PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Synthetic Lubricating Oils

We, Standard Oil Development Company, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

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 of branched chain structure, which are derived from primary monohydric aliphatic alcohols obtained as 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. 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 pre-

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sence 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:

$$C_nH_{2n} + CO + H_2 \rightarrow C_nH_{2n+1}CHO$$

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

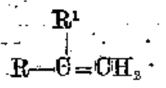
$$C_nH_{2n+1}CHO + H_2 \rightleftharpoons C_nH_{2n+1}CH_2OH$$

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^1, R^{11}, R^{111}, represent alkyl radicals:

Type I: $RCH=CH_2$

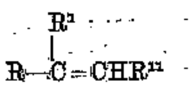
Type II: $RCH=CHR^1$

Type III:



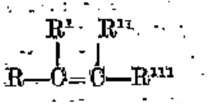
$$R-\overset{\overset{\displaystyle R^1}{|}}{C}=CH_3$$

Type IV:



$$R-\overset{\overset{\displaystyle R^1}{|}}{C}=CHR^{11}$$

Type V:



$$R-\overset{\overset{\displaystyle R^1}{|}}{C}=\overset{\overset{\displaystyle R^{11}}{|}}{C}-R^{111}$$

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 C_7 to C_{10}, which will produce alcohols of the C_8 to C_{20} 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 C_7 fraction isolated from the product of the polymerization of propylene or a mixture of C_3 or C_4 olefins may be employed in the production of C_8 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 mono-olefins, largely tertiary. Diisobutylene, produced by the cold acid polymerization of isobutylene, may be employed in the production of C_9 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 C_8 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. Under these conditions it may be desirable to have present a 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 were prepared by methods which have been described above. C_8 Oxo alcohol, for example, was prepared from a C_7 fraction of a product of the polymerization of C_3 and C_4 olefins. The olefinic content of this fraction consists of not more than 4% of Type I olefins. The C_9 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 C_{11} to C_{14} 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 C_{11} to C_{12} Oxo alcohols were obtained from a fraction boiling at 300—350°F., the C_{12} to C_{13} alcohols from a fraction boiling at 350—400°F., and the C_{13} to C_{14} 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 ester, 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 $POCl_3$ 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 desicant such as Drierite (anhydrous $CaSO_4$), 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*
C_8 Oxo	$\leqslant 35$	20.060	4.478	0.687	156	15	15
C_9 Oxo	$\leqslant 35$	15.990	3.770	0.711	146	12	—
C_{11}—C_{12} Oxo	$\leqslant 35$	38.700	6.950	0.658	140	15	15
C_{12}—C_{13} Oxo	$\leqslant 35$	40.230	7.322	0.643	142	15	13
C_{13}—C_{14} Oxo	$\leqslant 35$	110.2	14.220	0.613	126	15	5

* 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.

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 alone as synthetic lubricants, they are valuable for improving the film strength and oiliness properties 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 may 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 alloys 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. Buna is a Registered Trade Mark.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of preparing compositions suitable for use as lubricants or as additions to lubricants comprising reacting one molecular proportion of phosphorus oxychloride with three molecular proportions of a branched chain alcohol having from 8—20 carbon atoms in the molecule or a mixture of such alcohols obtained by the process of reacting carbon monoxide and hydrogen in the presence of a catalyst and an olefin or mixture of olefins containing from 7 to 19 carbon atoms per molecule and hydrogenating the resulting aldehyde.

2. A method as claimed in claim 1 wherein the alcohols contain from 8—14 and preferably 12 or 13 carbon atoms in the molecule.

3. A mtehod as claimed in claim 1 or 2 wherein the olefine is present in a hydrocarbon mixture containing olefines and of which not more than 20% are straight chain α olefins.

4. A method as claimed in any of claims 1—3 wherein the olefine is an olefine derived from the polymerization of a mixture of olefines containing 3 and 4 carbon atoms in the molecule.

5. A method as claimed in any of claims 1—4 wherein the olefine is diisobutylene.

6. A method as claimed in any of claims 1—6 wherein the olefine comprises a hydrocarbon fraction boiling from 300—500°F. obtained by the Fischer synthesis process from a mixture of carbon monoxide and hydrogen and containing olefines having from 10 to 13 carbon atoms in the molecule.

7. A method as claimed in any of the preceding claims wherein the reaction between the alcohol and the phosphorus oxychloride is carried out in the presence of a basic substance precerably pyridine to neutralize the hydrochloric acid liberated during the reaction.

8. Compounds suitable for use as lubricants or additions to lubricants comprising trialkyl esters of phosphoric acid having alkyl groups each containing from 8—20 carbon atoms when prepared by the methods claimed in any of claims 1—7.

9. A lubricant comprising a mineral oil and a trialkyl phosphate having branched chain alkyl groups that are residues of "oxo" alcohols each containing from 8 to 20 and preferably from 8—14 particularly 12 or 13 carbon atoms in the group.

10. A lubricant composition as claimed in claims 8 or 9 wherein the trialkyl phosphate is prepared by the method claimed in any of claims 1—8.

11. A lubricant composition as claimed in any of claims 8—10 wherein the quantity of the trialkyl phosphate used is from 1—10% by weight of the mixture.

Dated this 13th day of September, 1949.

J. T. TYSON.
Brettenham House, 6th Floor,
South Block, Lancaster Place,
London, W.C.2.
Agent for the Applicants.

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