

UNITED STATES PATENT OFFICE

2,623,018

EXTREME PRESSURE LUBRICANT

Elmer B. Cyphers, Cranford, N. J., and Alexander H. Popkin, New York, N. Y., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application December 17, 1949, Serial No. 133,661

6 Claims. (Cl. 252—46.7)

1

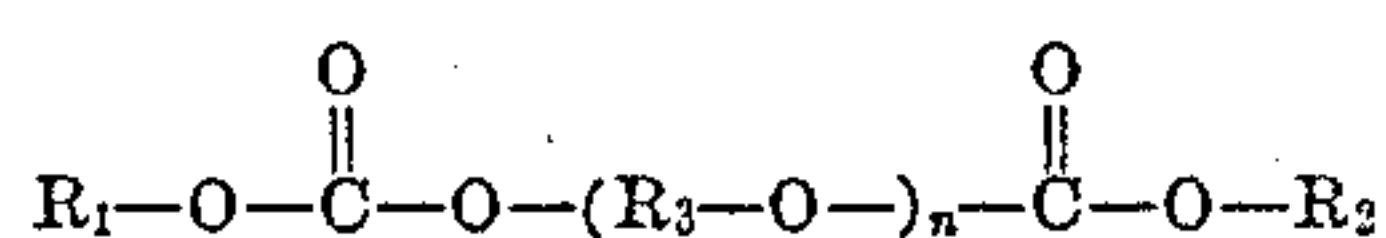
This invention relates to extreme pressure lubricating compositions. It relates particularly to lubricating compositions containing phosphorus, chlorine, and sulfur in active form. More particularly it relates to a lubricating composition having combined therein the condensation product of a halogenated polyalkylene glycol bis-carbonate with a compound containing phosphorus and sulfur.

It is known in the art that lubricating films are likely to fail under extreme pressures. For example, certain machine elements, such as the hypoid gears commonly used in automotive vehicles, may, at times, be subjected to pressures in the order of hundreds of thousands of pounds per square inch. If the lubricating film separating the opposed metallic surfaces fails, the surfaces will contact each other directly. This contact generates extremely high temperatures due to friction and results in seizure of the opposing elements, excessive wear, and early failure of the elements. Extreme pressure additives containing active sulfur, phosphorus, or chlorine, or mixtures of the same, are effective to prevent this excessive frictional wear. These active elements react with the metal surfaces at the high temperatures existent when the oil film fails, and form a protective metallic sulfide, phosphide, or chloride film which serves temporarily as a lubricating medium until the normal oil film between the metallic parts can be reestablished. Extreme pressure additives are known to the art, then, as materials which are reactive with the metals they lubricate to form extremely thin protective films thereon when the temperature of such metals rises due to failure of the normal lubricating film under extreme pressure.

This invention has as its object to furnish to the art a new and useful additive having extreme pressure and other valuable properties which contains, in an active form, chlorine, sulfur, and phosphorus. As a further object this invention contemplates lubricating compositions containing the new additive material which are useful for extreme pressure gear oils, cutting oils, greases, and other lubricants where high film strength properties are required.

Briefly stated the new additive material comprises a halogenated polyalkylene glycol bis-carbonate condensed with a compound containing both phosphorus and sulfur, such as an organic thiophosphoric or an organic thiophosphorous acid derivative.

The polyalkylene glycol bis-carbonates operable in forming the materials of this invention have the following general formula:



wherein n is an integer from 2 to 4, R_1 and R_2 may be the same or different and are alkyl, alicy-

2

clie, aralkyl, aryl, or alkoxy-alkyl radicals, and R_3 is an aliphatic hydrocarbon group, either straight or branched chain. In general R_1 and R_2 have from 3 to 22 carbon atoms each, preferably from 4 to 18 carbon atoms. Examples of these radicals are butyl, octyl, 2-ethyl hexyl, dodecyl, cetyl, oleyl, stearyl, butoxy-ethyl, phenyl, alkyl-phenyl, hydro abietyl, cyclohexyl, branched chain primary alcohols produced by the Oxo reaction on propylene-butylene copolymers, or mixtures of the above. The R_3 group contains from 2 to 4 carbon atoms such as occurs in glycols and polyglycols derived from ethylene, propylene, 1-butylene, 2-butylene, isobutylene, butadiene, etc.

Carbonate esters, in themselves, are known in the art. For instance, Fincke and Bartlett in U. S. Patent 2,263,265, disclose the use of a series of the esters of normal carbonic acid to improve spreading and penetration of mineral oils. The use of chloraralkyl esters of thio acids such as thiocarbonic acid is taught by Blake in U. S. Patent 2,438,599.

It has now been found that very effective extreme pressure additive compositions containing chlorine, sulfur and phosphorus can be made by chlorinating an organic carbonate ester and then condensing the chlorinated material with a dithiophosphoric acid derivative.

In accordance with this invention, polyalkylene glycol bis-carbonate is halogenated by any of the known methods until it contains a halogen content of from 10% to 40% by weight, preferably from 15% to 20% by weight. Direct chlorination with chlorine gas is an advantageous method for the halogenation step. Although any of the dialkyl esters of polyglycol carbonates wherein the alkyl group contains at least 3 carbon atoms may be used in this invention, it is preferred that the alkyl group contain from 4 to 18 carbon atoms, the dibutyl ester, the diamyl ester, the dihexyl ester and the di Oxo octyl ester of di-glycol carbonate being especially preferred.

The halogenated ester of polyglycol carbonate is then condensed with an alkali or alkaline earth metal salt of an organic dithiophosphoric or dithiophosphorous acid to obtain the final product. The proportions of the materials used in this condensation may vary widely depending upon the amount of phosphorus and sulfur desired in the final condensate. For most purposes a product obtained by condensing from 5 to 20 parts of the chlorinated organic ester of di-glycol carbonate with 1 part of the alkali metal salt is satisfactory, a preferred ratio being from 6 to 10 parts of the chlorinated ester to 1 part of the salt, all parts being by weight. The ratio of ingredients is to some extent dependent on the original chlorine content of the ester, it being preferred to remove by the condensation reaction from 20 to 50% of the original chlorine content.

The condensation may be advantageously carried out by refluxing in the presence of a solvent such as isopropyl alcohol or ethyl alcohol which is removed by heating after the condensation is completed. The time of the condensation reaction may vary from 1 to 10 hours.

The alkali metal salt of the acid used may first be prepared and then the salt and the chlorinated material admixed for condensation, or the salt may be formed in situ by adding the desired alkali metal hydroxide to a reaction mixture of the acid and the chlorinated material.

The invention will be explained more in detail by reference to the following example.

EXAMPLE I

466 grams of diethylene glycol bis(n-butylcarbonate), also known as butyl diglycol carbonate, were charged to a one liter, three-necked flask. The flask was equipped with a thermometer, a reflux condenser, and a diffusion stone for the introduction of gases. Chlorine gas was introduced at about 170° F. until the contents of the flask had gained 90 grams. The product was then blown with air for about 18 hours to remove dissolved HCl and chlorine. Analysis of the material showed a chlorine content of 14.98%.

180 grams of this chlorinated material were mixed with 20 grams of di-isopropyl dithiophosphoric acid, 16 grams of a 25% solution of NaOH and 200 grams of 91% isopropyl alcohol as a solvent. The mixture was then heated to reflux and the refluxing was continued for 3½ hours with constant stirring. The solvent was then removed by blowing with nitrogen while heating on a steam bath, followed by heating at about 212° F. in a vacuum oven. After filtration the product showed the following analysis:

	Percent
Chlorine -----	10.48
Sulfur -----	2.56
Phosphorus -----	1.86

To test the extreme pressure properties of this material, it was blended to a 10% concentration by weight in a base oil consisting of a blend of 45% of a steam refined Pennsylvania type cylinder oil and 55% of a solvent extracted Mid-Continent distillate, the blend having a viscosity at 210° F. of about 87 S. U. S. Tests reporting the extreme pressure characteristics, the well known SAE and Timken Machine extreme pressure tests, were run on the base oil, base oil-additive blend, and a blend of the base oil and a commercial extreme pressure additive. The results of these tests are reported in Table I below:

TABLE I

E. P. test data

Additive	Timken Machine			SAE Machine @ 1,000 R. P. M., Scale Lbs.
	Load, Lbs.	Scar, 1/64"	Lbs./sq. in.	
None-----	10	1.35	9,500	60
10%-----	43	2.85	19,300	450+
Comml. Agt., 10%-----	18	1.65	14,000	325

It will be noted from the table above that the material of this invention shows a pronounced improvement in resistance to extreme pressures over the base oil alone or the base oil-commercial additive blend.

Although for purposes of the laboratory tests a 10% blend of the additive of this invention was

made in a mineral base oil, concentrations of from 1% to 20% in either a naturally occurring mineral oil or a synthetic lubricating oil exhibit desirable extreme pressure properties. Preferred concentrations are from 5 to 15%.

The additive materials of this invention are compatible with other ingredients which may be blended in lubricating compositions, such as viscosity index improvers, pour depressants, sludge dispersers, oiliness agents, corrosion inhibitors, oxidation inhibitors and the like.

To summarize briefly, this invention comprises a new and useful additive material which may be blended with lubricating compositions, such as greases, gear oils, cutting oils, and the like, to impart extreme pressure resisting properties and other desirable properties to the blend. Generally speaking it comprises an additive prepared by condensing a halogenated organic ester of a polyglycol carbonate with a salt of an organic thiophosphoric or thiophosphorous acid in order to obtain a condensate having available halogen, sulfur, and phosphorus in active form.

What is claimed is:

1. A new and useful product having the property of increasing the extreme pressure resisting quality of a lubricant into which it is blended which comprises a condensation product of about 20 to 5 parts by weight of a di-alkyl ester of a di-glycol carbonate which contains from 15% to 20% by weight of active chlorine, each of said alkyl groups having from 4 to 18 carbon atoms, with about 1 part by weight of an alkali metal salt of a material selected from the class consisting of alkyl substituted dithiophosphoric acids and alkyl substituted thiophosphorous acids said product having been formed by heating together a mixture of said ester and said salt in the presence of a solvent for from 1 to 10 hours.

2. A new and useful product having the property of increasing the extreme pressure resisting quality of a lubricant into which it is blended which comprises a condensation product of about 10 to 6 parts by weight of a di-alkyl ester of a di-glycol carbonate which contains from 15% to 20% by weight of active chlorine, each of said alkyl groups having from 4 to 18 carbon atoms, with about 1 part by weight of an alkali metal salt of an alkyl substituted dithiophosphoric acid said product having been formed by heating together a mixture of said ester and said salt in the presence of a solvent for from 1 to 10 hours.

3. A new and useful product having the property of increasing the extreme pressure resisting quality of a lubricant into which it is blended which comprises a condensation product of about 9 parts by weight of the dibutyl ester of di-glycol carbonate containing about 15% active chlorine, with about 1 part by weight of the sodium salt of di-isopropyl dithiophosphoric acid said product having been formed by heating together a mixture of said ester and said salt in the presence of isopropyl alcohol for from 1 to 10 hours.

4. A lubricating composition having improved extreme pressure resisting properties which consists essentially of a major amount of a lubricant having combined therein from 5% to 15% by weight of a compound formed by heating together about 10 to 6 parts by weight of a di-alkyl ester of a di-glycol carbonate which contains from 15% to 20% by weight of active chlorine, each of said alkyl groups having from 4 to 18 carbon atoms, with about 1 part by weight of an alkali metal salt of an alkyl substituted dithiophosphoric acid said compound having been formed by heat-

5

ing together a mixture of said ester and said salt in the presence of a solvent for from 1 to 10 hours.

5. A lubricating composition having improved extreme pressure resisting properties which consists essentially of a major amount of a lubricant having combined therein from 5% to 15% by weight of a compound formed by heating together a mixture of about 9 parts by weight of the dibutyl ester of di-glycol carbonate containing about 15% active chlorine, with about 1 part by weight of the sodium salt of di-isopropyl dithiophosphoric acid in the presence of isopropyl alcohol for from 1 to 10 hours.

6. A lubricating composition having improved extreme pressure resisting characteristics which consists essentially of a major amount of a mineral base lubricating oil and having combined therein about 10% by weight of a product obtained by heating at about 178° F. for about 3½ hours, a mixture of about 90 parts by weight of the dibutyl ester of di-glycol carbonate which has

6

been chlorinated to a chlorine content of about 15% by weight, about 8 parts by weight of a 25% solution of sodium hydroxide, about 100 parts by weight of isopropyl alcohol, and about 10 parts by weight of di-isopropyl dithiophosphoric acid.

ELMER B. CYPHERS.

ALEXANDER H. POPKIN.

REFERENCES CITED

10 The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
15 2,198,915	MacAfee -----	Apr. 30, 1940
2,268,232	Whittier -----	Dec. 30, 1941
2,355,106	Prupton -----	Aug. 8, 1944
2,438,599	Blake -----	Mar. 30, 1948
2,448,037	Lincoln et al. -----	Aug. 31, 1948
20 2,494,332	Cyphers -----	Jan. 10, 1950
2,529,304	Mikeska -----	Nov. 7, 1950