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EXTREME PRESSURE LUBRICANT

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This invention has to do in a general way with the art of lubrication and is more particularly concerned with the production of improved lubricants from hydrocarbon oils by the incorporation of a small proportion of an improving agent therein. More specifically, our invention has to do with the development of lubricant compositions compounded from hydrocarbon oils which as a result of the addition agent are adapted for use under extreme pressure conditions.

As is well known to those familiar with the art, the ordinary type of hydrocarbon lubricant comprised only of a petroleum fraction is incapable of withstanding the enormous pressures encountered between engaged surfaces in various types of modern machinery such as the hypoid gears used in motor vehicles. This fact has led to the development of the so-called extreme pressure lubricant, which is comprised of a suitable carrying agent such as a hydrocarbon oil containing a minor proportion of an ingredient which under the extreme pressures encountered will provide or form between the engaged surfaces a lubricating film capable of withstanding these high pressures. Ingredients of the type just referred to are known as extreme pressure agents or extreme pressure (E. P.) bases, and numerous materials have been proposed for such use. Among the various E. P. bases which have been proposed and which have met with varying degrees of success are metal soaps, certain compounds of sulfur and certain classes of compounds containing sulfur and chlorine. Phosphorus compounds have also been proposed, as well as compounds containing phosphorus and nitrogen.

The present invention is predicated upon the discovery of a novel class of compounds containing phosphorus and sulfur and which may contain phosphorus, sulfur and chlorine, which when added in minor proportion to a suitable carrying medium, such as a hydrocarbon oil, will impart to such carrying medium outstanding extreme pressure characteristics. More specifically, the compounds or reaction products contemplated by this invention are obtained by reacting a halide of phosphorus with an alkali thiocarbonate.

The halides of phosphorus which may be employed as the first reactant mentioned above are typified in the chlorides by phosphorus trichloride (PCl_3), phosphorus pentachloride (PCl_5), phosphorus oxychloride ($POCl_3$) and phosphorus sulfochloride ($PSCl_3$).

As the alkali thiocarbonate we prefer to use such thiocarbonates which have been derived from alkyl or aliphatic thiocarbonic acids. Illustrative of these compounds may be mentioned the alkali alkyl monothiocarbonates and the alkali alkyl dithiocarbonates or alkali alkyl xanthates and alkali alkyl trithiocarbonates.

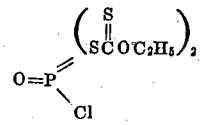
We are aware of the fact that the esters of the acids of phosphorus have been proposed and have been used with varying degrees of success as extreme pressure lubricant bases, and we therefore make no claim to the esters of the acids of phosphorus. The compounds of the present invention are distinguished from the esters of the acids of phosphorus in that they are mixed anhydrides of phosphorus acids and the organic, or more specifically, the aliphatic, thiocarbonic acids. The molecular composition of the products obtained by reacting halides of phosphorus with alkali thiocarbonates will vary not only with the reactants used but also with the molecular proportions of such reactants. For example, where one molecular proportion of phosphorus trichloride is reacted with three molecular proportions of an alkali alkyl trithiocarbonate, all of the chlorine in the PCl_3 combines with the alkali metal of the thiocarbonate to effect a substitution of three alkyl thiocarbonate groups on the phosphorus. If, on the other hand, only two or only one molecular proportion of the thiocarbonate is used with one molecular proportion of the phosphorus halide mentioned, one or two atoms respectively of the chlorine will remain in the product, which in turn will contain two or one of the thiocarbonate groups respectively. Although we do not wish to be specifically limited to our theory as to the chemical composition of the reaction product and prefer to identify the same merely as a reaction product, or as mixed anhydrides of alkyl thiocarbonic acids and acids of phosphorus, the preferred products contemplated herein may, in general, for purposes of description and further identification be represented by the general formula:

$$X_mPCl_n\left(\begin{matrix}Y\\ \|\\ SC-YR\end{matrix}\right)_{3-n} \quad I.$$

in which X represents sulfur or oxygen; m represents the number of X atoms in the molecule represented by the formula and is equal to zero or 1; n represents the number of chlorine atoms and is equal to zero, 1 or 2; Y represents sulfur or oxygen; and R represents an aliphatic hydrocarbon radical.

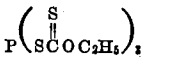
Illustrating the application of the foregoing general formula, if one molecular proportion of phosphorus oxychloride is reacted with two molecular proportions of an alkali alkyl dithio-

carbonate such as potassium ethyl xanthate, the product of such reaction has the probable formula:

II. 

in which case it will be observed that X of the general formula represents oxygen; *m* is one; *n* is one; and one of the Y's represents sulfur and the other oxygen, R being the ethyl group.

As a further example, if one molecular proportion of phosphorus trichloride is reacted with three molecular proportions of potassium ethyl xanthate, the product obtained would have the general formula:

III. 

The details in the procedure which may be followed in preparing the reaction products contemplated herein as extreme pressure lubricant bases will be best understood from the following examples in which various phosphorus halides have been employed and in which the reactants have been employed in various proportions. It will be observed in all of these examples that potassium ethyl xanthate is the thio-carbonate reactant but, as indicated above, the invention contemplates thiocarbonates other than the dithiocarbonate or xanthate and alkyl groups other than the ethyl group, such for example, as the propyl, butyl, amyl, etc.

EXAMPLE 1

PREPARATION OF PRODUCT FROM POTASSIUM ETHYL XANTHATE AND PHOSPHORUS TRICHLORIDE IN MOLECULAR PROPORTIONS OF THREE TO ONE

A solution of 24½ grams PCl_3 in 100 cc. acetone was added to 71 grams recrystallized

$KS.CS.OC_2H_5$

(potassium ethyl xanthate) in 400 cc. of acetone during 34 minutes with stirring and at a temperature of 0° to +3° C. After stirring for 80 minutes longer at room temperature, the mixture was suction-filtered to remove the inorganic reaction salt (KCl) and the filtrate concentrated by distillation at a liquid temperature of not over 50° C., under vacuum. The residue, a light brown, mobile liquid, weighed 41.5 grams. The product contained phosphorus, sulfur and a trace of chlorine and may be considered as a mixed anhydride of an alkyl (ethyl) xanthic acid and an acid of phosphorus.

EXAMPLE 2

REACTION PRODUCT OF POTASSIUM ETHYL XANTHATE AND PHOSPHORUS TRICHLORIDE IN MOLECULAR PROPORTIONS OF TWO TO ONE

Eighty grams of recrystallized $KS.CS.OC_2H_5$ were added gradually to a solution of 34 grams PCl_3 in 500 cc. acetone during 45 minutes, with stirring and at a temperature of 22° to 32° F. The mixture was then left over-night at a temperature of 70–75° F. and worked up as in the preceding experiment, yielding 127 grams of a brown, mobile liquid with a fairly pleasant odor, resembling that of mesityl oxide. The product, which contained phosphorus, sulfur and chlorine, was a mixed anhydride of ethyl xanthic acid and phosphorus acid, such mixed anhydride containing chemically combined halogen (chlorine).

EXAMPLE 3

REACTION PRODUCT OF POTASSIUM ETHYL XANTHATE AND PHOSPHORUS SULFOCHLORIDE IN MOLECULAR PROPORTIONS OF THREE TO ONE

To 55 grams of recrystallized $KS.CS.OC_2H_5$ in 300 cc. acetone was added, with stirring, a solution of 19–19.5 grams $PSCl_3$ in 100 cc. acetone during 22 minutes at a temperature of from −2° to 3° C. The mixture was stirred 35 minutes longer at room temperature and then worked up as in the preceding experiment, yielding 33 grams of a mobile, brown liquid. The product, containing phosphorus, sulfur and a trace of chlorine, may be considered to be a mixed anhydride of ethyl xanthic acid and thiophosphoric acid.

EXAMPLE 4

REACTION PRODUCT OF POTASSIUM ETHYL XANTHATE AND PHOSPHORUS SULFOCHLORIDE IN MOLECULAR PROPORTIONS OF TWO TO ONE

Eighty grams of $KS.CS.OC_2H_5$ were gradually added to a solution of 42 grams $PSCl_3$ in 300 cc. acetone during 50 minutes with stirring, and at a temperature of 0 to 5° C. The mixture stood over-night at room temperature and was then worked up as in the preceding experiments, yielding 86 grams of mobile, dark brown liquid. The product contained phosphorus, sulfur and chlorine and was a mixed anhydride of ethyl xanthic acid and thiophosphoric acid, such mixed anhydride containing chemically combined halogen (chlorine).

EXAMPLE 5

REACTION PRODUCT OF POTASSIUM ETHYL XANTHATE AND PHOSPHORUS OXYCHLORIDE IN MOLECULAR PROPORTIONS OF THREE TO ONE

Fifty-eight grams $KS.CS.OC_2H_5$ were added with stirring to a solution of 15.5 grams $POCl_3$ in 200 cc. CS_2 during 30 minutes at a temperature of 0° to 5° C. The temperature was then held at 40–45° C. for an hour and at 30–40° C. for 4 hours additional. The reaction mixture was then allowed to stand over-night, after which it was filtered and worked up as in the preceding experiment, yielding 28 grams of mobile light yellow liquid. The product, a mixed anhydride of ethyl xanthic acid and phosphoric acid, contained phosphorus, sulfur and a trace of chlorine.

To demonstrate the effectiveness of the materials contemplated by this invention as extreme pressure lubricant ingredients we have prepared and tested compositions comprised of the reaction products prepared under the foregoing examples as the E. P. ingredients and mineral oil as the carrying agent. The mineral oil used was one having a Saybolt viscosity of from 80 to 90 seconds at 210° F. and the reaction products from the examples described above were added thereto in amounts of 5 per cent. Examples of these extreme pressure lubricant blends were subjected to the Almen pin test described by Wolf and Mougey, Proc. A. P. I., 1932, pages 118–130, and the S. A. E. test, described in S. A. E. Journal 39, 23–4 (1936). These two tests are commonly accepted in the art as standards to determine extreme pressure characteristics of a lubricant. In the table given below we show the results obtained with such tests using the oil without the addition agent and samples of the same oil blended with the reaction products from Examples 1 to 5 inclusive described above.

Table I

Lubricant	E. P. tests (pounds failed)	
	Almen	S. A. E./1,000 R. P. M. rubbing ratio 14.6:1; loading rate 83.5 lbs./sec.
Oil alone	3,000–4,000	10–15
Oil+5% material from Example 1	28,000	580+
Oil+5% material from Example 2	30,000+	580+
Oil+5% material from Example 3	25,000	580+
Oil+5% material from Example 4	24,000	580+
Oil+5% material from Example 5	16,000+	580+

From the foregoing examples it will be seen that the phosphorus halide-thiocarbonate reaction products or mixed anhydrides of alkyl thiocarbonic acid (specifically alkyl xanthic acid) and acids of phosphorus contemplated by this invention are highly efficient extreme pressure lubricant bases. The amount of these materials which may be used to give a satisfactory extreme pressure lubricant may be varied from about 1 per cent to about 20 per cent, but in general amounts in the neighborhood of 5 per cent are preferred.

Although we have indicated from the foregoing description that a mineral lubricating oil is a preferred carrying agent for the extreme pressure ingredients contemplated herein, it is not our intention that the invention be limited to any particular carrying or blending medium, but the invention includes broadly extreme pressure lubricants containing these reaction products dissolved, dispersed or emulsified, in any other suitable carrying medium, such for example as fatty, vegetable or animal oils; light petroleum hydrocarbons such as kerosene, etc.; benzene and related hydrocarbons; alcohols; esters; ethers, etc.

We claim:

1. An extreme pressure lubricant composition comprising a mineral lubricating oil containing as an extreme pressure ingredient the mixed anhydrides of an alkyl thiocarbonic acid and an acid of phosphorus characterized by the general formula

$$X_mPCl_n(S\overset{\overset{Y}{\|}}{C}-YR)_{3-n}$$

in which X and Y represent elements selected from the group consisting of sulfur and oxygen; m represents the number of X atoms in the molecule and is equal to zero or one; n represents the number of chlorine atoms in the molecule and is equal to zero, one or two; and R represents an aliphatic hydrocarbon radical.

2. An extreme pressure lubricant composition comprising a hydrocarbon oil and a small proportion of an extreme pressure base comprised of mixed anhydrides of an alkyl thiocarbonic acid and an acid of phosphorus.

3. An extreme pressure lubricant composition comprising a hydrocarbon oil and a small proportion of an extreme pressure base comprised of mixed anhydrides of an alkyl xanthic acid and an acid of phosphorus.

4. An extreme pressure lubricant composition comprising a hydrocarbon oil and a small proportion of extreme pressure base comprised of halogen-bearing mixed anhydrides of an alkyl thiocarbonic acid and an acid of phosphorus.

5. An extreme pressure lubricant composition comprising a hydrocarbon oil and a small proportion of extreme pressure base comprised of a halogen-bearing mixed anhydride of alkyl xanthic acid and an acid of phosphorus.

6. A lubricant composition comprising a hydrocarbon oil and a small proportion of mixed anhydrides of an alkyl thiocarbonic acid and an acid of phosphorus, said mixed anhydrides having been obtained by the reaction of a halide of phosphorus with an alkali alkyl thiocarbonate.

7. A lubricant composition comprising a hydrocarbon oil and a small proportion of mixed anhydrides of an alkyl thiocarbonic acid and an acid of phosphorus, said mixed anhydrides having been obtained by the reaction of a halide of phosphorus selected from the group consisting of PCl_3, PCl_5, $POCl_3$ and $PSCl_3$ with an alkali alkyl thiocarbonate.

8. A lubricant composition comprising a hydrocarbon oil and a small proportion of mixed anhydrides of an alkyl thiocarbonic acid and an acid of phosphorus, said mixed anhydrides having been obtained by the reaction of a halide of phosphorus selected from the group consisting of PCl_3, PCl_5, $POCl_3$ and $PSCl_3$ with an alkali alkyl thiocarbonate selected from the group consisting of alkali alkyl monothiocarbonates, alkali alkyl dithiocarbonates and alkali alkyl trithiocarbonates.

9. A lubricant composition comprising a hydrocarbon oil and in admixture therewith from about one per cent to about twenty per cent of mixed anhydrides of an alkyl thiocarbonic acid and an acid of phosphorus, said mixed anhydrides having been obtained by the reaction of a halide of phosphorus selected from the group consisting of PCl_3, PCl_5, $POCl_3$ and $PSCl_3$ with an alkali alkyl thiocarbonate selected from the group consisting of alkali alkyl monothiocarbonates, alkali alkyl dithiocarbonates, and alkali alkyl trithiocarbonates.

10. A lubricant composition comprising a hydrocarbon oil and a small proportion of mixed anhydrides of an alkyl xanthic acid and an acid of phosphorus, said mixed anhydrides having been obtained by the reaction of about one molecular proportion of a halide of phosphorus with from about two to about three molecular proportions of an alkali alkyl xanthate.

11. A lubricant composition comprising a hydrocarbon oil and a small proportion of mixed anhydrides of ethyl xanthic acid and an acid of phosphorus, said mixed anhydrides having been obtained by the reaction of about one molecular proportion of a halide of phosphorus with from about two to about three molecular proportions of an alkali ethyl xanthate.

12. A lubricant composition comprising a hydrocarbon oil and in admixture therewith from about one per cent to about twenty per cent of mixed anhydrides of ethyl xanthic acid and an acid of phosphorus, said mixed anhydrides having been obtained by the reaction of about one molecular proportion of a halide of phosphorus with from about two to about three molecular proportions of an alkali ethyl xanthate.

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