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The present invention relates to organic materials useful as synthetic lubricants and for various other purposes. More specifically, the invention pertains to improved synthetic materials having excellent lubricating and plasticizing properties and to methods for making these materials. In its broadest aspect, the invention provides for the manufacture of lubricants and other valuable materials, such as plasticizers for resins, rubbers, etc. on the basis of certain organic carbonates having the general formula $RO-CO-OR'$.

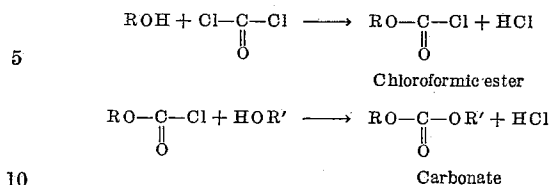
Prior to the present invention it has been suggested to use certain synthetic oils, particularly certain esters of dibasic aliphatic acids as an oil constituent for greases, engine oils, extreme pressure lubricants and related materials. While lubricants prepared on the basis of these esters have highly desirable lubricating qualities as well as excellent high and low temperature characteristics, many of these esters are easily hydrolyzed. In addition, the field of available raw materials is rather limited. In view of the rapidly increasing demand for synthetic lubricating oils in many fields, a broadening of the raw material basis is highly desirable. Similar conditions prevail in the field of plasticizers and related materials.

It has now been found that certain organic carbonates may be substituted for low boiling mineral oil fractions and synthetic oils of the type described above in the production of lubricants, plasticizers and for various other uses. These carbonates have excellent lubricating qualities and combine relatively high boiling points with desirably low pour points, high flash points, low viscosity-temperature coefficients and high chemical stability.

Organic carbonates may be prepared by contacting phosgene with a suitable alcohol at temperatures of about 260° to 350° F. Phosgene may either be bubbled through the alcohol maintained at reaction temperatures or the phosgene may be dissolved in a solvent, such as toluene, and the alcohol added to the solution maintained at reaction temperatures, preferably in the presence of a base, e. g. a tertiary amine such as trimethyl or triethylamine, dimethylaniline, pyridine or an inorganic base such as alkali metal hydroxides or carbonates.

The process may be carried out in stages as follows. The chloroformic ester of the alcohol used may first be formed by adding 1 mol of alcohol to 1 mol of phosgene as described above. Thereafter, 1 mol of the same or of a different alcohol may be added to this chloroformic ester, preferably in the presence of a base to form a

simple or mixed carbonate depending on the character of the second alcohol. The equation is as follows:



The organic carbonates which may be used for the purposes of the invention have the general formula $\text{RO}-\text{CO}-\text{OR}'$ wherein R and R' are hydrocarbon radicals having at least 8 carbon atoms. While this broad group of compounds has utility in the fields of synthetic lubricants and plasticizers, those representatives of the group which have pour points below -20°F. and flash points above 300°F. have been found to be most suitable as lubricating oil bases in general and for the production of low temperature greases in particular.

In accordance with the preferred embodiment of the invention, the carbonates used have branched-chain hydrocarbon radicals R and R', each radical containing at least 8 carbon atoms. These compounds may be obtained by reacting phosgene with branched-chain monohydric or polyhydric alcohols in the manner described above. Examples of such carbonates are those derived from 6-methyl-1-heptanol, 2-n-propyl-1-pentanol, 3-n-propyl-1-hexanol, 2,2-dimethyl-1-octanol, 10,10-dimethyl-1-undecanol, 3-isopropyl-1-heptanol.

However, it has further been found that good results are consistently obtained when using a group of new carbonates which are derived from the product or by-product alcohols of the well known "Oxo" synthesis. This process involves the catalytic reaction of olefins with carbon monoxide and hydrogen at elevated temperatures of about 300°–400° F. and pressures of about 2500 to 4000 p. s. i. g. to form, particularly in the presence of cobalt catalysts, aldehydes having one carbon atom more than the olefin originally used. The aldehyde is catalytically hydrogenated to the corresponding alcohol which is recovered as overhead product by distillation of the reaction mixture. The distillation residue, i. e. the so-called "Oxo-bottoms," is rich in by-product alcohols of higher molecular weight.

While the exact composition of all these alcohols is not known, it is well established that they are mixtures of primary alcohols, at least a substantial proportion of which is of the branched-chain type. The overhead 50 alcohol product consists of a mixture of such alcohols averaging 1 carbon atom more than the olefin originally fed to the "Oxo" synthesis. It has been found that these alcohols may be reacted with phosgene as described above to produce new carbonates of the general type 55 defined above. Oxo-alcohol carbonates which have branched-chain hydrocarbon radicals containing at least 8, and preferably 10-20, carbon atoms each are preferred for the purposes of the present invention.

Novel carbonates having excellent properties for the purposes of the invention may be obtained by the re-

action of phosgene with Oxo-alcohols produced by reacting polymers and copolymers of C₃ and C₄ mono-olefins in the presence of oxonation catalysts as described above. Suitable mixtures of these mono-olefins are readily available in refinery gases and processes for their conversion into liquid copolymers are well known in the art. In accordance with the most widely used of these processes, the olefins are contacted in liquid phase with a polymerization catalyst comprising phosphoric acid supported on kieselguhr. Other similar processes use as catalyst silica gel impregnated with phosphoric acid, or sulfuric acid, Friedel-Crafts catalysts, activated clays, and others. Polymerization conditions in the presence of phosphoric acid catalysts include temperatures of about 300°–500° F. and pressures of about 250–5,000 p. s. i. g. The olefinic feed stocks normally contain about 15–60 mol percent of propylene, about 0.5–50 mol percent of butylenes and from 0.1–10 mol percent of isobutylene, the remainder being saturated hydrocarbons having 2–4 carbon atoms per molecule. In place of or together with these olefin mixtures the dimer and trimer of isobutylene as well as tri, tetra and penta propylene may be used.

The composition and structure of the C₈ Oxo-alcohols obtained from a mixture of C₇ olefins of the type described above and more specifically of C₇ olefins derived from a refinery gas stream containing propylene and mixed normal and iso-butylenes are now well understood. These Oxo-alcohols have the following analysis:

Structure of C ₈ Oxo-alcohols prepared from C ₃ -C ₄ copolymer heptenes	Percent
	29.35
	25
	17.40
	16
	45
	2.3
	50
	1.4
2-alkyl-alkanols	4.3
Others	5.0
Total	100.0

Other Oxo-alcohols are believed to have compositions generally analogous to that specified above, chain lengths and degree of branching depending on the type of olefins used. It is noted in this respect that even when pure straight-chain olefins are used as the starting materials, the alcohols obtained consist predominantly of branched-chain compounds.

Examples of carbonates having utility as lubricating oil bases, plasticizers, etc. are tabulated below together with some of their more important characteristics.

Carbonate of—	Pour, °F.	Flash, °F.	Viscosity in centistokes at—	
			210° F.	100° F.
C ₁₀ Oxo alcohol	–75	355	2.43	9.27
C ₁₂ Oxo alcohol	–70	410	4.32	23.8
C ₁₄ Oxo alcohol	–40	455	8.32	78.6

The addition of some polymers improves the viscosity of the Oxo carbonates as shown in the table below.

	Viscosity kinematic Saybolt at—		
	100° F.	210° F.	–40° F.
C ₁₂ Oxo Carbonate+0.5% polyacrylate ester (mol. wt. 6,000–10,000)	120.7	41.2	25,301.0
C ₁₂ Oxo Carbonate+1.0% Polyacrylate Ester (mol. wt. 6,000–10,000)	128.6	42.3	26,678.0
C ₁₂ Oxo Carbonate+1.5% Polyacrylate Ester (mol. wt. 6,000–10,000)	131.7	42.7	27,020.0
C ₁₂ Oxo Carbonate+0.5% polybutene (mol. wt. 12,000)	130.3	42.2	28,771.0
C ₁₂ Oxo Carbonate+1.0 polybutene (mol. wt. 12,000)	155.6	45.2	35,431.0
C ₁₂ Oxo Carbonate+1.5 polybutene (mol. wt. 12,000)	180.8	47.9	44,034.0

Other carbonates having similarly desirable properties include those obtained by reacting phosgene with Oxo-alcohols to form di-“iso”octyl carbonate and di-“iso”undecyl carbonate.

Some of the critical properties of carbonates prepared from Oxo alcohols in the manner described above are tabulated below in comparison with those of some prior art mineral and synthetic lubricants.

Lubricant	Prepared by Oxo synthesis from—	Pour	Flash	Viscosity in centistokes at—	
				210° F.	100° F.
Di-C ₈ Oxo adipate	C ₇ copolymer of butylene and propylene	<–75	400	2.81	9.84
Di-C ₁₀ Oxo adipate	C ₈ polypropylene	<–75	465	4.70	20.83
Specifications for complex ester-type of lubricating oil		–60	470	10.1	52.0
Extracted Mid-Continent mineral oil		–5	410	4.99	29.8
Carbonate of C ₁₂ Oxo alcohol	C ₁₂ polypropylene	–70	410	4.32	23.8
Carbonate of C ₁₄ Oxo alcohol	C ₁₄ polypropylene	–40	465	8.32	78.6

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The above table shows that the new Oxo carbonates of the invention compare favorably with synthetic lubricants as well as mineral oils.

These carbonates may also be used as plasticizers. The results on Mooney viscosity for C₁₃ Oxo carbonate in GR-I butyl rubber (isobutylene-diolefin copolymer) and GR-S styrene butadiene copolymer rubber are recorded in table form below.

Rubber-type	C ₁₃ carbonate added, Percent	Mooney viscosities recorded at 1/2 minute intervals at 212° F. large rotor					
		1/2'	1'	1 1/2'	2'	2 1/2'	3'
GR-I-----	0	80	79	78	78	78	78
GR-I-----	25	30	29	28	28	28	28
GR-I-----	50	11	10	10	10	10	9
GR-S-----	0	44	40	39	39	40	41
GR-S-----	25	18	16	15	15	14	14
GR-S-----	50	6	6	5	5	5	5

It is to be noted that the C₁₃ Oxo carbonate at 25% as well as at 50% concentrations reduces the Mooney viscosity value of these rubbers at 212° F. to a very low value. The preferred range of plasticizer in these rubbers is about 15-30%. Good results have also been obtained when adding C₁₃ Oxo alcohol carbonate to ethyl cellulose. The carbonate is compatible with ethyl cellulose and acts as a plasticizer for the latter in concentrations as low as 10%.

As to other specific uses, extreme pressure lubricants may be produced by incorporating small percentages, e. g. 2-30 wt. percent of an extreme pressure agent containing sulfur, phosphorus and/or halogen, such as well known hydrocarbon derivatives containing both active halogen and active sulfur into the carbonates of the present invention. Carbonates such as those of the C₁₀ to C₁₆ Oxo alcohols are particularly suitable for this purpose.

For example, when 3% of tri cresyl phosphate was added to the carbonate of C₁₆ Oxo alcohol the lubricant carried all 15 weights on the Almen machine, under both gradual and shock loading conditions.

Lubricating greases in accordance with the invention may be prepared by incorporating into the carbonate grease-making proportions, say about 5-40 wt. percent of a suitable metal soap, preferably an alkali or alkaline earth metal soap of a high molecular weight fatty acid having 10-30 carbon atoms per molecule or of a soap-salt complex consisting of the soaps of higher molecular weight fatty acids and the salts of low molecular weight fatty acids, such as acetic, furoic, acrylic, or similar acids. The metal soap or soap-salt complex may be added as such particularly when carbonates are used which contain hydrocarbon radicals having only 5 carbon atoms or less which have a strong tendency to hydrolyze at soap-forming conditions. In this case, the preformed dry soap or complex may be slurried into the carbonate and the mixture heated to 300°-500° F. while stirring until a homogeneous mass is obtained which is cooled to form the finished grease.

The preparation of greases in accordance with the invention will be illustrated by the following example.

A C₁₃ Oxo alcohol produced by catalytic oxonation of C₁₂ olefin polymer was converted into the carbonate as follows: Phosgene was bubbled through the alcohol which was heated to 284° F. until HCl evolution ceased. The product was washed with water, hydrochloric acid and sodium hydroxide solutions and distilled, the fraction distilling at 338°-360° F. at 7 mm. pressure being taken as product. This carbonate had the following properties:

Flash, ° F. -----	405
Viscosity, centistokes:	
210° F. -----	4.38
100° F. -----	23.8
-40° F. -----	23765
Pour, ° F. -----	-65

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A lubricating grease of excellent stability was prepared as follows:

Ingredients:	Wt. percent
Complex lithium soap -----	20
C ₁₃ Oxo carbonate -----	80

For preparing the complex lithium soap, a mixture of acetic acid and hydrofol acid (hydrogenated fish oil acids) in a 1:1 mol ratio was conneutralized with lithium hydroxide. The finished dry soap contained a small excess (about 1.0%) of free alkali.

The preformed dry soap was slurried in the carbonate and then stirred while heating to 450° F. The fluid molten grease was cooled without further agitation. The finished product was extremely hard and tended to become crumbly on homogenization. The soap concentration was further diluted with an equal weight of carbonate and reheated to 450° F. and allowed to cool. The finished inhibited grease had the following formulation:

Ingredients:	
Complex lithium soap ----	9.0 wt. percent.
C ₁₃ Oxo carbonate -----	90.0 wt. percent.
Phenyl - alpha - naphthyl-amine oxidation inhibitor.	1.0 wt. percent.
Inspection and properties:	
Dropping point, ° F. ----	360.
Penetrations, 77° F. mm./10:	
Unworked -----	265.
Worked, 60 strokes ---	285.
Worked, 60,000 strokes	290.
Water solubility -----	Insoluble.
Appearance -----	Smooth, uniform, homogeneous grease. Light homogenization however results in greater smoothness.

It is noted that the above grease-making example is presented to illustrate the utility of the carbonates of the present invention as a synthetic lubricating oil base. Greases based on the carbonates of this invention and processes for preparing such greases are claimed and described in greater detail in the copending Morway, Cottle and Young application, Serial No. 296,935, filed of even date with the present application and assigned to the same interests.

The invention is not limited to the specific figures of the foregoing examples. The relative proportions of the materials used may be varied within the limits indicated in the specification to obtain products of varying characteristics.

What is claimed is:

1. A synthetic lubricating composition which comprises a major proportion of a mixture of organic carbonates of the formula



wherein R and R' are branched chain alkyl groups derived from C₁₀ to C₂₀ alcohols, containing combined therein a minor but extreme pressure-improving amount of tricresyl phosphate, said mixture of organic carbonates having a pour point below about -20° F. and a flash point above about 300° F., said alcohols being predominantly isomeric mixtures of branched-chain saturated aliphatic primary alcohols.

2. A synthetic lubricating composition according to claim 1 wherein said alkyl groups contain from about 13 to about 16 carbon atoms.

3. A synthetic lubricating composition according to claim 1 wherein said alkyl groups contain about 13 carbon atoms.

4. A synthetic lubricating composition according to

claim 1 wherein said alkyl groups contain about 16 carbon atoms.

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