. Still more particularly, the invention relates to a process for preparing complex formals in the synthetic lubricating oil range by a one-step process of formal interchange. The concept of the invention contemplates a formal interchange between a simple formal of the type

$$R—O—CH_2—O—R'$$

wherein R and R' are C_4 to C_{26} alkyl radicals with a glycol in the presence of a catalyst.

In recent efforts to obtain superior lubricating compositions which have unusual and specific properties, there have been developed entirely new synthetic materials with lubricating properties. In general, these new synthetic lubricants are characterized by viscosity properties that are outstanding at both low and high 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 lubricating 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 he 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 a corresponding increase in lubricant life, increased power factor from fuel, and a general overall improvement in engine operation.

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 below about +20° F. has sufficient low temperature lability to make it satisfactory in these respects for general use. 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 30 and 110 Saybolt seconds, Universal. To prevent undue lubricant loss, due to volatility and general molecular disintegration and to insure against explosion hazards

at higher temperatures sometimes encountered, a lubricating composition should have a flash point in excess of about 350° F. These requisites are inherent in the term "lubricating compositions," as used in this specification, and the formals prepared by the process of this invention are limited to those within these operable ranges. 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 35 to 70 Saybolt seconds, Universal at 210° F. It has been found that formals having between about 20 to 130 carbon atoms are useful as synthetic lubricants and particularly between about 25 and 100 carbon atoms. The materials prepared in accordance with the inventive concept are within this range.

As was stated above, the instant improved process for the preparation of complex formal synthetic lubricants involves a simple formal interchange procedure in the presence of a suitable catalyst. In this improved process a glycol or glycol reactant is admixed with a simple formal and subjected to the proper conditions of temperature and pressure to effect a removal of the desired interchanged material. This simplified one-step procedure may eliminate time-consuming and costly washing procedures and subsequent neutralization steps which have hitherto been found necessary in the preparation of materials of this type. The catalysts that are operable and the preferred conditions of temperature and pressure are set out more in detail below. In order to more explicitly illustrate the inventive process, the following detailed examples are given:

EXAMPLE I

One molecular proportion of isooctyl formal was admixed with one molecular proportion of triethylene glycol in a one-liter distillation flask. Toluene sulfonic acid (0.5 wt. percent) was added as the catalyst. The mixture was heated at 25 mm./Hg until about one mol of isooctyl alcohol was evolved (B. P. 90°–112° C./25 mm./Hg). This amount of alcohol was evolved in about 90 minutes of heating time.

The product obtained was submitted to the standard inspection tests for synthetic lubes and the data is set out in Table I below.

EXAMPLE II

A mixture of 4 mols of isooctyl formal, one mol of triethylene glycol, and 0.25 wt. percent of toluene sulfonic acid was heated for 4 hours at 30 mm./Hg pressure. Two mols of isooctyl alcohol was removed overhead, having a boiling point of 90°–100° C. at this pressure. The product was washed with caustic and again with water.

The material was then stripped to a temperature of 210° C. at 8 mm./Hg pressure and the resulting product submitted to the standard inspection tests. Data obtained are set out in Table I below.

EXAMPLE III

A mixture of two mols of isooctyl formal and one mol of triethylene glycol was heated at 30 mm./Hg pressure for 3 hours. No catalyst was used in this preparation. At the end of the three-hour heating period, the product was stripped to a liquid temperature at 210° C. at 0.05 mm./Hg pressure.

The product obtained had the properties set out in Table I below.

EXAMPLE IV

Two mols of triisodecyl formal, one mole of tetraethylene glycol, and 0.4 wt. percent of toluene sulfonic acid was heated for three hours at 8 mm./Hg pressure. 1.7

mols of triisodecyl alcohol was distilled overhead at 122°–129° C.

The product was washed with caustic and then with water. After washing, the material was stripped to a liquid temperature of 210° C. at 8 mm./Hg pressure. The final product had the properties set out in Table I below.

EXAMPLE V

One mol of isodecyl formal, one mol of tetraethylene glycol, and 0.5 wt. percent of sodium acid sulfate were heated for one hour at 30 mm./Hg pressure. 0.5 mol of isodecyl alcohol was removed overhead (B. P. 116°–135° C./30 mm./Hg). The product was washed with caustic and with water and stripped to a liquid temperature of 185° C. at 6 mm./Hg pressure. The resulting material had the properties set out in Table I below.

EXAMPLE VI

Two mols of isodecyl formal, one mol of tetraethylene glycol and 0.5 wt. percent of toluene sulfonic acid were heated for one hour at 25 mm./Hg pressure. One mol of isodecyl alcohol was removed (B. P. 110°–112° C./25 mm./Hg). This material was caustic washed and then water washed. After stripping to a liquid temperature of 220° C. at 5 mm./Hg pressure, the product had the properties set out in Table I below.

EXAMPLE VII

A glycol of the type formula triethylene glycol (formal-triethylene glycol)$_2$, that is,

$$HO—(C_2H_4O)_3—[CH_2O—(C_2H_4O)_3]_2—H$$

was prepared as follows:

2253 grams (15 mols) of triethylene glycol, 330 grams of paraformaldehyde, equivalent to 11 mols of formaldehyde (10% excess), 200 grams hexane, and 11.2 grams sodium acid sulfate catalyst were heated (refluxed) to a maximum temperature of 108° C. over a period of 7 hours to give 2453 grams (5 mols) of the triethylene glycol formal-hexane mixture exclusive of the water of reaction and the catalyst.

245 grams (½ mol) of this complex glycol formal-hexane mixture was heated with 373 grams (1 mol) of a C_{10} Oxo alcohol formal in the presence of 3.5 grams of sodium acid sulfate as a catalyst. The maximum temperature during the 9 hours heating period was 165° C. The material obtained was filtered and divided into two 284 gram portions A and B.

Portion A was stripped to a liquid temperature of 230° C. at 0.5 mm./Hg. 190 grams of distillate was obtained overhead, leaving as a product 80 grams of a material having the properties set out in Table I below.

Portion B was diluted with 200 grams of hexane and washed with saturated sodium carbonate solution. This washing was followed by a water wash and by a sodium chloride solution wash. After the washing steps, the product was filtered and stripped to a liquid temperature of 200° C. at 0.1 mm./Hg pressure. 119 grams of a material was obtained which had the properties set out in Table I below.

An examination of the data of Examples I–VII shows that the process of this invention may be used to prepare complex formal synthetic lubricants which have excellent properties, making them especially suitable for use as lubricating oil bases or components.

The glycol reactant which is operable in the improved process of this invention may be selected from a large number of materials. Exemplary are glycols of the formula HO—R—OH wherein R is an alkyl group containing from about 2 to about 30 carbon atoms. The glycol reactant may be of branched or straight chain configuration. For instance, polyalkylene glycols, the butane diols, the pentane diols, are operable as are the substituted diols such as 2-alkoxymethyl-2,4-dimethyl pentanediol-1,5. In the preferred embodiment of this invention, polyalkylene glycols are contemplated which have the formula $HO(C_nH_{2n}O)_yH$ wherein n and y are numbers of from 1 to 6. Particularly preferred are the polyalkylene glycols of the formula wherein n is 2 and wherein y is a number of from 2 to 6.

The formal component of the improved process is prepared by reacting two mols of the desired alcohol with formaldehyde or a formaldehyde donor in the presence of a suitable catalyst. Other operable conditions are temperatures in the order of 50° to 225° C. and pressures ranging from about 250 to about 1 mm./Hg.

The formals may also be prepared by reacting a molar proportion of the desired alcohol with formaldehyde or a formaldehyde donor in the presence of hydrogen chloride to produce a chloromethylether. One mol of the chloromethylether so formed is then further reacted with a mol of an alcohol to give the desired formal liberating a mol of hydrogen chloride. The formals operable in the invention have the generic formula

$$R'—O—CH_2—O—R''$$

wherein R' and R'' are alkyl groups of the reacting alcohol and contain from about 4 to about 26 carbon atoms.

Particularly preferred are the formals of the highly branched chain primary alcohols obtained by carbonylation and hydrogenation of olefins in the Oxo process. These alcohols are well known to the art and are generally referred to as "Oxo" alcohols.

As was stated above, the final complex formal will contain from about 20 to about 130 carbon atoms, preferably 25 to 100 carbon atoms, and the initial reactants will be chosen so as to obtain a product having the desired structure and carbon chain composition.

Although in the examples given as illustrative, toluene sulfonic acid and sodium acid sulfate were used as catalysts, it is to be understood that any of the commonly known esterification catalysts may be employed in the process of this invention, for instance, such catalysts as sodium acid sulfate, p-toluene sulfonic acid, sulfosalicyclic acid, phosphoric acid, etc. Ordinarily, from about 0.2 wt. percent to about 1.0 wt. percent of the catalyst is sufficient, with from 0.3 to 0.5 wt. percent being preferred. The percentage of catalyst used is based on the weight of the total composition.

The proportions of the complex formal and the formal which are used in the improved process will depend

Table I.—Complex formal synthetic lubricants

	Ex. I	Ex. II	Ex. III	Ex. IV	Ex. V	Ex. VI	Example VII	
							Portion A	Portion B
Viscosity (SUS):								
210° F.	126	37.8	52.4	41.3	40.7	48.2	254	44.0
100° F.	785	67.8	167.7	107.7	103.0	146.4	1850	121.0
0° F.	53,000	965	4,850	3,900	3,350	4,850		4,010
Viscosity Index	139	172	161	140	108	160	132	156
Pour Point, (° F.)	<−35	<−35	<−35	−70	<−75	−65	−25	−70
Flash Point, (° F.)	>425	370	370	395	370	405	>425	375
Acid No. (mg.KOH/g.)	1.9	0.6	0.7	0.3	0.2	0.3	0.40	0.4
Hydroxyl No. (mg.KOH/g.)	47	8.0	6.6	23	105	17		47

somewhat upon the desired final product. Satisfactory synthetic lubricating oils may be obtained by utilization of from 2 to 12 mols of a formal with from about 1 to 6 mols of a glycol reactant.

The temperatures and pressures utilized in the process of this invention may vary between about 50° and 250° C. and from about 0.1 to about 760 mm./Hg. Preferred operating conditions are from 90° to 190° C. and from 5 to 30 mm./Hg. The time of the reaction will be dependent upon the product desired but ordinarily the theoretical quantity of displaced alcohol will be distilled overhead in from about 1 to about 3 hours.

As was stated above and as is shown by the examples, the time-consuming and expensive washing procedures may be eliminated by the process of this invention. However, outstanding synthetic lubricants are obtained by finishing the product with a caustic wash usually followed by a water wash and/or a wash with a salt solution.

The desired viscosity is obtained by stripping the reaction product to remove materials of lower viscosity and lower boiling points. Although the stripping conditions will depend on the final product desired, liquid temperatures of from about 150° to about 200° C. at 0.5 to 10 mm./Hg pressure have been found to result in synthetic lubricants of the desired properties.

The synthetic lubricants prepared by the inventive process are compatible with various additive materials with which the art is familiar. Particularly, viscosity index improvers, pour point depressants, sludge dispersants, oxidation inhibitors and the like may be blended with these formals to enhance special properties thereof.

To summarize briefly, the instant invention relates to an improved process for the preparation of complex formal type synthetic lubricants. Improved process comprises the steps of mixing from about 1 to 6 mols of a glycol reactant with from about 2 to 12 mols of a formal in the presence of from 0.2 to 1.0 wt. percent of a catalyst and subjecting the mixture to a temperature of from about 50° to 200° C. and at a pressure of from about 250 to 1 mm./Hg. The reaction is carried out until theoretical alcohol is removed overhead and the product is stripped to a liquid temperature of about 200° C. at a pressure of about 0.5 to 10 mm./Hg. If desired, the product, prior to the stripping step, may be caustic washed followed by other washing steps, although this procedure is not necessary. The preferred glycols have the formula $HO(C_nH_{2n}O)_yH$ wherein n and y are numbers of from 1 to 6, preferably 2 to 6. The preferred formal has the formula $R—O—CH_2—O—R'$ wherein R and R' are alkyl groups having from 4 to 26 carbon atoms, preferably from 6 to 18 carbon atoms. The highly branched chain alkyl groups of the well-known Oxo alcohols are particularly desirable.

What is claimed is:

1. In a process for the preparation of complex formal lubricating compositions having an ASTM pour point below about +20° F., a viscosity at 210° F. of between 30 and 110 S. U. S. and a flash point above about 350° F., by reacting a formal of the formula

$$R—O—CH_2—O—R'$$

wherein R and R' are alkyl groups containing from about 4 to 26 carbon atoms with a glycol at a temperature within the range of about 50° to 250° C. for about 2 to 20 hours, and recovering a complex formal having from about 20 to 130 carbon atoms per molecule, the improvement which comprises reacting said formal with said glycol in the molar ratio of about 2 to 4 moles of formal to 1 mole of glycol.

2. In a process for the preparation of complex formals containing 20 to 130 carbon atoms, having ASTM pour points below about +20° F., flash points above about 350° F., and viscosities at 210° F. within the range of from about 30 to about 110 S. U. S., by reacting a formal of the formula $R—O—CH_2—O—R'$ wherein R and R' are alkyl groups containing about 6 to 18 carbon atoms, with a glycol having the formula $HO(C_2H_4O)_yH$ wherein y is a number of 2 to 6, at a temperature of about 90 to 190° C. under pressures of about 0.1 to 760.0 mm./Hg, for about 2 to 20 hours in the presence of an acid catalyst and stripping the reaction product to recover said complex formals, the improvement which comprises reacting said formal with said glycol in the molar ratio of 2 to 4 moles of formal per mole of glycol.

3. A process according to claim 2 wherein R and R' contain 8 carbon atoms and wherein y is 4.

4. A process according to claim 1 wherein said glycol is prepared by reacting 15 mols of triethylene glycol with paraformaldehyde in an amount equivalent to 11 mols of formaldehyde.

5. A process according to claim 2 wherein R and R' are the alkyl radicals of highly branched chain alcohols having from 6 to 18 carbon atoms obtained by carbonylation and hydrogenation of olefins in the Oxo process.

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