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EXTREME PRESSURE LUBRICANT

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This invention, which is a continuation in part of that disclosed in our copending application Serial No. 177,891, filed December 3, 1937, has to do in a general way with the art of lubrication and is more particularly concerned with the development of a lubricant composition 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 mineral oil, containing a minor proportion of an ingredient which under the extreme pressure conditions 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 ingredients 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 organic materials which contain sulfur and chlorine. Our present invention is related to this general type of compound.

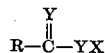
It is a primary object of this invention to provide an extreme pressure lubricant which contains a new and novel sulfur-and-chlorine-containing material or compound capable of giving extreme pressure lubricant properties to a carrying agent such as a hydrocarbon lubricant oil otherwise incapable of withstanding these extreme pressure conditions. In this regard, we have discovered that the class or group of compounds or reaction products obtained by reacting various reactive organic compounds with perchloromethylmercaptan are very effective extreme pressure lubricant addition agents. These materials have the advantage of being cheap and easily prepared. Perchloromethylmercaptan itself and its low molecular weight derivatives and very effective E. P. bases, but we prefer to use the higher molecular weight derivatives because they are more desirable from the standpoint of odor.

The perchloromethylmercaptan derivatives which we have found to be particularly useful as E. P. bases may be broadly divided into two general classifications: namely, (1) products obtained by reacting perchloromethylmercaptan

with organic compounds containing an active hydrogen or an active metal atom, or both; and (2) products obtained by reacting perchloromethylmercaptan with unsaturated organic materials such as animal and vegetable oils, cracked petroleum stocks, etc. Reaction products of the type encompassed by class 2 above were made the subject of our application Serial No. 177,890, filed December 3, 1937. The present application is broadly directed to the reaction products of group 1, wherein the secondary reactant is an organic compound containing an active hydrogen atom or an active metal atom or both.

Typical compounds contemplated under the broad aspect of this invention as organic compounds containing an active hydrogen atom or an active metal atom are: (a) aromatic hydrocarbons (specifically disclosed and claimed in our copending application Serial No. 358,207, filed September 25, 1940); (b) organic amines (specifically disclosed and claimed in our copending application Serial No. 358,286, filed September 25, 1940); (c) organic compounds having the general formula ROX , where R is alkyl, aryl, aralkyl, or alkaryl and X is hydrogen or the hydrogen equivalent of a metal (this latter group includes the alcohols, phenols, metal alcoholates, metal phenolates, etc., and is specifically disclosed and claimed in our application Serial No. 358,288, filed September 25, 1940); and (d) compounds having the general formula RSX , where R is alkyl, aryl, aralkyl, or alkaryl and X is hydrogen or the hydrogen equivalent of a metal (this group of compounds includes the mercaptans, mercaptides, the thiophenols and their metal derivatives and is specifically disclosed and claimed in our copending application Serial No. 362,373, filed concurrently herewith).

In its more specific aspect our present invention is directed to still another class of perchloromethylmercaptan reaction products, wherein the compound containing active hydrogen or active metal is one selected from the class consisting of the organic thio acids and their metal salts. The organic thio acids and their corresponding metal derivatives contemplated for obtaining the reaction products forming the specific subject matter of this invention may be represented by the general formula



wherein the Ys represent oxygen or sulfur, at least one Y being sulfur; X represents hydrogen or the hydrogen equivalent of a metal and R rep-

resents alkyl, aryl, aralkyl, alkaryl or one of the radicals R'S-; R'O-or



wherein R' represents a hydrocarbon radical and R'' represents hydrogen or a hydrocarbon radical. Typical thio acids which with their metal salts are contemplated herein for reaction with perchloromethylmercaptan are listed below with their general formulae.

Carbothiolic acids (R.CO.SH)
Carbolthionic acids (R.CS.OH)
Carbithionic acids (R.CS.SH)
Monothiocarbonic acids (R.O.CO.SH)
Dithiocarbonic (xanthic) acids (R.O.CS.SH)
Trithiocarbonic acids (R.S.CS.SH)
Thiocarbamic acids (R(R')N.CS.SH)

Perchloromethylmercaptan, the primary reactant used in synthesizing the reaction products contemplated herein, is a chlorinated substituted sulfur chloride having the formula $\text{Cl}_3\text{C}-\text{SCl}$. It can be prepared by the chlorination of carbon disulfide according to the method of Helfrich and Reid (Jour. American Chem. Soc. 43, 591 (1921)). For example, carbon disulfide containing about 4 per cent by weight of iodine was chlorinated in the absence of direct sunlight at a temperature maintained below 25° C. until the volume of the reaction mixture had doubled. This crude reaction product, which contains carbon tetrachloride and sulfur chlorides in addition to perchloromethylmercaptan, can be used in the preparation of the reaction products contemplated by this invention, but it is preferable to purify the crude product by distillation on a water bath at 100° C., followed by steam-distillation. Subsequent vacuum-distillation of the material refined in this manner indicated that the steam-distilled material was practically pure.

The procedure for preparing the general class of reaction products contemplated herein may be obtained from the following examples describing the synthesis of reaction products which typify those forming the specific subject matter of the present invention.

EXAMPLE ONE

Reaction of perchloromethylmercaptan with potassium ethyl xanthate

Potassium ethyl xanthate (potassium ethyl dithiocarbonate) was slowly added to an equal weight of perchloromethylmercaptan in an acetone solution. The strongly exothermic reaction required water cooling. The reaction mixture was drowned in water, and the heavy red liquid which separated was washed with dilute sodium sulfide and dried by filtration. This reaction product contained 41.3 per cent sulfur and 23.6 per cent chlorine.

EXAMPLE TWO

Reaction of perchloromethylmercaptan with potassium amyl dithiocarbonate

Potassium amyl dithiocarbonate was reacted with perchloromethylmercaptan in a procedure similar to that described above, and the small excess of perchloromethylmercaptan was removed from the product of reaction. After the water was separated from the product, the latter was ready for use. This product contained 37.5 per cent sulfur and 27.7 per cent chlorine.

EXAMPLE THREE

Reaction of Perchloromethylmercaptan with crude commercial sodium ethyl trithiocarbonate

Two molecular proportions of crude commercial sodium ethyl trithiocarbonate (assuming its purity as 100 per cent) were reacted with one molecular proportion of perchloromethylmercaptan in acetone solution. The perchloromethylmercaptan used in this reaction was the crude material above referred to, and the product obtained was isolated by filtering, distilling off the solvent, drying azeotropically with benzol, and filtering again. The product obtained through this procedure contained 60.9 per cent sulfur and 6.5 per cent chlorine.

EXAMPLE FOUR

Reaction of perchloromethylmercaptan and sodium dimethyl dithiocarbamate

A water solution of sodium dimethyl dithiocarbamate was prepared by shaking 35 grams (0.25 mole) of the compound with 250 cc. of water. The turbid solution was added to 45 grams (.25 mole) of perchloromethylmercaptan in petroleum ether, and the mixture stirred for 1 hour at room temperature. There was an initial temperature rise of 10° C., which was brought down by means of a water bath. The petroleum ether solution was then water-washed and the ether distilled off to yield 29 grams of a dark brown oil.

EXAMPLE FIVE

Reaction of perchloromethylmercaptan and ethyl xanthic acid

Ethyl xanthic acid ($\text{C}_2\text{H}_5\text{OCSSH}$) was formed by dissolving 60 grams (0.375 mole) of potassium ethyl xanthate in water cooled in ice to under 5° C. and then adding an excess of sulfuric acid. The xanthic acid thus formed was extracted with cold petroleum ether and added to a cold solution of 46.5 grams (0.25 mole) of perchloromethylmercaptan in petroleum ether with the temperature maintained at about 0° C. The mixture was then allowed to warm up slowly to room temperature, after which it was water-washed and the solvent removed under vacuum. The product was topped to a pot temperature of 72° C. at 2.7 mm. in a stream of nitrogen gas to yield a yellow oil.

In the foregoing examples we have mentioned several typical compounds of the specific class contemplated herein which may be reacted with perchloromethylmercaptan to obtain effective E. P. ingredients. Other compounds falling into the aforesaid specific classification of organic thio acid and their metal salts are as follows:

$\text{C}_2\text{H}_5\text{COSH}$ thiopropionic acid
 $\text{C}_2\text{H}_5\text{COSK}$ potassium salt of thiopropionic acid
 $\text{C}_6\text{H}_5\text{CSOH}$ thiobenzoic acid
 $\text{C}_6\text{H}_5\text{CSSH}$ dithiobenzoic acid
 $\text{C}_6\text{H}_5\text{CSSNa}$ sodium salt of dithiobenzoic acid
 $\text{C}_4\text{H}_9\text{CSSNa}$ sodium salt of dithiovaleric acid
 $\text{C}_3\text{H}_7\text{OCOSNa}$ sodium salt of propylthiocarbonic acid
 $\text{C}_2\text{H}_5\text{SCSSH}$ ethyl trithiocarbonic acid
 $(\text{CH}_3)_2\text{NCSSH}$ dimethyl dithiocarbamic acid

To demonstrate the effectiveness of the reaction products contemplated by this invention as extreme pressure lubricant ingredients we have prepared and tested compositions comprised of these ingredients and mineral oil as the carrying agent. More specifically, we have added a minor

proportion of each of the reaction products prepared according to the foregoing illustrative examples to a mineral oil having a Saybolt Universal viscosity of 80-90 seconds at 210° F. and have subjected samples of such blended lubricants 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 the extreme pressure characteristics of a lubricant. In Table I below we show the results obtained with such tests, using the oil without the addition agent and samples of the same oil blended with perchloromethylmercaptan derivatives of the type contemplated by this invention.

TABLE I

Reaction product added	Percent in oil	Extreme pressure tests (lbs. failed)	
		Almen	S. A. E. (755 R. P. M.; 14.6:1 rubbing ratio; 8.35 lbs./sec. loading rate)
None		3,000	40-70
Cl ₃ CSCl+potassium ethyl xanthate	5	30,000+	580+
Cl ₃ CSCl+potassium amyl trithiocarbonate	5	30,000+	580+
Cl ₃ CSCl+commercial sodium ethyl trithiocarbonate	5	30,000+	580+
Cl ₃ CSCl+sodium dimethyl dithiocarbamate	3	30,000+	580+*
Cl ₃ CSCl+ethyl xanthic acid	3	30,000+	325*

*These values were obtained at 1000 R. P. M. instead of 755 R. P. M. The blank oil failed in the test at 1000 R. P. M. with a 20 pound load.

From the foregoing examples it will be seen that the perchloromethylmercaptan condensation products contemplated by this invention are highly efficient extreme pressure lubricant bases. The amount of these materials used may vary from say .5 per cent to 20 per cent, but in general lower percentages ranging from .5 per cent to 10 per cent are preferred.

Although we have indicated in the foregoing description that a mineral lubricating oil is a preferred carrying agent for the extreme pressure ingredients contemplated by our invention, 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 the perchloromethylmercaptan condensation products dissolved, dispersed or emulsified in any other suitable carrying medium such, for example, as fatty vegetable and animal oils; light petroleum hydrocarbons such as kerosene, etc.; benzene and related hydrocarbons; alcohols; esters; ethers, etc.

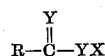
We claim:

1. An extreme pressure lubricant composition comprising a hydrocarbon oil and in admixture therewith a minor proportion of the product obtained by the reaction of perchloromethylmercaptan with a compound selected from the group consisting of organic compounds containing reactive hydrogen atoms and organic compounds containing reactive metallic atoms, said reaction product containing both sulfur and chlorine and being present in the oil in an amount sufficient to increase its load-carrying capacity.

2. An extreme pressure lubricant composition comprising a hydrocarbon oil and in admixture therewith a minor proportion of the product ob-

tained by the reaction of perchloromethylmercaptan with a compound selected from the group consisting of organic thio acids and their metal salts, said reaction product containing both sulfur and chlorine and being present in the oil in an amount sufficient to increase its load-carrying capacity.

3. An extreme pressure lubricant composition comprising a hydrocarbon oil and in admixture therewith a minor proportion of the product obtained by the reaction of perchloromethylmercaptan with a compound having the general formula



wherein the Y's represent oxygen or sulfur and at least one Y is sulfur, X represents hydrogen or the hydrogen equivalent of a metal and R is selected from the group consisting of hydrocarbon radicals and the radicals R'S—, R'O— and



wherein R' is a hydrocarbon radical and R'' is selected from the group consisting of hydrogen and hydrocarbon radicals.

4. An extreme pressure lubricant comprising a hydrocarbon lubricant oil and in admixture therewith a minor proportion of the product obtained by the reaction of perchloromethylmercaptan with an alkali thiocarbonate, said product containing both sulfur and chlorine.

5. An extreme pressure lubricant comprising a hydrocarbon lubricant oil and in admixture therewith a minor proportion of the product obtained by the reaction of perchloromethylmercaptan with an alkali thiocarbamate, said product containing both sulfur and chlorine.

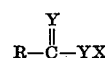
6. An extreme pressure lubricant comprising a hydrocarbon oil and in admixture therewith a minor proportion of the product obtained by the reaction of perchloromethylmercaptan with an alkali alkyl dithiocarbonate.

7. An extreme pressure lubricant comprising a hydrocarbon oil and in admixture therewith a minor proportion of the product obtained by reacting perchloromethylmercaptan with an alkali alkyl trithiocarbonate.

8. An extreme pressure lubricant comprising a hydrocarbon oil and in admixture therewith a minor proportion of the product obtained by reacting perchloromethylmercaptan with an alkali alkyl dithiocarbamate.

9. An extreme pressure lubricant comprising a hydrocarbon oil and in admixture therewith a minor proportion of the product obtained by reacting perchloromethylmercaptan with a compound selected from the group consisting of: potassium ethyl xanthate; potassium amyl trithiocarbonate; sodium ethyl trithiocarbonate and sodium dimethyl dithiocarbamate.

10. An extreme pressure lubricant composition comprising a minor proportion of the chlorine-and-sulfur-containing product obtained by the reaction of perchloromethylmercaptan with a compound having the general formula



wherein the Y's represent oxygen or sulfur and at least one Y is sulfur, X represents hydrogen or the hydrogen equivalent of a metal and R is

selected from the group consisting of hydrocarbon radicals and the radicals $R'S-$, $R'O-$, and



wherein R' is a hydrocarbon radical and R'' is selected from the group consisting of hydrocarbon radicals and hydrogen, the said product being in admixture with a major proportion of a carrying medium, which composition when applied to metallic bearing surfaces will form a lubricant film capable of withstanding extreme pressure conditions.

11. An extreme pressure lubricant composition comprising a minor proportion of the chlorine-and-sulfur-containing product obtained by the reaction of perchloromethylmercaptan with the metal salt of an organic thio acid, in admixture with a major proportion of carrying medium, which composition, when applied to metallic bearing surfaces, will form a lubricant film capable of withstanding extreme pressure conditions.

12. An extreme pressure lubricant composition comprising a minor proportion of the chlorine-and-sulfur-containing product obtained by the reaction of perchloromethylmercaptan with an alkali thiocarbonate, in admixture with a major proportion of carrying medium, which composition, when applied to metallic bearing surfaces, will form a lubricant film capable of withstanding extreme pressure conditions.

13. An extreme pressure lubricant composition comprising a minor proportion of the chlorine-and-sulfur-containing product obtained by the reaction of perchloromethylmercaptan with an alkali thiocarbamate, in admixture with a major proportion of carrying medium, which composition, when applied to metallic bearing surfaces, will form a lubricant film capable of withstanding extreme pressure conditions.

14. An extreme pressure lubricant composition

comprising a minor proportion of the chlorine-and-sulfur-containing product obtained by the reaction of perchloromethylmercaptan with a compound selected from the group consisting of

5 potassium ethyl xanthate; potassium amyl tri-thiocarbonate; sodium ethyl trithiocarbonate; and sodium dimethyl dithiocarbamate, the said product being in admixture with a major proportion of carrying medium and the said lubricant composition, when applied to metallic bearing surfaces, forming a lubricant film capable of withstanding extreme pressure conditions.

15. An extreme pressure lubricant comprising a minor proportion of the chlorine-and-sulfur containing product obtained by the reaction of perchloromethylmercaptan and an organic thio acid, in admixture with a major proportion of a carrying medium, which composition, when applied to metallic bearing surfaces, will form a lubricant film capable of withstanding extreme pressure conditions.

16. An extreme pressure lubricant comprising a minor proportion of the chlorine-and-sulfur containing product obtained by the reaction of perchloromethylmercaptan and a thiocarbonic acid in admixture with a major proportion of a carrying medium, which composition, when applied to metallic bearing surfaces, will form a lubricant film capable of withstanding extreme pressure conditions.

17. An extreme pressure lubricant comprising a minor proportion of the chlorine-and-sulfur containing product obtained by the reaction of perchloromethylmercaptan and ethyl xanthic acid in admixture with a major proportion of a carrying medium, which composition, when applied to metallic bearing surfaces, will form a lubricant film capable of withstanding extreme pressure conditions.

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