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SYNTHETIC LUBRICATING OIL

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This invention relates to a new class of compounds which have been found to be particularly suitable for use as synthetic lubricants because of their low pour point, high viscosity index and unusually good load carrying properties. These compounds have also been found to be useful as addition agents for mineral lubricating oils, in which they serve as improvers of the load carrying properties of the same.

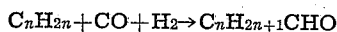
In the lubricant art, considerable progress has been realized in recent years in the production of lubricants characterized by one or more specific properties and adapted for particular uses. In the main, this progress can be attributed to two developments: the first, new refining procedures, and the second, addition agents capable of imparting particular properties to available lubricants. Thus, viscosity index improvers and pour depressants are added to automotive lubricants to render the lubricants more adaptable to wide changes in temperature conditions, while other agents are added to improve the load carrying properties of a lubricant which is to be employed, for example, under extreme pressure conditions.

Recently, in an effort to obtain superior lubricants endowed with specific and superior characteristics, a new field has been explored, namely, the synthesis of lubricants from various materials. Esters represent one class of materials which have attracted unusual interest as synthetic lubricants. In general, they are characterized by higher viscosity indices and lower pour points than mineral oils of corresponding viscosity. The esters described in the present specification have been found to exhibit very low pour points, high viscosity indices and, in addition, unusually good load carrying properties. Lubricants possessing such properties are of special value in the lubrication of engines which are subjected to high temperatures such as combustion turbine engines, particularly those of the "prop-jet" type. Mineral oil lubricants containing added viscosity index improvers, thickeners or other highly non-volatile additives are undesirable for use in such engines because of the tendency to leave a residue which would accumulate and interfere with the operation of the engine. A synthetic lubricant of the type described in the present specification is especially adapted to use under such conditions, since the lubricant contains no additives and thus tends to leave no residue upon volatilization.

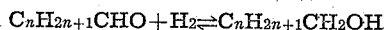
The new compounds of the present invention, adapted particularly for use as synthetic lubricants, comprise a new class of trialkyl phosphates, in which the alkyl groups contain 8 to 20 carbon atoms each and may be alike or different and are

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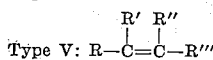
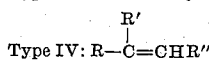
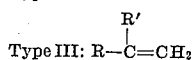
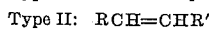
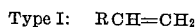
of branched chain structure, being derived from a primary monohydric aliphatic alcohol obtained as a product of the "Oxo" synthesis. The Oxo process may be described as the catalytic reaction of mono-olefins with carbon monoxide and hydrogen at a temperature of 300-350° F. and under a pressure of about 3000 lbs./sq. in. to form aldehydes and the subsequent hydrogenation of the aldehydes to form primary alcohols. This process was first developed in Germany and first described in this country in the Roelen U. S. Patent 2,327,066, granted August 17, 1943. Cobalt catalysts are employed in the reaction of the olefin with carbon monoxide and hydrogen, and conventional hydrogenation catalysts are employed for the reduction of the aldehydes. In the presence of the cobalt catalyst, one mol of olefin reacts with one mol of carbon monoxide and one mol of hydrogen to form an aldehyde containing one more carbon atom per molecule than the olefin, according to the reaction:



The aldehydes thus formed may be hydrogenated to the corresponding primary alcohols, according to the reaction:



In the present specification a number of different types of olefins will be referred to, and for convenience these may be defined by the following formulas, in which R, R', etc., represent alkyl radicals:



In the reactions of the Oxo process, described above, there is no invariable point of attack on the olefinic double bond, and in the case of reactions with Type I olefins both normal and iso-alcohols are formed. However, with all of the other types of olefins defined above branched chain alcohols greatly predominate in the products. For the production of esters having properties which make them suitable for use as lubricating oils it is desirable to employ alcohols which are chiefly of a branched chain structure, and accordingly it is desirable to employ as starting materials olefins or olefin mixtures which contain

not more than 20% of Type I olefins having a straight chain hydrocarbon radical. Except for this limitation the olefins may be of any type, provided they are essentially of chain length from C₇ to C₁₉, which will produce alcohols of the C₈ to C₂₀ range.

For the commercial production of Oxo alcohols useful in accordance with the present invention a large variety of olefin-containing commercial products may be employed. For example, a C₇ fraction isolated from the product of the polymerization of propylene or a mixture of C₃ or C₄ olefins may be employed in the production of C₈ Oxo alcohols, since the fraction contains no more than a trace of diolefins and the unsaturated hydrocarbon content of the same consists almost entirely of monoolefins, largely tertiary. Diisobutylene, produced by the cold acid polymerization of isobutylene, may be employed in the production of C₉ Oxo alcohols. For the production of alcohols having 12 to 14 carbon atoms a convenient source of olefins is a Fischer synthesis product, boiling above about 350° F., which, after treatment with bauxite, contains about 50% of mono-olefins of which not more than a trace consists of Type I straight chain olefins. This product may be fractionated to narrow the range of carbon content in the alcohol product.

The alcohols formed by applying the Oxo process to the olefinic materials described above will naturally consist of complex mixtures, and the exact composition of many of these products is not known. The C₈ Oxo alcohols obtained from the propylene polymers described above have been found to comprise a mixture of isomers having, on the average, two alkyl side groups along a carbon chain 4 to 6 carbon atoms in length. The Oxo nonyl alcohol product formed from commercial diisobutylene prepared by the cold acid polymerization of isobutylene consists of 3,5,5-trimethylhexanol-1, 2-isopropyl-3,3-dimethylbutanol-1, and 2,2,4,4-tetramethylpentanol-1.

The phosphate esters of the present invention may be conveniently prepared by contacting about three molecular proportions of a suitable Oxo alcohol or mixture of Oxo alcohols with one molecular proportion of phosphorus oxychloride in the presence of a suitable medium such as benzene. When phosphorus oxychloride is employed it may be desirable to have present a

were prepared by methods which have been described above. C₈ Oxo alcohol, for example, was prepared from a C₇ fraction of a product of the polymerization of C₃ and C₄ olefins. The olefinic content of this fraction consists of not more than 4% of Type I olefins. The C₉ Oxo alcohol was prepared from commercial diisobutylene consisting of about 80% of Type III and 20% of Type IV olefins and the alcohols derived therefrom consisted of three isomers as explained above. The C₁₁ to C₁₄ alcohols were obtained from fractions of Fischer synthesis products which had been submitted to treatment with bauxite at 850°-950° F., the rate of flow being 1 to 6 v./v./hour. The C₁₁ to C₁₂ Oxo alcohols were obtained from a fraction boiling at 300-350° F., the C₁₂ to C₁₃ alcohols from a fraction boiling at 350-400° F., and the C₁₃ to C₁₄ alcohols from a fraction boiling at 400-450° F.

In the following table are shown a number of properties of the Oxo alcohols employed in preparing the esters:

	C ₈	C ₉	C ₁₁₋₁₂	C ₁₂₋₁₃	C ₁₃₋₁₄
Hydroxyl No.....	408	373	317	260	269
Carbonyl No.....	4	4	7	7	1
Saponification No.....	13	11	8	19	8
Acid No.....	0.2	0.1	0.3	0.1	0.06

The above described alcohols were each reacted with phosphorus oxychloride to form phosphate esters, the following procedure being followed in each case: A mixture of one gram mol of the alcohol, 1.1 gram mols of pyridine, and 92 ml. of benzene was cooled to -5° C., and then 51.1 g. (1/3 mol) of POCl₃ was dropped in at such a rate that the temperature did not exceed 10° C. When the addition was complete, the mixture was refluxed for two hours, after which 150 ml. of water was added and the benzene layer separated. The latter was washed several times with water or with dilute aqueous alkali until it was neutral. After drying over a desiccant such as Drierite (anhydrous CaSO₄), the solvent was distilled off at 5 mm. pressure and a bath temperature of 200-225° C. (In this process an excess of alcohol may be employed if desired.)

In the table below are shown properties of the phosphate esters, prepared as described above, which indicate their particular suitability for use as synthetic lubricants.

Alcohol Reacted with POCl ₃	ASTM Pour Point (° F.)	Kinematic Viscosity		ASTM Slope	Viscosity Index	Almen Machine Weights Carried (Gradual Loading)	
		100° F.	210° F.			Alone	6% in Mineral Oil ¹
C ₈ Oxo.....	<-35	20.060	4.478	0.687	156	15	15
C ₉ Oxo.....	<-35	15.990	3.770	0.711	146	12	15
C ₁₁ -C ₁₂ Oxo.....	<-35	38.700	6.950	0.658	140	15	13
C ₁₂ -C ₁₃ Oxo.....	<-35	40.230	7.322	0.643	142	15	13
C ₁₃ -C ₁₄ Oxo.....	<-35	110.2	14.220	0.613	126	15	5

¹ Conventionally refined Coastal naphthenic oil of 42 seconds Saybolt viscosity at 210° F. The unblended mineral oil carried only two weights on the Almen machine.

basic substance such as pyridine to absorb the hydrogen chloride produced in the reaction. A typical method suitable for preparing any of the compounds of the present invention will be described in detail below.

Data will be given below showing properties of five typical examples of trialkyl phosphates illustrating the present invention. The alcohols employed in the preparation of these esters

The above data indicate that the materials tested possess an uncommonly low pour point, high viscosity index and high load-carrying characteristics, and since these materials have a viscosity within the lubricating oil range they are of particular interest as synthetic lubricants. In addition to the use of these materials along as synthetic lubricants, they are valuable for improving the film strength and oiliness proper-

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ties of mineral oils with which they are blended. For this purpose, they are preferably blended in proportions ranging from 1% to 10% by weight of the mineral oil. The data in the last column of the above table show the usefulness of these compounds when blended with a mineral oil. The unblended mineral oil employed in these tests was capable of carrying only two weights on the Almen machine under similar conditions of test.

The mineral lubricating oil base stocks which may be improved in load-carrying capacity by the addition of the new compounds of the present invention may be derived from the various types of crude petroleum and many consist of distillates or blends of various kinds which have been refined by any of the conventional methods. Synthetic oils may also be used, such as those obtained by the polymerization of olefins or by the hydrogenation of coal or its products. The base oils may vary considerably in viscosity and other properties depending upon the particular use for which they are desired.

If desired, other known addition agents, such as thickeners, pour depressants, antioxidants, dyes, etc., may be added to the mineral oil composition prepared in accordance with the present invention.

The above described esters are also useful as plasticizers for synthetic resins, e. g., of the polyvinyl chloride or vinyl chloride-vinyl acetate copolymer type, and for synthetic rubbers, e. g., of the Buna N type.

What is claimed is:

1. A synthetic lubricating oil having an ASTM pour point below about -35° F., a viscosity index above about 125, a viscosity at 210° F. of at least 3.0 centistokes and a flash point of at least 450° F., said oil consisting predominantly of C_8 to C_{14}

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highly branched trialkyl esters of phosphoric acid, the ester portions of said phosphoric acid esters being derived from a primary monohydric alcohol boiling below about 450° F. which is obtained by Oxo synthesis wherein there is employed as the olefinic substance a hydrocarbon material whose olefin content consists of not more than 20% by weight based on the total olefin of an olefin of the type $RHC=CH_2$ where R is a straight chain saturated aliphatic hydrocarbon radical.

2. A composition according to claim 1 in which the alkyl groups are C_8 groups.

3. A composition according to claim 1 in which the alkyl groups are derived from a C_9 Oxo alcohol obtained by Oxo synthesis from diisobutylene.

4. A composition according to claim 1 in which the alkyl groups are derived from a C_{12} - C_{13} Oxo alcohol.

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