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LUBRICATING COMPOSITION

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1 Claim. (Cl. 252—48)

This invention relates to lubricating oils and more particularly to improved lubricating oils of high film strength, high resistance to oxidation, and markedly reduced formation of corrosive products during use.

Present-day mechanical devices require lubricating oils of high film strength, of high oiliness characteristics, and of low tendency to oxidize during use. It has been found that the present-day hydrocarbon lubricants of the very highest quality are deficient in these very important characteristics. These three properties are of vital importance under conditions of thin film lubrication where the lubricant has been squeezed from between the friction surfaces because of high pressure, slow speeds, and other causes. In modern engines, large surfaces of oil are exposed to the action of atmospheric oxygen, promoting rapid oxidation. It is readily seen that the viscosity or the body of the lubricant plays no part in thin film lubrication and that the remaining film of oil must have a very high film strength and be of high oiliness value to prevent rupture of the film of the lubricant, which would cause seizure. The oil film must tend to keep the coefficient of friction as low as possible. The oil must resist oxidation when these thin film are heated in the presence of atmospheric oxygen as they are in use.

Mechanical devices are being designed for higher pressure operation, and the film strength of the best quality straight hydrocarbon lubricant has been found to be too low for satisfactory service. It will be obvious that an invention which provides a means of improving the film strength of these lubricants is of great importance to the art of lubricant manufacture and to the designer and fabricator of mechanical devices.

Substantially all machines operate in part or at times totally under conditions of boundary or thin film lubrication, under which conditions the oiliness or unctuosity of the lubricant is the first and primary requisite of efficient operation. Those skilled in the art of lubricant manufacture or machine manufacture will readily appreciate the value of an invention that will improve the oiliness of these otherwise high-quality lubricants. Furthermore, sludge and acid are especially deleterious under conditions of thin film lubrication. The sludge is not a lubricant in any sense of the word, and the soluble acid is particularly corrosive to bearing metals such as cadmium-silver, copper-lead, and the like.

In starting idle mechanical equipment which is lubricated from a sump by pumping or circulating the lubricant, there is always a short period of

time in which the rubbing surfaces must operate under conditions of dry friction if ordinary hydrocarbon lubricants are used. With dry friction, the wear on friction surfaces is extreme; and during cold weather when the lubricant is sluggish or during periods when the lubricating system is not functioning properly for one reason or another, rubbing surfaces may not only suffer considerable wear but may be damaged to the point where they must be replaced. The product of our invention has a very important property of reacting with the metal surfaces, penetrating or adsorbing on the metal surfaces, and leaving a film of lubricant with high oiliness character, which remains on the metal surface irrespective of the length of time the machine has been idle.

This high oiliness film gives very even and smooth operation, which may be easily discerned by the experienced operator or lubricating engineer.

When the hydrocarbon lubricants are diluted with unburned fuel or with other light hydrocarbons, the small degree of oiliness of the original hydrocarbon lubricant is greatly decreased. We have found that the addition of the products of our invention to hydrocarbon lubricants more than compensates for the loss in oiliness and load-carrying ability from dilution.

It is well known that, in order to obtain lubricants which are preeminently satisfactory from the standpoint of oxidation in use, it is necessary to refine the oil thoroughly and then to add an inhibitor of oxidation. The thorough refining may consist of more and heavier acid treatments or solvent treating so as to remove a considerable part of the oil and leave only the most stable portion. Such drastic refining is necessary in order to obtain stability with respect to sludge formation, but the oil is then subject to easy oxidation to form soluble acids and other corrosive materials. This can be prevented by the addition to the refined oil of small amounts of materials which either prevent the formation of these corrosive products or by some action render them inert. Furthermore, such well-refined oils are susceptible to the formation during use of lacquer-like materials which tend to stick rings. This results in blow-by and hence loss of power, failure of lubrication, scratching, scoring, overheating, and eventually replacement of parts. It is practically impossible to refine a lubricant in such a manner as to avoid all three of these difficulties, namely, soluble corrosive products, sludge, and lacquer. It is considerably more ad-

vantageous to add the materials of our invention and avoid these difficulties by this method.

Certain compounds are adsorbed or absorbed by metals thus forming tenacious films at the surface of metals; these films are able to stand high pressures. X-ray diffraction methods have shown that compounds containing highly polar molecules, that is, molecules of unsymmetrical electrical character containing an atom or group of atoms exhibiting a secondary or residual valence, tend to produce regimentation of the molecules of hydrocarbon oil when added thereto. A metal immersed in a strongly polar compound will show a film of the compound in which there is a regimentation of molecules oriented with respect to the surface of the metal by which they are adsorbed or absorbed.

Many of our additive materials are effective when added to poorly refined or even wholly unrefined lubricants. The addends may thus be substituted in whole or in part for the usual refining processes.

In the prior art of applying these principles to the manufacture of lubricants, many diverse types of materials have been suggested to be added to obtain improvement in various characteristics. It has been found that the addition of various compounds frequently improves film strength, oxidation resistance, noncorrosiveness, and other characteristics.

One object of our invention is to provide improved inhibitors of oxidation and corrosion for addition to lubricants.

Another object of our invention is to provide film strength improving addition agents suitable for use in lubricants and especially in crankcase lubricants.

Other and further objects of our invention will appear in the course of the following description.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereinafter fully described and particularly pointed out in the claims.

In general, our invention contemplates an oil of lubricating viscosity having added thereto a small amount of an organic thiocarbonate of the general formula



in which C represents carbon, X represents either oxygen or sulfur (at least one of the X's must be sulfur) and R and R' are organic radicals one or both of which contain carbon, hydrogen, and at least one other element besides halogen. Halogen may be present in the R's but in that case another characterizing element must also be present. The elements which we refer to here as "characterizing elements" include oxygen, sulfur, selenium, tellurium, nitrogen, phosphorus, arsenic, and metallic elements, such as, tin, antimony, bismuth, and the like. The R's may be aliphatic, carbocyclic, or heterocyclic in character. It will be apparent that by thiocarbonate in the appended claims we mean to include mono- and trithiocarbonates as well as the dithiocarbonates (xanthates).

The introduction of this characterizing element into our thiocarbonates permits of an extraordinary flexibility in the design of the addend for a particular use. Thus it permits the introduction of additional sulfur if the sulfur in the thiocarbonate is insufficient in amount or the introduction of other forms of sulfur if the thio-

carbonate sulfur is too stable or too unstable. The additional inhibiting action of phosphorus, nitrogen, or organo-metallic groups may be added to the molecule to produce an extremely effective inhibitor of oxidation and/or corrosion. Furthermore the newly introduced elements have a considerable effect on the activity of the thiocarbonate sulfur and it may be activated or depressed by the use of suitable groups in the R's of our thiocarbonates. Chlorine may in turn have an activating effect on the characterizing element or elements.

The substituted thiocarbonates of our invention show an unexpected improvement over the corresponding unsubstituted thiocarbonates and even over mixtures of the unsubstituted thiocarbonates with other compounds having the same substituting groups. Thus a xanthate containing a triphenyltin group in the organic radical shows a greater effect as an antioxidant than the triphenyltin group in, say, tetraphenyltin plus the same xanthate without the triphenyltin group. Similar unexpected results are obtained on the introduction of oxygen as an oiliness factor, halogen, nitrogen, phosphorus, sulfur metal and the like as film strength or inhibiting factors.

The particular thiocarbonates of this invention have a dual action in a lubricant. One action involves increased load-carrying ability and/or oiliness, while another action is directed to the stability of the lubricant. For load-carrying capacity, quantities ranging from 0.1 per cent to about 10 per cent may be added. As an anti-corrosive agent and/or an anti-sludging agent, much smaller amounts may be required ranging from approximately 0.001 to 1.0 per cent. The action of our thiocarbonates is specific but difficult to understand. These compounds may be added to any type of hydrocarbon lubricants but show an unusual value in highly refined and solvent treated lubricants. By oil having lubricating viscosity in the appended claims, we mean to include the so called mineral oils and various hydrogenated, polymerized and otherwise synthetically treated oils such as voltolized oils, aluminum chloride treated oils, and the like. Furthermore the lubricating oil may consist in whole or in part of shale oil, animal or vegetable oils such as castor oil, lard oil, corn oil, cottonseed oil, and the like.

In practice, it is better to employ compounds whose boiling point is above 250° F. in order that the addition compound will not be evaporated or distilled in use. The selection of a particular compound or compounds to be used as an addition agent to the hydrocarbon or other oil is to be made considering the physical and chemical properties of the various compounds and the use to which the blend is put. Thus, if water is likely to be present during use, a salt or combination of salts is selected which is not affected by water. If a particular added compound proves too volatile for its application, a higher boiling material should be used and the more volatile compound used for blending in an oil intended for duty at lower temperatures. In general, for automotive crankcase lubricants, we prefer to use compounds having vapor pressures of less than atmospheric at 250° F.

The following compounds may be used in accordance with our invention. All and each of these are to be considered as examples of our invention when blended in minor proportion in an oil of lubricating viscosity.

One or both of the organic radicals in our

mono-, di-, or trithiocarbonates may be of various types as shown in the following classification. Each of the following organic, or organo-metallic radicals may be combined with mono-, di- and trithiocarbonate radicals as further examples of our invention.

I—Aliphatic types

A. Containing oxygen

a. Alcohols

1. Hydroxyethyl ethylxanthate
2. Reaction product of potassium laurylxanthate and glycerol monochlorohydrin or glycerol dichlorohydrin. 10
3. Reaction product of potassium ethoxyethylxanthate with chlorinated, hydroxylated paraffin wax which has been chlorinated to 20 per cent chlorine and had half the chlorine removed by treatment with aqueous caustic under pressure to form the hydroxy compound. 15

b. Ethers

4. Butoxyethyl butoxyethylxanthate
5. Reaction product of potassium amyltrithiocarbonate with paraffin wax chlorinated to 23 per cent chlorine and treated with sodium butylate to remove about one-third of the chlorine to make the butyl ether. 20
6. Reaction product of potassium amylxanthate with beta, beta prime-dichloroethyl ether.
7. Methyl ethoxyamylxanthate 25

c. Ketones

8. Reaction product of potassium amylxanthate with chloroacetone
9. Reaction product of potassium amylxanthate with symmetrical dichloroacetone so as to form di(amylxanthylmethyl) ketone.
10. Reaction product of potassium amylxanthate with symmetrical dichloroacetone so as to form amylxanthylmethyl chloromethyl ketone. 30
11. Unsaponifiable oxidation products of paraffin wax chlorinated and part or all of the chlorine removed by condensation with sodium ethylxanthate 35

d. Aldehydes

12. Alpha-butylxanthylbutyraldehyde
13. Alpha-ethoxyethylxanthylcinnamaldehyde

e. Acids and salts

14. Alpha-amylxanthylstearic acid
15. Calcium amylxanthylchlorostearate
- 15a. Tin amylxanthylchlorostearate
16. Ethoxyethylxanthylphenylstearic acid
17. Aluminum ethoxyethylxanthylphenylstearate

f. Esters

18. n-Butyl ethylxanthylacetate
A mixture of 65 parts of finely powdered potassium ethylxanthate, 65 parts of n-butyl chloroacetate, and 200 parts of acetone was agitated and heated for five hours. The acetone solution was drawn off, concentrated, and the residual oil distilled at 128–135 at one mm. pressure. 45
19. Methyl ethylxanthylchlorostearate
A mixture of 48 parts of finely powdered potassium ethylxanthate, 102.5 parts of methyl dichlorostearate, and 100 parts of acetone was similarly refluxed and separated. The residual oil contained 4.05 per cent sulfur. A one per cent blend of this material in a S. A. E. 30 mineral oil showed a Timken film strength of 28 pounds on the arm. The mineral oil alone had a Timken film strength of only 9 pounds on the arm. 50

g. Amides

20. Amylxanthylsuccinylamide
21. Laurylxanthylauramide

B. Containing sulfur

a. Mercaptans

22. Mercaptoamyl butoxyethoxyethylxanthate 60

b. Sulfides and polysulfides

23. Amylxanthyl mercaptomethylstearate
24. Reaction product of sodium laurylxanthate with beta, beta prime-dichloroethyl sulfide
25. Reaction product of sodium amyltrithiocarbonate with dichloroamyl trisulfide. 65

c. Thioacids and derivatives

26. Reaction product of sodium amylmonothiocarbonate with methyl alpha-chlorothioacetate
27. Reaction product of lithium isobutylxanthate with alphas-bromothiovaleramide. 70

d. Sulfones and sulfoxides

28. Reaction product of sodium ethoxyethylxanthate with omega-chloroamylsulfone
29. Reaction product of sodium hexylxanthate with omega-chloroamylsulfoxide 75

e. Sulfurized aliphatic compounds

30. Reaction product of potassium hexylxanthate with sulfur and chlorine bearing methyl oleate
31. Reaction product of potassium ethylxanthate with sulfur chloride treated methyl linoleate
32. Reaction product of potassium benzylxanthate with sulfur chloride treated methyl esters of soy bean or corn oil acids

C. Containing nitrogen

a. Amines

33. Beta-aminoethyl ethylxanthate
34. Reaction product of potassium octadecylxanthate with 3-amino-2-chloropentane
35. Reaction product of potassium amylxanthate with 3-dimethylamino-2-chloropentane

b. Nitro compounds

36. Omega-nitroamyl amylxanthate
37. Reaction product of potassium butylxanthate with nitro-chloro-paraffin wax

c. Cyanides, isocyanides, thiocyanides, cyanates

38. Thiocyanato-ethyl laurylxanthate
39. Reaction product of sodium ethoxyethylxanthate with chloroacetoneitrile
40. Reaction product of sodium propylxanthate with omega-chloroamyl isocyanide
41. Reaction product of sodium amylxanthate with omega-chloroamyl cyanate.

D. Containing phosphorus

42. Tri(ethoxyethylxanthyl)phosphate
43. Tri(ethoxyethylxanthyl)phosphite
44. Tri(ethoxyethylxanthyl)thiophosphate
45. Methyl butoxyethylxanthyl phosphinostearate
46. Diethylphosphinoethyl amylxanthate

E. Containing metals

a. Group IV

47. Triethylstannylamyl amylxanthate
48. Triethylplumbylethyl amyltrithiocarbonate
49. Triamylstannylethyl ethoxyethylxanthate

b. Group V

50. Diethylarsenylamyl ethylxanthate
51. Diethylantimonylamyl ethylmonothiocarbonate
52. Diethylbismuthylamyl ethylxanthate

c. Group VI

53. Amylseleniumethyl ethoxyethylxanthate
54. Amyltelluriumethyl butylxanthate

II—Carbocyclic types

A. Containing oxygen

a. Phenols

55. Hydroxyphenyl ethylxanthate
56. Omega-hydroxyphenylamyl amylxanthate
57. Reaction product of potassium amylxanthate with chlororesorcinol
58. Reaction product of potassium amylxanthate with halogenated paraffin wax substituted phenol

b. Alcohols

59. Reaction product of sodium butoxyethylxanthate with o-chlorobenzyl alcohol
60. Reaction product of sodium butylxanthate with hydroxylated, halogenated phenylated wax

c. Ethers

61. Anisyl laurylxanthate
62. Omega-phenoxyamyl amylxanthate
63. Phenoxyphenyl laurylxanthate
64. Reaction product of potassium benzylxanthate with chlororesorcinol dimethyl ether

d. Ketones

65. Reaction product of sodium ethylxanthate with chlorobenzophenone
66. Omega-amylxanthylacetophenone
67. Reaction product of potassium isobutylxanthate with chlorostearoyltetralin

e. Aldehydes

68. Reaction product of sodium benzylxanthate with o-chlorobenzaldehyde
69. Reaction product of sodium ethoxyethylxanthate with omega-chlorotolu-aldehyde

f. Acids and salts

70. Reaction product of potassium amylxanthate with cinnamic acid dichloride
71. Reaction product of sodium ethylxanthate with chlorine-bearing dinaphthylstearic acid
72. Calcium salt of the reaction product of sodium laurylxanthate with o-chlorobenzoylbenzoic acid

g. Esters

73. Reaction product of potassium amylxanthate and chlorinated phenyl benzoate
74. Phenyl ethoxyethylxanthyl phenylstearate

75. Chlorinated wax condensed (Friedel-Crafts) with phenyl benzoate and sodium amylxanthate
- b. Amides
 76. Potassium butoxyethylxanthate condensed with chloro-stearanilide
 77. Chloro-amylxanthylsteartoluidide
13. Containing sulfur
 - a. Mercaptans and thiophenols
 78. Mercapto-dodecalhydro-diphenyl ethylxanthate
 79. Reaction product of potassium butylmonothiocarbonate and o-chlorophenyl ethylmercaptan
 - b. Sulfides and polysulfides
 80. Reaction product of chlorobenzyldisulfide and potassium hexyltrithiocarbonate
 81. Reaction product of sodium amyltrithiocarbonate and chlorophenylethyl disulfide
 82. Reaction product of sodium amylmonothiocarbonate with chlorodiphenyltrisulfide
 83. Reaction product of potassium amylxanthate with chlorodiphenylsulfide
 - c. Thioacids and derivatives
 84. Reaction product of sodium laurylxanthate with omega-chlorothiobutolulic acid
 85. Reaction product of sodium benzylxanthate with alphasbromothiobutyramide
 - d. Sulfones and sulfoxides
 86. Reaction product of potassium octadecylxanthate with chlorodiphenylsulfone
 87. Reaction product of potassium ethyltrithiocarbonate with chlorodibenzylsulfone
 88. Reaction product of sodium ethylmonothiocarbonate with chlorodibenzylsulfide
- C. Containing nitrogen
 - a. Amines
 89. Reaction product of lithium butylxanthate with chlorodiphenylamine
 90. Reaction product of sodium benzylxanthate with o-chlorodimethylaniline
 - b. Nitro compounds
 91. Nitrocresyl thiocarbonate
 92. Amyl nitrobenzylxanthate
 - c. Azo compounds
 93. Reaction product of potassium amylxanthate with the product of coupling diazotized p-chloroaniline with alpha-naphthol
- D. Containing phosphorus
 94. Reaction product of sodium ethoxyethyl trithiocarbonate with chlorophosphazobenzene
 95. Reaction product of sodium butoxyethoxyethylxanthate with p-chlorophosphinobenzene
- E. Containing metals
 96. Reaction product of triphenyl-omega-chloroamyltin with sodium amyltrithiocarbonate
 97. Triethylstannylphenyl benzylxanthate
 98. Triethylplumblyphenyl amylxanthate
 99. Ethylmercuriiphenyl amylxanthate
- III—Heterocyclic types
 - A. Containing oxygen
 100. Reaction product of potassium butylxanthate with chlorodioxane
 101. Reaction product of potassium ethylxanthate with chlorodiphenylene oxide
 102. Reaction product of chlorohydroxythiophene with sodium butoxyethylxanthate
 - B. Containing sulfur
 103. Reaction product of potassium ethoxyethylxanthate with chlorothianthrene
 - C. Containing nitrogen
 104. Reaction product of potassium amylxanthate with alpha-chloropyridine

Any of these compounds or other members of the classes represented may be used within the scope of our invention.

The thiocarbonates have varying degrees of solubility in hydrocarbon and other oils. In some cases it is necessary to use a solvent for the compound or to form colloidal suspensions of the compound in oil. While some of these compounds have only limited solubility in hydrocarbon oils, it is to be remembered that because of their great efficiency extremely small amounts are often effective. Thus we may use as little as 0.001 per cent of some of these compounds, and it will be seen that a fairly insoluble material may dissolve to a sufficient extent to be satisfactory for our purpose. In general, more than 0.001 per cent of

our addition agents are used, and we may add one, two, or even five per cent or more.

Furthermore, it is well known that different types of oils have different capabilities of dissolving a given material. For some purposes therefore, we prefer paraffinic, for other purposes, asphaltic, and for still other purposes, naphthenic or mixed base lubricants. Another method of obtaining a satisfactory mixture of addition agent with the hydrocarbon oil is the use of a mutual solvent to bring the addend into solution. Alternatively, peptizing agents may be added to maintain the thiocarbonates in permanent suspension.

Many of the more difficultly soluble materials are rendered more soluble by the introduction of alkyl groups, particularly those containing four or more carbon atoms. The isoamyl, octyl, lauryl, and octadecyl radicals and radicals from paraffin wax greatly increase the solubility of organic compounds in oil. One or more of such groups may be introduced as required.

It is sometimes advantageous to combine more than one of these compounds in a blend to obtain particular properties. We accomplish this by mixing two or more of these compounds together and blending the mixture with the hydrocarbon oil or by blending one in the hydrocarbon oil, blending the second into this mixture, and so on until the composition is complete.

The various thiocarbonates usually improve both the film strength and oxidation characteristics of the hydrocarbon oil. For example, the sludging tendencies may be decreased by as little as 0.001 per cent of our thiocarbonates. The oxidation characteristics of lubricants are very important, and these are markedly improved by our compounds. The ability to reduce friction is another feature contributed to lubricants by some of our compounds.

It may be desirable to include in one and the same blend, in addition to the addends here described, other addends for specific purposes. Thus, we may add a pour point depressor such as a naphthalenechlor wax condensation product, a viscosity index improver such as certain resins or polymerized hydrocarbons, and sulfur or phosphorus containing inhibitors, such as alkyl and aryl phosphite esters and alkyl and aryl phosphate esters in addition to our thiocarbonates. Furthermore, various metallic compounds may be added to the blend without interfering with the action of our ingredients. Indeed, in some cases it is advantageous to combine with our compounds in a hydrocarbon oil blend such materials as calcium dichlorostearate, sodium stearate, sodium oleate, sodium chloroleate, tin oleate, sodium naphthenates, tin naphthenate, chromium oleate, aluminum stearate, and other metallic soaps or inorganic-organic salts.

Our invention also contemplates the use in lubricating compositions comprising a major proportion of lubricating oil of minor amounts of the previously identified sulphur compounds with a separate organic halogen compound. The halogen compounds which may thus be employed may be classified as follows:

Cyclic compounds, such as halogenated

- I—Benzene and related compounds such as:
 - (1) Halogenated benzene, e. g.
 - (a) Chlorinated benzene, e. g. The dichlorobenzenes, notably the ortho compound
 - (b) Brominated benzene, e. g. Ortho-dibrom benzene
 - (c) Fluorinated benzene

- (2) Halogenated derivatives of benzene such as:
- Halogenated homologs of benzene, e. g.
Mono-chlor toluene
Mono-chlor xylene
Mono-chlor cymene
Ethyl mono-chlor benzenes
Propyl mono-chlor benzenes
Di-ethyl dichlor benzenes
Propyl dichlor benzenes
Di-ethyl tetrachlor benzenes
 - Halogenated amino derivatives of benzene, e. g.
Chlorinated aniline
Mono-chlor aniline (preferably the ortho-compound)
Mono-chlor di-methyl aniline
Chlorinated toluidines
Chlorinated xylidines
Chlorinated diphenylamine
 - Halogenated hydrobenzenes, e. g.
Hydrogenated dichlor-benzenes
Dichlorhexahydrobenzene
(Dichlor cyclohexane)
- II—Polyphenyls, and related compounds, including diphenyl, diphenyl benzenes, etc., such as
- Halogenated diphenyl, e. g.
 - Chlorinated diphenyl, e. g.
Mono-chlor diphenyls
Di-chlor diphenyls
Tri-chlor diphenyls
 - Brominated diphenyl, e. g.
The mono-brom diphenyls
 - Fluorinated diphenyl
 - Halogenated derivatives of diphenyl, such as,
 - Halogenated homologs of diphenyl, e. g.
Chlorinated phenyl-toluenes
Ethylated, or propylated, chlorinated diphenyl, e. g. di-ethyl tetrachlor diphenyl
 - Halogenated amino derivatives of diphenyl, e. g.
Chlorinated phenyl-anilines
Chlorinated phenyl-toluidines
Chlorinated diphenyl amines (xenyl amines)
 - Halogenated hydridiphenyls, e. g.
Chlorinated phenyl hexahydrobenzene
Chlorinated dodecahydridiphenyl
- III—Naphthalene and related compounds, such as
- Halogenated naphthalene
 - Chlorinated naphthalene, e. g. -mono-chlor naphthalene
 - Brominated naphthalenes, e. g. -mono-brom naphthalene
 - Fluorinated naphthalene
 - Halogenated derivatives of naphthalenes, such as:
 - Halogenated homologs of naphthalenes, e. g.
Chlorinated methyl naphthalenes, such as -methyl naphthalene
Chlorinated ethyl, propyl, or isopropyl naphthalenes
 - Halogenated amino derivatives of naphthalene, e. g.
Chlorinated naphthylamines
Mono-chlor naphthyl amine
 - Halogenated hydronaphthalenes, e. g.
Chlorinated decahydronaphthalene
Chlorinated tetrahydronaphthalene
- IV—Phenanthrene and anthracene and related compounds, such as:
- Chlorinated phenanthrene, chlorinated anthracene
 - Halogenated derivatives of phenanthrene and anthracene, such as:
 - Halogenated homologs, e. g.
Chlorinated 1-methyl phenanthrene
Chlorinated 3-methyl phenanthrene
Chlorinated 9,10 dimethyl phenanthrene
Chlorinated propyl and isopropyl derivatives of phenanthrene such as retene
Chlorinated dimethyl anthracenes
Chlorinated -methyl anthracene
Chlorinated propyl and isopropyl derivatives of anthracene
 - Halogenated amino derivatives, e. g.
Chlorinated phenanthrylamines
Chlorinated anthramines
 - Halogenated hydrophenanthrenes and Halogenated hydroanthracenes, e. g.
Chlorinated retene oil (contains hydro retene)
- V—Chrysene, picene, and related compounds, including their derivatives, such as homologs, amino derivatives and other substitution products.
- VI—Bridged ring compounds, such as the terpenes and related compounds, and their derivatives, e. g. chlorinated pinene.
- VII—Heterocyclic compounds, such as pyridine, quinoline, pyrrole, thiophene, and derivatives of them, e. g. mono-chlor pyridine.
- VIII—Nitriles derived from any of the above compounds, e. g.
- Chlorinated:
- Benzonitrile
 - Tolunitriles
 - Benzyl cyanide
 - Naphthyl cyanide
 - Xenyl cyanide
 - Cyclohexyl cyanide
- IX—Sulphides derived from any of the above compounds, e. g.
- Chlorinated:
- Diphenyl sulphide
 - Dibenzyl sulphide
 - Dixyl sulphides
 - Di-naphthyl sulphides
 - Dixenyl sulphides
 - Dicyclohexyl sulphide
- X—Mercaptans derived from any of the above compounds, e. g.
- Chlorinated:
- Benzyl mercaptan
 - Phenyl benzyl mercaptans
 - Naphthyl mercaptans
 - Phenyl propyl mercaptans
 - Cyclohexyl mercaptan
- XI—Thiocyanates, e. g.
- Chlorinated:
- Benzyl thiocyanate
 - Phenyl ethyl thiocyanate
 - Phenyl propyl thiocyanate
 - Cyclohexyl thiocyanate
- Halogen-bearing aliphatic compounds**
- I. Hydrocarbons, e. g.
- Chlorinated or fluorinated hydrocarbons which contain from four to ten or more carbon atoms and certain others containing less than four carbon atoms, e. g.
- Hexachlor ethane
 - Pentachlor ethane
 - Chlor propane
 - Chlor butane
 - Chlor pentane
 - Fluor hexane
 - Fluor octane
 - Fluor decane
 - Tetrachlor ethylene
 - Hexachlor propylene
 - Chlor butylenes
 - Chlor pentenes
 - Chlorinated unsaturated hydrocarbons obtained from products of partial pyrolytic decomposition of high boiling petroleum hydrocarbons.
 - Chlorinated petroleum wax
 - Chlorinated paraffin wax
 - Chlorinated petrolatum
 - Chlorinated aliphatic fractions of mineral oil
- II. Amines, e. g.
- Primary, secondary, and tertiary, e. g.
- Fluorinated tri-butyl amines
 - Fluorinated tri-amyl amines
 - Fluorinated hexyl amines
- III. Nitriles, e. g.
- Chlorinated or fluorinated
- Ethyl cyanide
 - Butyl cyanide
 - Octyl cyanide
 - Lauryl nitrile
 - Stearyl nitrile
- 45 The halogen bearing compounds which may thus be advantageously employed in combination with the sulphur compounds of the type above identified may also desirably contain oxygen and such halogen and oxygen bearing organic compounds may be classified as follows:
- Halogen and oxygen-bearing organic ring compounds**
- Oxygen-bearing derivatives of:
- A. "Carbon ring" type compounds
- of the aromatic, or allied type, including oxygen-bearing derivatives of benzene, naphthalene, anthracene, etc., also compounds of the bridged ring type, such as the terpenes, and related compounds.
 - of the class including the cycloparaffins, cyclo-olefines, etc. Examples of this class are oxygen-bearing derivatives of the following:
 - Hydrogenation products of benzene (e. g. cyclohexane, cyclohexene, cyclohexadiene), such as hydrogenated phenol, notably
Cyclohexanol
Di-hydro phenol
Tetra-hydro phenol
 - Hydrogenation products of naphthalene (e. g. decahydronaphthalene, tetrahydronaphthalene, etc.), such as the hydrogenated naphthols.
 - Naphthenes, such as naphthenic acid, etc.
 - of mixed type such as derivatives of indene, hydrindene, hydranthracene, etc.
- B. "Heterocyclic" type compounds
- of the aromatic or allied type including derivatives of pyridine, quinoline, etc.
 - other types such as furane and its derivatives and derivatives of thiophene, pyrrole, etc.

Halogen and oxygen-bearing aliphatic compounds

- Alcohols (mono-, di-, and tri-hydric) e. g.
 Ethylene chlorhydrin
 Glyceryl monochlorhydrin
 Fluorinated octyl alcohol
 Fluorinated decyl alcohol
 Fluorinated lauryl alcohol
 Chlorinated octadecyl alcohol
- Esters and salts, e. g.
 Methyl chlorpropionate
 Ethyl chlorlaurate
 Methyl dichlorstearate
 Chlorinated mono- and di-glycol esters of propionic, lauric, and stearic acids
 Chlorinated mono-, di-, and tri-glycerol esters of propionic, lauric, and stearic acids
 Methyl dichlorpalmitate
 Sodium chlorhydroxy stearate
 Calcium di-chloro stearate
 Aluminum di-chloro stearate
- Ethers, e. g.
 Chloromethyl propyl ether
 Chlor butyl ether
 Chlor amyl ether
 Chlor methyl lauryl ether
- Ketones, e. g.
 Chloromethyl ethyl ketone
 Chloridibutyl ketone
 Chlor palmitone
 Chlor laurone
 Chlor stearone
- Aldehydes, e. g.
 Chlorbutanal
 Chlorpentanal
- Acids, e. g.
 Chlorpropionic acid
 Chlorlauric acid
 Chlormyristic acid
 Chlorpalmitic acid
 Chlorstearic acid
 Chlorhydrostearic acid
 Chlorricinoleic acid
 Chlor crotonic acid
 Chlor acrylic acid
 Chlor oleic acid

Other halogen containing compounds which may be employed to advantage in lubricating compositions along with the previously identified sulphur compounds are as follows:

Halogenated aliphatic phosphorus-containing compounds

- Chlor-lauryl phosphine
 Chlor-octyl phosphine
 Chlor-di-ethyl di-thiophosphine sulfide
 Chlor-amyl phosphite
 Chlor-butyl phosphite
 Chlor-lauryl phosphite
 Chlor-lauryl thiophosphite
 Chlor-lauryl thiophosphite

Halogenated aliphatic compounds containing sulfur and nitrogen

- Chlor-lauryl thiocyanide
 Chlor-butyl thiocyanate

Halogenated aliphatic compounds containing sulfur

- Chlor-amyl sulfide
 Chlor-butyl disulfide

While the above compounds have been disclosed primarily as separate halogen compounds which may be used in conjunction with our thiocarbonates, they may also serve another use. Many of them may be used to react with alkali metal thiocarbonates to form the substituted thiocarbonates which are the principal products of our invention. For these secondary uses, the halogen in these compounds may be replaced in whole or in part. It will be obvious to those skilled in the art that most of these compounds are useful only in introducing the second R of our thiocarbonates since the first is derived from an alcoholic compound, carbon bisulfide and a caustic metal hydroxide. Furthermore it will be obvious that in order to come within the scope

of our claims the halogenated hydrocarbons listed above may be used only with such alkali thiocarbonates as contain in the first R group one of the characterizing elements.

Our addends are admirably adapted for use in lubricating oils of all types including those designed for use in automotive crankcases, Diesel oils, and any other oils of lubricating viscosity. Certain lubricating compositions containing certain of the addition agents above mentioned will be found particularly useful in the lubrication bearings formed of cadmium or lead containing bearing metals such as, for example, cadmium-silver and copper-lead bearings. Furthermore, our addends are advantageously blended in gasoline and other petroleum fuels either directly or after being blended first in a lubricating oil and then added to the fuel. Soap-thickened mineral oils of all types ranging from those showing only a slight increase in viscosity over that of the mineral oil alone to the semi-solid and solid greases containing fifty per cent or more of soap are amenable to treatment according to our invention. In making these greases, the usual soaps such as sodium stearate, aluminum stearate, calcium soaps of beta fat, and the like may be used to form the large part of the necessary soap. Various other thickening ingredients or materials for other purposes may be added. These include yarn, hair, graphite, glycerol, water, lampblack, mica, zinc, dust, litharge, and the like.

In making a lubricating gasoline, we blend 0.5 per cent of the product of Example 19 with gasoline. It is to be understood, however, that the hydrocarbon oil in the treated fuels may be of a viscosity of from about 35 seconds at 100° F. S. S. U. to 350 seconds or more and the amount of oil blended with the thiocarbonate to form the fuel addend may vary between 0% to 99.5%. In some cases the fuel may be prepared without adding any hydrocarbon oil. The quantity of thiocarbonate in the final blended fuel may vary from 0.0001 to 1.0% or slightly more.

It will be understood that certain features and sub-combinations may be employed without reference to other species or combinations. This is contemplated by and is within the scope of our claim. It is further obvious that various changes may be made in details within the scope of our claim without departing from the spirit of our invention. It is therefore to be understood that our invention is not to be limited to the details described.

Other forms may be employed embodying the features of our invention instead of the one here explained, change being made in the form or construction, provided the elements stated by the following claim or the equivalent of such stated elements be employed.

We therefore particularly point out and distinctly claim as our invention:

A lubricant comprising in combination a major proportion of an oil of lubricating viscosity and a minor proportion of methyl ethylxanthylchlorostearate.

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