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LUBRICATING OIL COMPOSITION

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17 Claims. (Cl. 252—48.4)

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This invention relates to lubricating compositions and to methods of preparing the same and more particularly to lubricating compositions adapted for use under extreme pressure conditions.

Various types of modern machinery such as the hypoid gears in motor vehicles develop enormous pressures between engaged surfaces. The ordinary type of hydrocarbon lubricant composed only of a petroleum fraction is incapable of satisfying the severe requirements demanded in the proper lubrication of hypoid gears, bearing surfaces, metal cutting tools and the like, subjected to unusually heavy loads per unit area of surface. This fact has led to the development of the so-called extreme pressure lubricant which is composed of a suitable carrying agent, such as mineral oil, and another ingredient which imparts to the lubricating composition the property of maintaining between the engaged surfaces a lubricating film under the high pressures encountered.

Among the various E. P. bases which have been prepared and which have met with varying degrees of success are organic materials which contain sulfur or both sulfur and chlorine. The present invention relates to the general type of organic materials which contain both sulfur and chlorine. The presence of chlorine frequently increases the effectiveness of organic sulfur compounds but this increased effectiveness is accompanied by increased corrosiveness and decreased stability. However, the new adjuvants while considerably more effective than the corresponding chlorine free sulfur compounds actually appear to be more stable and are not corrosive.

A primary object of this invention is to provide a new and novel sulfur-and-chlorine-containing material capable of imparting extreme pressure lubricant properties to a lubricating oil composition otherwise incapable of withstanding extreme pressure conditions. A further object is to provide a mineral oil adjuvant which is not corrosive and yet is a very effective extreme pressure addition agent. Still further objects are to provide extreme pressure addition agents which are cheap and easily prepared.

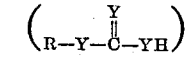
In accordance with this invention it has been discovered that chloraralkyl esters of thio acids are very effective extreme pressure lubricant agents. The addition to hydrocarbon or fatty lubricating oils of small amounts of chloraralkyl esters of thio acids provides lubricating compositions which not only satisfy all of the primary requirements of extreme pressure lubricants but,

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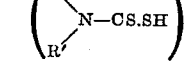
in addition do not tend to form gum, foul or corrode metal surfaces nor separate into their constituent parts in long continued use. Examples of suitable thio acids from which the new E. P. agents may be derived include carbothiolic acids (R—CO.SH), carbothionic acids

(R—CH.OH)

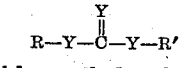
carbodithioic acids (R—CS.SH), mono-, di- and trithiocarbonic acids



where Y is oxygen or sulfur, at least one Y being sulfur, and thiocarbamic acids



In general derivatives of thiocarbonic acids are preferred, that is to say products of the structure



where R is a chloraralkyl radicle, Y is sulfur or oxygen at least one of them being sulfur and R′ represents alkyl, aryl, aralkyl or alkyaryl.

The amounts of chloraralkyl esters required to be added to hydrocarbon or fatty lubricating oils for the preparation of compositions of this invention vary somewhat, depending upon the character of the lubricating stock used as a base, and the severity of the service for which they are designed; however, the active agent is always present in minor amounts with respect to the oil base and in general varies between about 1% and about 10% of the oil base by weight although amounts outside of this range can be used where convenient or desirable. Since most of the preferred adjuvants are freely soluble in lubricating oils, a wide range of homogeneous compositions can be prepared. Where desired concentrates can be prepared containing relatively large amounts, as for example 50%, of chloraralkyl esters of a thio acid. Such concentrates may be stored or transported in this form and diluted to the desired concentration before actual use. Complete solution is not always necessary and incorporation of the less soluble active agents in suspended form is sufficient to allow them to function in decreasing film strength in actual use.

There are a variety of procedures suitable for the preparation of the new adjuvants and in general any of the methods suitable for the prep-

aration of esters of thio acids can be used. A particularly convenient synthesis which has been found to give excellent yields is to react a chloraralkyl chloride with an alkali metal salt of the thio acids and separate the salt split out in the formation of the desired ester. The following examples describe in detail the synthesis of chloraralkyl esters typical of the new class of adjuvants but it is to be understood that the invention is not limited thereto.

Preparation of trichlor benzyl chloride

Substantially 1500 parts by weight of dry toluene were charged into a chlorinator of suitable capacity. Substantially 15 parts by weight of iron filings were added as catalyst carrier for ring chlorination and chlorine introduced at about 20° C. until the increase in weight corresponded to that calculated for trichlor toluene. The temperature was increased to 70° C. during the last part of the reaction and the flow of chlorine interrupted when the product analyzed 54.8% chlorine. The trichlor toluene was washed with 10% caustic and filtered through a bed of clay in order to remove the iron and chlorinated at 160° C. in the presence of ultra violet light until the gain in weight was that calculated for trichlor benzyl chloride. Analysis of the product for chlorine at this point gave 61.8%.

EXAMPLE I

Trichlor Benzyl Trithiocarbonate

Into a vessel of suitable capacity there was charged 316 parts by weight (substantially 1.32 molecular proportions) of $Na_2S.9H_2O$, 138 parts by weight (substantially 1.82 molecular proportions) of carbon disulfide and substantially 2500 parts by weight of methanol. The mass was stirred for about four and one-half hours and then 550 parts by weight (substantially 2.39 molecular proportions) of trichlor benzyl chloride added in a slow stream during which the temperature of the reaction mixture was held at 25–30° C. After the addition was complete, the temperature was raised to refluxing temperature for about four hours and the solvent removed as for example, by distillation under a vacuum and the residue washed with water and dried. The product was a brown liquid which was readily soluble in mineral hydrocarbon oils.

EXAMPLE II

Trichlor Benzyl Butyl Trithiocarbonate

A mixture of 181.5 parts by weight (substantially 2.02 molecular proportions) of butyl mercaptan and substantially 1200 parts by weight of ethanol was added to 79 parts by weight of 96.5% caustic soda (substantially 1.90 molecular proportions). The mass was cooled to 15° C. and 200 parts by weight (substantially 2.63 molecular proportions) of carbon disulfide added thereto which caused the temperature to rise to about 28° C. 400 parts by weight (substantially 1.74 molecular proportions) of trichlor benzyl chloride was added in a slow stream during which the temperature of the mass was kept at 30–40° C. The mixture was then heated to refluxing temperature for four hours and the solvent removed as for example by distillation under a vacuum and the residue washed with water and dried. The product was a brown liquid very soluble in mineral hydrocarbon oils.

EXAMPLE III

O-Chlor Benzyl Butyl Trithiocarbonate

Into a reaction vessel of suitable capacity there was charged 49.5 parts by weight (substantially 0.55 molecular proportion) of butyl mercaptan and 20.7 parts by weight of 96.5% caustic soda (substantially 0.50 molecular proportion). The mixture was diluted somewhat with ethyl alcohol, cooled to 10° C. and 42.0 parts by weight (substantially 0.55 molecular proportion) of carbon disulfide added. The temperature rose to 28° C. The mixture was then stirred for about 12 hours without heating and 72.5 parts by weight (substantially 0.45 molecular proportion) of ortho chlor benzyl chloride added in a slow stream after which the mixture was heated at refluxing temperature for about three hours. The alcohol was removed by distillation and the last traces stripped out by heating mildly under a vacuum. The residue was washed with water and dried leaving in good yield a reddish yellow liquid freely soluble in mineral hydrocarbon lubricating oils.

EXAMPLE IV

Di(O-Chlor Benzyl) Trithiocarbonate

To a solution of 80 parts by weight (substantially 0.33 molecular proportion) of $Na_2S.9H_2O$ in substantially 400 parts by weight of methanol was added 27.8 parts by weight (substantially 0.37 molecular proportion) of carbon disulfide keeping the temperature below 30° C. The cold solution was stirred for several hours after which 107.3 parts by weight (substantially 0.67 molecular proportion) of o-chlor benzyl chloride was added in a slow stream while keeping the temperature below 30° C. by suitable cooling. Stirring was continued for about 12 hours after the addition of the chloride and the solvent then removed as for example by distillation, the last traces being stripped out by mild heating under a vacuum. The residue was washed with water and dried leaving, in good yield, a yellow liquid freely soluble in mineral hydrocarbon lubricating oils.

EXAMPLE V

O-Ethyl S-Trichlor Benzyl Trithiocarbonate

The potassium salt of thio ethyl carbonate commonly known as Bender's salt (24 parts by weight or substantially 0.167 molecular proportion) was dissolved in substantially 200 parts by weight of ethyl alcohol. To this solution 36.5 parts by weight (substantially 0.159 molecular proportion) of trichlor benzyl chloride was added in a slow stream while keeping the temperature of the reaction mixture at 20–25° C. Stirring was continued for several hours and the mixture allowed to stand for about 12 hours after which it was poured into an excess of water and the oil extracted with ether or other suitable solvent. The solvent was removed and the residue dried by heating at 80° C. under good vacuum. A dark brown liquid was obtained in good yield.

EXAMPLE VI

Trichlor Benzyl Diethyl Dithiocarbamate

Substantially 80.5 parts by weight (substantially 0.35 molecular proportion) of trichlor benzyl chloride was added in a slow stream to an ethanol solution of the diethyl amine salt of diethyl dithiocarbamic acid prepared by reacting at 15–25° C. 58.4 parts by weight (substantially 0.80 molecular proportion) of diethyl amine and

40.4 parts by weight (substantially 0.53 molecular proportion) of carbon disulfide in substantially 315 parts by weight of ethanol. The temperature was kept at 15°–20° C. during the addition of the chloride. Without heating, the reaction mixture was stirred for about five hours and the solvent then removed by heating up to 40° C. under a good vacuum. The residue was washed with water, then dilute hydrochloric acid and finally with water again until neutral to litmus. The washing of the oil is facilitated by dilution with a suitable water immiscible solvent such as ether. After removal of solvent, drying and filtering through a bed of clay, a good yield of a brown viscous oil was obtained.

EXAMPLE VII

Dichlor Diethyl Phenyl Ethyl, Ethyl Xanthate

Freshly distilled triethyl benzene was chlorinated at 75° C. in the presence of ultra violet light until the increase in weight corresponded to that calculated for the introduction of one chlorine atom into each side chain. The chlorinated product contained 40.1% chlorine by analysis. 186.0 parts by weight (substantially 0.7 molecular proportion) of the trichlor ethyl benzene so prepared was dissolved in substantially 238 parts by weight of acetone and the solution heated to refluxing temperature. Over a period of two hours 122.5 parts by weight of 91.5% potassium ethyl xanthate (substantially 0.7 molecular proportion) was added to the refluxing solution. Heating was continued for four hours, then the solvent removed, the residue washed with water, dried and filtered through a bed of clay. An oily product was obtained in excellent yield and was soluble in mineral hydrocarbon oils.

EXAMPLE VIII

α-(2,4 Dichlor Phenyl) Ethyl Trithiocarbonate

Substantially 209.5 parts by weight (substantially 1.0 molecular proportion) of α-(2,4-dichlor phenyl) ethyl chloride was added in a slow stream to a solution of substantially 86 parts by weight (substantially 0.5 molecular proportion) of Na_2CS_3 in substantially 800 parts by weight of methanol. The mixture was stirred without heating for about an hour after the chloride had been added and then heated to refluxing temperature for about six hours after which the solvent was removed, preferably by distillation and the residue dissolved in a suitable water immiscible solvent, as for example benzene, and washed with water. The solvent was again removed and the residue dried leaving in excellent yield a thin orange liquid soluble in hydrocarbon mineral lubricating oils.

Chlorination of Diethyl Benzene

Chlorine was introduced into substantially 721 parts by weight of diethyl benzene at 90–110° C. in the presence of ultra violet light. Samples were withdrawn corresponding to the di, tri, tetra and penta chlorinated products. Analysis for chlorine gave the following:

Per cent Chlorine	Found	Calculated
Dichloride	36.9	35.0
Trichloride	46.1	44.9
Tetrachloride	53.2	52.2
Pentachloride	59.0	57.9

The fractions so obtained were reacted as hereinafter described.

EXAMPLE IX

Di(Chlor Ethyl Phenyl Ethyl) Trithiocarbonate

Substantially 84.2 parts by weight (substantially 0.5 molecular proportion) of diethyl benzene dichlorine was added slowly to a solution of sodium trithiocarbonate prepared by mixing 60 parts by weight of $Na_2S.9H_2O$ (substantially 0.25 molecular proportion) and 38 parts by weight (substantially 0.50 molecular proportion) of carbon disulfide in substantially 200 parts by weight of methanol. The temperature rose to 34° C. during the addition. Stirring was continued for four hours and the mass was then poured into water and the oil dissolved in ether or other suitable solvent and dried. A red oil was obtained after removal of the solvent which was soluble in mineral hydrocarbon lubricating oils. Analysis for sulfur and chlorine indicated that the product was essentially di(chlor ethyl phenyl ethyl) trithiocarbonate.

EXAMPLE X

Di-Dichlor Ethyl Phenyl Ethyl) Trithiocarbonate

Substantially 47.5 parts by weight (substantially 0.2 molecular proportion) of diethyl benzene trichloride was added slowly to a solution of sodium trithiocarbonate prepared by mixing 24 parts by weight of $Na_2S.9H_2O$ (substantially 0.1 molecular proportion) and 18.7 parts by weight (substantially 0.24 molecular proportion) of carbon disulfide in substantially 200 parts by weight of methanol. Stirring was continued for four hours and the solvent removed as for example by distillation and the residue washed with water and dried. Substantially theoretical yield of a reddish oil was obtained which was freely soluble in mineral hydrocarbon lubricating oils. Analysis for sulfur and chlorine indicated the product was essentially di(dichlor ethyl phenyl ethyl) trithiocarbonate.

EXAMPLE XI

Di(Trichlor Ethyl Phenyl Ethyl) Trithiocarbonate

Substantially 54.5 parts by weight (substantially 0.2 molecular proportion) of diethyl benzene tetrachloride was added slowly to a solution of sodium trithiocarbonate prepared by mixing 24 parts by weight of $Na_2S.9H_2O$ (substantially 0.1 molecular proportion) and 18.7 parts by weight (substantially 0.24 molecular proportion) of carbon disulfide in substantially 200 parts by weight of methanol. Stirring was continued for four hours and the solvent removed as for example by distillation and the residue washed with water and dried. Substantially theoretical yield of a reddish oil was obtained which was moderately soluble in mineral hydrocarbon lubricating oils. Analysis for sulfur and chlorine indicated the product was essentially di(trichlor ethyl phenyl ethyl) trithiocarbonate.

EXAMPLE XII

Di(Tetrachlor Ethyl Phenyl Ethyl) Trithiocarbonate

Substantially 61.3 parts by weight (substantially 0.2 molecular proportion) of diethyl benzene pentachloride was added slowly to a solution of sodium trithiocarbonate prepared by mix-

ing 24 parts by weight of $Na_2S.9H_2O$ (substantially 0.1 molecular proportion) and 18.7 parts by weight (substantially 0.24 molecular proportion) of carbon disulfide in substantially 200 parts by weight of methanol. Stirring was continued for four hours and the solvent removed as for example by distillation and the residue washed with water and dried. Substantially theoretical yield of a reddish oil was obtained which was moderately soluble in mineral hydrocarbon lubricating oils.

EXAMPLE XIII

Trichlor Benzyl Ester of Benzothiolic Acid

The potassium salt of benzothiolic acid was prepared by saturating in the cold an alcoholic solution of KOH with hydrogen sulfide and slowly adding benzoyl chloride to the cold solution containing an excess of KSH. The free acid was precipitated by the addition of hydrochloric acid and then purified by dissolving in aqueous KOH until alkaline to phenolphthalein and the solution evaporated. The salt was then dried at 100° C.

Substantially 40 parts by weight of the salt so prepared (substantially 0.227 molecular proportion) was suspended in substantially 237 parts by weight of alcohol and 47.1 parts by weight (substantially 0.205 molecular proportion) of trichlor benzyl chloride added in a slow stream. The reaction was slightly exothermic. After the addition of the trichlor benzylchloride the mixture was heated to refluxing temperature for about three hours and the solvent removed. The residue was washed with water, preferably after dissolving in a water immiscible solvent, then dried and the solvent removed leaving the desired ester as a residue. The product was soluble in mineral hydrocarbon oils. Analysis for sulfur and chlorine without further purification gave 9.2% sulfur and 33.8% chlorine as compared to calculated values of 9.7% sulfur and 32.1% chlorine.

EXAMPLE XIV

Trichlor Phenyl Ethyl, Ethyl Xanthate

Mono ethyl benzene was chlorinated at 60–80° C. in the presence of iron until the gain in weight approximated that calculated for ethyl trichlor benzene. The product was distilled and the fraction boiling at 98–104° C. was chlorinated at 130–140° C. in the absence of iron until the gain in weight approximated that calculated for trichlor phenyl ethyl chloride.

Sodium ethyl xanthate was prepared by reacting below 45° C. substantially 76 parts by weight (1.0 molecular proportion) of carbon disulfide, 36.6 parts by weight (substantially 0.88 molecular proportion) of sodium hydroxide and substantially 316 parts by weight of ethyl alcohol. Substantially 195.5 parts by weight (0.8 molecular proportion) of trichlor phenyl ethyl chloride was added and the reaction mixture heated to refluxing temperature for about three hours. The excess alcohol was removed by distillation and the residue washed with water until neutral. Further purification was effected by mildly heating under a vacuum and then filtering through a bed of clay. The trichlor phenyl ethyl ethyl xanthate so prepared was freely soluble in mineral hydrocarbon lubricating oils.

The effectiveness of the chloraralkyl esters of thio acids is demonstrated by the conventional tests on compositions comprised of these ingredients and a lubricating oil carrying agent. More specifically a minor amount of chloraralkyl ester was aded to a high viscosity hydrocarbon lubricating oil (Saybolt Universal viscosity of 101 seconds at 210° F.) and samples of the blended lubricant 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 the extreme pressure characteristics of a lubricant.

In order for chlorine to effectively improve the E. P. properties of organic sulfur compounds, it has generally been considered necessary that the chlorine be linked to an aliphatic radicle. On the other hand, the results set forth in the table below demonstrate that in the case of the new adjuvants chlorine linked to the aromatic radicle markedly improves their effectiveness. An admixture of benzyl butyl thiocarbonate and an Arochlor, which is the trade marked name of chlorinated diphenyl, was aded to a mineral oil base and compared with the same oil base containing trichlor benzyl butyl trithiocarbonate in amount such that the chlorine and sulfur content of the oil compositions were identical.

Table I

Product Added	Per cent in Oil	Per cent S in Oil	Per cent Cl in Oil	Extreme pressure Tests lbs. failed	
				S. A. E. (1000 R. P. M. 14:6:1 rubbing ratio; 77–79 lbs./sec. loading rate)	Almen
Dibenzyl trithiocarbonate	2.85	.9	3.3	234	18
Arochlor #1258	3.25				
Di(trichlorbenzyl) trithiocarbonate	7	.9	3.3	365	40
Benzyl diethyl dithiocarbamate	7	1.8	0.0	225	8
Trichlor benzyl diethyl dithiocarbamate	7	1.3	2.2	328	40

From the foregoing examples it will be seen that the chloraralkyl esters of this invention are highly efficient extreme pressure lubricant bases and that the chlorine, although it may be linked to the aryl group, markedly improves the effectiveness. This is further brought out by the data set forth in Table II. In addition to tests on the Almen machine the increase in viscosity caused by heating the oil in the presence of the additive, were also determined. The viscosity determinations were made by heating the oil containing the E. P. additive for 100 hours at 300° F. in open beakers. The viscosity of the oil compositions was determined at 210° F. before and after heating and the increase in viscosity in percent calculated from the results obtained. A marked increase in viscosity indicates that viscous gummy constituents were formed as the result of oxidation and decomposition of the oil or the product added or both.

Table II

Product added	Per cent in Oil	Almen	Viscosity Increase, Per cent
Benzyl butyl trithiocarbamate	7	8	23.5
o-Chlor benzyl butyl trithiocarbonate	7	40	16.7
Trichlor benzyl butyl trithiocarbonate	7	40	15.4
Dibenzyl trithiocarbonate	7	12	25.0
Di(trichlorbenzyl)trithiocarbonate	7	40	14.9

The foregoing examples bring out the fact that the presence of the chlorine actually seems to stabilize the oil compositions while at the same time improving the E. P. properties.

Other examples of the new lubricating oil compositions are set forth in Table III.

Table III

Product added	Per cent in Oil	S. A. E. (1000 R. P. M., 14:6:1 rubbing ratio; 77-79 lbs./sec. loading rate) lbs. failed
Di(chloro ethyl phenyl ethyl) trithiocarbonate	9.3	360
Di(dichlor ethyl phenyl ethyl) trithiocarbonate	7.3	350
Di(trichlor ethyl phenyl ethyl) trithiocarbonate	6.4	310
Di(tetrachlor ethyl phenyl ethyl) trithiocarbonate	5.9	300
Dichloro diethyl phenyl ethyl, ethyl xanthate	10.0	370
O-ethyl S-trichlor benzyl monothiocarbonate	10.0	313
Di(o-chlor benzyl) trithiocarbonate	7.0	340
α-(2,4 dichlor phenyl) ethyl trithiocarbonate	10.0	354
Trichlor benzyl ester of benzothiolic acid	10.0	370
Trichlor phenyl ethyl, ethyl xanthate	10.0	358

The above data show the high efficiency of the new oil compositions. Obviously, other chloraralkyl esters of thio acids can be used where convenient or desirable. Particular mention may be made of α-(2,4 dichlor phenyl) ethyl, ethyl xanthate, di(methyl chlor benzyl) trithiocarbonate, dichlor phenyl ethyl diethyl dithiocarbamate, trichlor phenyl ethyl methyl xanthate, trichor phenyl ethyl amyl xanthate and the trichlor phenyl ethyl ester of benzothiolic acid.

Again, the foregoing examples are to be taken as illustrative of the invention and not limitative thereof. While the character of the invention has been described in considerable detail and numerous examples furnished of the preparation of the new additives and of the preparation and properties of the new oil compositions, it will be obvious to one skilled in the art that numerous modifications and changes can be made. For example, the carrying agent for the extreme pressure agent can be varied widely. The inventon includes broadly the chloraralkyl esters of thio acids dissolved, dispersed or emulsified in any suitable carrying agent such as kerosene or other light petroleum hydrocarbons, benzene and other related hydrocarbons, alcohols, esters, ethers, fatty vegetable and animal oils as well as mineral hydrocarbon lubricating oils. This invention is limited solely by the claims attached hereto as part of the present specification.

What is claimed is:

1. A composition of matter comprising an admixture of a hydrocarbon lubricating oil base admixed with minor amounts sufficient to impart E. P. properties to the lubricant of a chlor phenalkyl ester in which the ester forming group consists of carbon, hydrogen and chlorine of a thio acid the chlorine being attached to the phenyl nucleus of the said phenalkyl group.

2. A composition of matter comprising an admixture of a hydrocarbon lubricating oil base admixed with minor amounts sufficient to impart E. P. properties to the lubricant of a chlor phenalkyl ester in which the ester forming group consists of carbon, hydrogen and chlorine, of trithiocarbonic acid the chlorine being attached to the phenyl nucleus of the said phenalkyl group.

3. A composition of matter comprising an admixture of a hydrocarbon lubricating oil base admixed with minor amounts sufficient to impart E. P. properties to the lubricant of a chlor benzyl ester in which the ester forming group consists of carbon, hydrogen and chlorine of a thio acid the chlorine being attached to the phenyl nucleus of the said benzyl group.

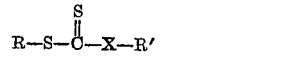
4. A composition of matter comprising a base lubricating oil admixed with minor amounts sufficient to impart E. P. properties to the lubricant of a chlor benzyl ester in which the ester forming group consists of carbon, hydrogen and chlorine, of a thiocarbonic acid the chlorine being attached to the phenyl nucleus of the said benzyl group.

5. A composition of matter comprising an admixture of a hydrocarbon lubricating oil base admixed with minor amounts sufficient to impart E. P. properties to the lubricant of a chlor benzyl ester in which the ester forming group consists of carbon, hydrogen and chlorine of a thiocarbonic acid the chlorine being attached to the phenyl nucleus of the said benzyl group.

6. A composition of matter comprising an admixture of a hydrocarbon lubricating oil base admixed with minor amounts sufficient to impart E. P. properties to the lubricant of a chlor benzyl ester in which the ester forming group consists of carbon, hydrogen and chlorine of a thiocarbamic acid the chlorine being attached to the phenyl nucleus of the said benzyl group.

7. A composition of matter comprising an admixture of a hydrocarbon lubricating oil base admixed with minor amounts sufficient to impart E. P. properties to the lubricant of a chlor benzyl ester in which the ester forming group consists of carbon, hydrogen and chlorine of a trithiocarbonic acid the chlorine being attached to the phenyl nucleus of the said benzyl group.

8. A composition of matter comprising an admixture of a hydrocarbon lubricating oil base admixed with minor amounts sufficient to impart E. P. properties to the lubricant of a compound of the type



where R represents a radicle consisting of carbon, hydrogen and chlorine in the form of a chlor substituted aralkyl radicle having the chlorine attached to the nucleus of the aryl group and R′ represents any aliphatic or aromatic radicle and X represents an element of group VI of the periodic table of atomic number not more than 16.

9. An extreme pressure lubricant comprising an hydrocarbon lubricating oil base and in admixture therewith a minor amount sufficient to impart E. P. properties to the oil of a chloraralkyl ester of a thiocarbonic acid the chlorine being attached to the aryl nucleus of the said aralkyl group.

10. An extreme pressure lubricant comprising

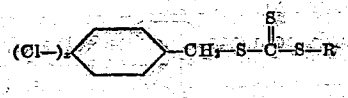
an hydrocarbon lubricating oil and in admixture therewith a minor amount but sufficient to impart E. P. properties to the oil of a chlor benzyl ester of a thiocarbonic acid the chlorine being attached to the phenyl nucleus of the said benzyl group.

11. An extreme pressure lubricant comprising an hydrocarbon lubricating oil base and in admixture therewith a minor amount sufficient to impart E. P. properties to the oil of a chlor benzyl ester of trithiocarbonic acid the chlorine being attached to the phenyl nucleus of the said benzyl group.

12. An extreme pressure lubricant comprising an hydrocarbon lubricating oil base and in admixture therewith a minor amount sufficient to impart E. P. properties to the oil of a chlor benzyl ester of a dithiocarbamic acid the chlorine being attached to the phenyl nucleus of the said benzyl group.

13. An extreme pressure lubricant comprising an hydrocarbon lubricating oil base and in admixture therewith a minor amount sufficient to impart E. P. properties to the oil of a trichlor benzyl ester of a dithiocarbamic acid the chlorine being attached to the phenyl nucleus of the said benzyl group.

14. An extreme pressure lubricant comprising an hydrocarbon lubricating oil base and in admixture therewith a minor amount sufficient to impart E. P. properties to the oil of a product of the structure



where x is an integer less than 4 and R is an organic ester forming group.

15. An extreme pressure lubricant comprising an hydrocarbon lubricating oil base and in admixture therewith a minor amount but sufficient to impart E. P. properties to the oil of di(trichlor benzyl) trithiocarbonate.

16. An extreme pressure lubricant comprising an hydrocarbon lubricating oil base and in admixture therewith a minor amount but sufficient to impart E. P. properties to the oil of trichlor benzyl butyl trithiocarbonate.

17. An extreme pressure lubricant comprising an hydrocarbon lubricating oil base and in admixture therewith a minor amount but sufficient to impart E. P. properties to the oil of trichlor benzyl diethyl dithiocarbamate.

EDWARD S. BLAKE.

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Certificate of Correction

Patent No. 2,438,599. March 30, 1948.

EDWARD S. BLAKE

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 2, line 8, in the formula, for "(R–CH.OH)" read (*R–CS.OH*); column 6, line 9, for "dichlorine" read *dichloride*; column 9, lines 71 and 72, and column 10, lines 4 and 5, lines 12 and 13, lines 28 and 29, lines 36 and 37, lines 44 and 45, and lines 52 and 53, claims 1, 2, 3, 5, 6, 7, and 8 respectively, strike out the words "an admixture of"; column 10, line 72, and column 11, lines 4, 11, 18, and 25, claims 9 to 13 inclusive, after "ester" insert *in which the ester forming group consists of carbon, hydrogen and chlorine*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of July, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.