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GEAR LUBRICANT

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1

This invention relates to the art of extreme pressure lubricant and is more particularly concerned with new and improved lubricant compositions which are capable of maintaining an effective lubricant film between engaged surfaces under high load pressures and high rubbing speeds.

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 so called extreme pressure lubricants. Such lubricants are composed of a lubricating oil base having incorporated therein a small amount of a chemical ingredient which will form, or which is capable of reaction under extreme pressure conditions to form, a lubricant film capable of withstanding these abnormally high pressures. The added ingredients are known to the art as E. P. (extreme pressure) additives, or E. P. bases. Among the substances which have been used for this purpose are sulfur, both free and chemically combined. Various chlorine and phosphorus compounds have also been used, principally chlorinated hydrocarbons and esters of various phosphorus acids. Combinations of these types of chemical ingredients have also been employed. None of the E. P. base formulations proposed up to the present time, however, have proved satisfactory over the range of service conditions encountered in automotive hypoid gears. Thus, whereas one E. P. lubricant will provide satisfactory lubrication under conditions of high speed shock loading and another under conditions of low speed, high torque operation, no one lubricant has been found to give adequate lubrication protection under both of these types of service conditions.

It is the object of this invention to provide an E. P. lubricant which is capable of maintaining a lubricant film, and thus providing highly efficient lubrication, under the extreme pressure conditions of both high speed and heavy load service. Other objects will appear from the following detailed description of the invention.

The invention resides in our discovery of a unique combination of three base ingredients, which combination provides outstanding effectiveness as an E. P. additive for hypoid gear lubricants. These three ingredients are the following:

1. A chlorinated aliphatic material in which the more reactive part of the chlorine has been replaced with a thiocarbonate group.

2. An ester obtained by reacting two moles of commercial hydroabietyl alcohol with one mole of malic acid.

2

3. A phosphorus acid ester obtained by reacting three moles of an alkyl-substituted phenol with approximately one mole of phosphorus pentoxide.

5 In order that our invention may be readily and fully understood, the several components which make up our novel extreme pressure lubricant will now be described in detail, including examples of procedures which may be followed in preparing these materials and test results demonstrating the outstanding effectiveness of the contemplated lubricant compositions.

LUBRICANT OIL BASE

15 The oil which forms the major proportion, from about 85 to about 99 per cent, by weight, of the gear lubricant composition herein contemplated may be any suitable lubricating oil, such as an oil derived from the refinement of a petroleum crude oil. The viscosity of the oil may vary, depending upon the intended application of the finished lubricant, from about 1 to about 10,000 centistokes at 100° F. Particularly preferred for use in this invention, i. e. in the hypoid gears of automotive vehicles, are lubricating oils having viscosities from about 10 to about 1500 centistokes at 100° F. The oil should, of course, also be selected on the basis of suitable pour point and viscosity index characteristics for the specific purpose intended, it being understood that the desired characteristics of the finished lubricant may be obtained by the addition of lubricating oil additives known to provide the desired effects on these properties in the oil.

CHLORINATED ALIPHATIC COMPOUND-THIOCARBONATE REACTION PRODUCT

As indicated hereinabove, this component of our composite additive is a polychlorinated aliphatic material, or a polychlorinated material predominantly aliphatic in nature, in which part of the chlorine is replaced by a thiocarbonate group.

45 The preferred procedure which may be followed in synthesizing this material involves substantial chlorination of an aliphatic compound or a predominantly aliphatic material, such as a petroleum naphtha, followed by reaction of the chlorinated material with an alkali or an alkaline earth metal salt of an alkyl thiocarbonic acid in such proportions and under such conditions that only part, preferably about one-third, of the chlorine (that is, the more reactive chlorine) is replaced by the alkyl thiocarbonate group.

55 In the chlorination step, the aliphatic material is chlorinated to such an extent that the final chlorinated product corresponds to a polychlor compound, and in the case of petroleum naphtha the chlorination is preferably carried to a point at which the product has an average composition corresponding to a tetra-chloronaph-

tha. In general, it may be said that chlorination should be carried to the point at which the chlorine content is from about forty per cent to about sixty per cent, although materials of lower and higher chlorine content may be used, depending upon the aliphatic constituent.

The range of aliphatic materials which may be chlorinated as the starting material extends from ethane to petroleum wax, the former being a compound containing two carbon atoms and the latter being a predominantly aliphatic material corresponding to a compound having about twenty-four carbon atoms. We have found, however, that the extremely short-chain compounds, represented by the ethane, and the extremely long-chain compounds, represented by petroleum wax, are somewhat more difficult to react and are somewhat less efficient in their effect in the final formulation than hydrocarbons of an intermediate range, and for this reason preference is given to aliphatic materials within the range of from about 5 to about 15 carbon atoms, particular preference being given to petroleum naphtha (or kerosene), a hydrocarbon material predominantly aliphatic in nature corresponding to a compound having about 10 carbon atoms and having a boiling range of from about 150° C. to about 275° C.

The thiocarbonate group which is used to replace a part of the chlorine is, as has been indicated above, derived from an alkali or alkaline earth metal salt of a thiocarbonic acid, preferably an alkyl thiocarbonic acid. The thiocarbonate radical may be a mono-, di- or trithiocarbonate, but in general preference is given to the dithiocarbonate (xanthate) compounds, characterized by the divalent group (OCS_2). The trithiocarbonate type of compounds, characterized by the divalent group (CS_3) have also been prepared and have been found to form effective extreme pressure agents in combination with the chlorinated aliphatic material, but from the standpoint of odor and cost, preference is to products in which the thiocarbonate constituent is a xanthate (divalent OCS_2) group.

As to the alkyl substituents in the thiocarbonate or xanthate groups, which are substituted in the chlorinated aliphatic material, it is preferable that such substituents be derived from aliphatic compounds of relatively low molecular weight. There is no particular advantage to be gained by having a long-chain alkyl group in the xanthate or thiocarbonate substituent from the standpoint of solubility, etc., and the lower molecular weight alkyl groups give a finished product in which the content of chlorine and characterizing divalent thiocarbonate groups (O_2CS , OCS_2 , or CS_3) is somewhat more highly concentrated.

As examples of the thiocarbonate or xanthate materials which may be reacted with chlorinated aliphatic materials to provide extreme pressure agents of the type contemplated by this invention, we may use sodium or potassium methyl, ethyl, propyl, isopropyl, benzyl, butyl, or amyl xanthates or the corresponding mono- or trithiocarbonates.

It is highly important, as stated above, that the proportions of reactants used and the conditions of reaction be controlled so that the final product contains both chlorine and thiocarbonate characterizing groups in chemical combination with the aliphatic hydrocarbon material. The relative amounts of chlorine and sulphur, or, more specifically, of chlorine and thio-

carbonate characterizing groups, in the finished product may be varied over a relatively wide range, but in general it may be said that the finished product should preferably be one which contains from about twenty-five to forty per cent chlorine and from about seven to fifteen per cent sulphur. Expressing the sulphur content as the equivalent amount of characterizing thiocarbonate groups present in the product, such preferred products are more accurately identified as containing from about ten per cent to about twenty-two per cent characterizing dithiocarbonate or xanthate (divalent OCS_2) groups or from about seven per cent to about seventeen per cent characterizing trithiocarbonate (divalent CS_3) groups. For general purposes it may be said that the characterizing-thiocarbonate-group-content is preferably from about seven per cent to about twenty-two per cent.

The reaction between the chlorinated aliphatic material and the alkali thiocarbonate is preferably carried out in the presence of a relatively low boiling point solvent. For convenience in reaction and purification, the solvent is preferably one in which the chlorinated aliphatic material and the reaction product are highly soluble but in which the alkali thiocarbonate and the alkali chloride are of low solubility. As an example of such a solvent we have found acetone to be highly satisfactory, although other solvents, such as methyl ethyl ketone, may be used. Alcohols may also be used as solvents in this reaction. Solvents such as acetone and methyl ethyl ketone are particularly desirable since they permit the reaction to proceed but tend to precipitate residual alkali thiocarbonate and chloride, thus permitting the process to be performed and the product substantially purified all in one step.

The general preferred procedure followed in effecting the replacement of the more highly reactive chlorine in chlorinated aliphatic materials with the thiocarbonate group is to dissolve the chlorinated aliphatic material in the solvent and add the alkali alkyl thiocarbonate in an amount sufficient to give a product having the desired chlorine and sulphur ratio. Under the conditions of reaction which we employ we have prepared materials using from about one-fourth to about twice as much alkali thiocarbonate (xanthate) as chlornaphtha. The preferred ratio, however, is to use a weighted amount of alkali thiocarbonate corresponding to from about forty per cent to about seventy per cent of the weight of the chlornaphtha used. It will be understood, of course, that these ratios vary with other chlorinated aliphatic materials, depending upon their hydrocarbon and chlorine content, and should also take into consideration the alkyl substituent which is attached to the characterizing thiocarbonate group.

As aforesaid, the preferred products contemplated by this invention are those obtained by replacing a part of the chlorine in chlorinated petroleum naphtha with an alkyl xanthate group. These materials are preferred to others in this general class of materials because of their ease of synthesis, their cost, etc. An exemplary procedure for preparing such a product, which we may term "chlornaphtha-xanthate reaction product" or "xantho-chlornaphtha" is the following:

EXAMPLE I

Chlornaphtha-xanthate reaction product

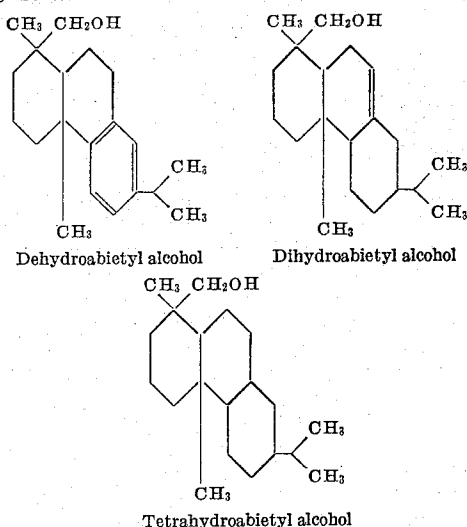
A chlorinated naphtha was first prepared by chlorinating petroleum naphtha (Stoddard sol-

vent) until it contained about fifty-four per cent by weight of chlorine. 200 parts of the chlornaphtha were dissolved in about 500 parts of acetone and placed in a reaction vessel heated by a water jacket and equipped with stirrer and reflux condenser. To this solution 120 parts of potassium ethyl xanthate were added and the mixture held at boiling temperature with stirring under reflux for about two hours. The resulting mixture was cooled to room temperature, filtered, and the filtrate subjected to distillation to remove the acetone. After removal of the acetone the product was washed to remove potassium salts and was dried and filtered. The finished reaction product obtained by the foregoing procedure, which for purposes of description herein may be termed "chlornaphtha-xanthate reaction product" or "chlornaphtha-ethyl xanthate reaction product" was a dark brown liquid containing about twelve per cent sulphur, or more specifically about seventeen per cent of the characterizing xanthate (divalent OCS_2) group, and thirty-seven per cent chlorine.

Variation in xanthate and chlorine content of the reaction product can be obtained by varying the degree of chlorination of the naphtha; by varying the amount of alkali xanthate used; and by varying the hydrocarbon substituent in the alkali xanthate. Thus products of widely varying chlorine and xanthate content are readily possible. In general, as indicated above, we prefer a product containing from about ten per cent to about twenty-two per cent of the characterizing xanthate group and from about twenty-five per cent to about forty per cent of chlorine.

Dihydroabietyl malate

This material is prepared by reacting 2 moles of hydroabietyl alcohol with 1 mole of malic acid. The hydroabietyl alcohol reactant used is the commercial mixture marketed by the Hercules Powder Co. This mixture of alcohols is comprised of three alcohols having the following structures:



The average proportions by weight of these alcohols in the commercial mixture are: 15 per cent dehydroabietyl, 40 per cent dihydroabietyl and 45 per cent tetrahydroabietyl. The commercial product also contains an average of about 15 per cent of non-alcoholic materials, which is considered as being comprised chiefly of methyl esters of hydrogenated rosin and hydrocarbons occurring in hydrogenated rosin.

Considering the average molecular weight of the alcohol portion of the commercial product which represents 1 equivalent of hydroxyl group, to be approximately 290, it is seen that since the mixture contains 15 per cent of non-alcoholic materials, then 341 grams will be required to provide one equivalent weight of the hydroxyl group. Consequently, when preparing dihydroabietyl malate from 0.375 mole of malic acid which contains two carboxyl groups, 0.75 mole, i. e. $341 \times 0.75 = 255.7$ grams of the commercial material will be required.

The following example will serve to illustrate a preferred procedure for preparing the dihydroabietyl malate ester.

EXAMPLE II

Preparation of dihydroabietyl malate

A reaction mixture consisting of 255.7 grams (0.75 mole) of commercial hydroabietyl alcohol and 50.2 grams (0.375 mole) of dl-malic acid were placed in a 500 ml. flask, provided with a thermometer, a mechanical stirrer and a condenser device (reflux water take-off) for removing water from the reaction as it evolved as an azeotrope of water and benzene. The mixture was heated to 130–135° C. and digested at this temperature for ½ hour. The reflux water take-off was filled with benzene and an amount of benzene was added to the reaction mixture such that the solvent refluxed while the flask contents were at 130–135° C. After 6 hours of refluxing, 11 ml. of water had been collected and the solvent was removed by gradually reducing the pressure in the system. The solvent-free product was warmed to 130° C. and suction filtered to remove an estimated 5 grams of residue. The filtered product had a neutralization number of 13.3, indicative of a neutral ester content of 89 per cent.

Alkyl phenol- P_2O_5 reaction product

This product may be prepared by reacting P_2O_5 with an alkylated phenol. The preferred alkylated phenols are mono-tertiary octyl phenol and di-tertiary amyl phenol, although other alkylated phenols, such as di-secondary amyl phenol, cetyl phenol, octadecyl phenol and wax phenols can also be used. The products obtained with the latter compounds are, however, somewhat less effective than those obtained with the preferred reactants.

The reaction is carried out by heating the alkylated phenol with P_2O_5 at temperatures of from about 75° C. to about 125° C. for several hours, preferably from about 1 to 15 hours. The preferred products are obtained when three moles of the alkylated phenol are reacted with approximately one mole of P_2O_5 .

The following examples will serve to illustrate convenient procedures for the preparation of our preferred materials.

EXAMPLE III

Di-tertiary amyl phenol- P_2O_5 reaction product

Reaction mixture:

Ditert-amyl phenol.. 468 grams (2 moles)
 P_2O_5 94.5 grams ($\frac{2}{3}$ mole)

The diamyl phenol was placed in a 1-liter, 4 necked, round bottom flask containing a reflux condenser, thermometer and mechanically-driven stirrer. After heating to 100° C., P_2O_5 was gradually added over a 3-hour period. Following this, the temperature was maintained

at 100° C. for eight hours. The reaction mixture was then filtered through Hyflo Super-Cel (a diatomaceous filter-aid) contained on a heated Buchner funnel. The filtrate, representing the finished product, contained 7.18% phosphorus and had a neutralization number of 176.

EXAMPLE IV

Octyl phenol-P₂O₅ reaction product

Reaction mixture:

Mono-tertiary octyl phenol	1900 grams (4.35 moles)
P ₂ O ₅	226 grams (1.59 moles)

The octyl phenol was placed in a 3-liter, 4-necked, round bottom flask containing a reflux condenser, thermometer and mechanically-driven stirrer. After heating to 100° C., P₂O₅ was gradually added over a 2-hour period. The mixture was then heated for 8 hours at 100° C.-105° C. Following this, the reaction mixture was diluted with 1025 grams of mineral oil and the product filtered through Hyflo Super-Cel contained on a heated Buchner funnel. The filtrate, representing the finished product, contained 4.6% phosphorus and had a neutralization number of 107.

EXAMPLE V

Wax phenol-P₂O₅ reaction product

A. ALKYLATION OF PHENOL

A paraffin wax melting at approximately 120° F. and predominantly comprised of compounds having at least about twenty, and an average of about 24, carbon atoms in their molecules is melted and heated to about 200° F. after which chlorine is bubbled therethrough until the wax has absorbed about 14% of chlorine, such product having an average composition between a monochlor wax and a dichlor wax. Preferably, the chlorination is continued until about one-sixth the weight of the "chlorwax" formed is chlorine. A quantity of chlorwax thus obtained, containing three atomic proportions of chlorine, is heated to a temperature varying from just above its melting point to not over 150° F., and one mole of phenol (C₆H₅OH) is admixed therewith. The mixture is heated to about 150° F., and a quantity of anhydrous aluminum chloride corresponding to about 3% of the weight of chlorwax in the mixture is slowly added with active stirring. The rate of addition of the aluminum chloride should be sufficiently slow to avoid violent foaming, and during such addition the temperature should be held at about 150° F. After the aluminum chloride has been added, the temperature of the mixture may be increased slowly over a period of from 15 to 25 minutes to a temperature of about 250° F. and then should be more slowly increased to about 350° F. To control the evolution of HCl gas the temperature of the mixture is preferably raised from 250° F. to 350° F. at a rate of approximately one degree per minute, the whole heating operation occupying approximately two hours from the time of adding the aluminum chloride. If the emission of HCl gas has not ceased when the final temperature is reached, the mixture may be held at 350° F. for a short time to allow completion of the reaction. However, to avoid possible cracking of the wax, the mixture should not be heated appreciably above 350° F., nor should it be held at that temperature for any extended length of time.

It is important that all unreacted or non-

alkylated hydroxyaromatic material (phenol) remaining after the alkylation reaction be removed. Such removal can be effected generally by water-washing, but it is preferable to treat the water-washed product with superheated steam, thereby insuring complete removal of the unreacted material and accomplishing the drying of the product in the same operation.

A wax-substituted phenol prepared according to the above procedure in which a quantity of chlorwax containing three atomic proportions of chlorine and having a chlorine content of 14% is reacted with one mole of phenol will be hereinafter designated as "wax phenol (3-14)."

B. WAX PHENOL-P₂O₅ PRODUCT

Reaction mixture:

Wax phenol (3-14)	300 grams (.360 mole)
P ₂ O ₅	18 grams (.127 mole)
Toluene	300 ml.

The wax phenol (3-14) and toluene were placed in a 2-liter, 4-necked, round bottom flask containing a reflux condenser, thermometer and mechanically-driven stirrer. After heating to 100° C., P₂O₅ was gradually added to the mixture over a four-hour period. Following this the temperature of the mixture was held at 100° C. for a period of 8 hours to insure complete reaction. The product was then clay filtered and the filtrate topped to 150° C. under diminished pressure to remove the toluene solvent. The residue, representing the finished product, contained 2.2 per cent phosphorus and had a neutralization number of 62.5.

EVALUATION OF ADDITIVE FORMULATION

To demonstrate the effectiveness of the composite additive formulation herein contemplated, we have conducted laboratory tests and actual road tests on oil blends of the composite additive formulation and on blends containing only one or two of the individual components. The laboratory tests were those contained in U. S. Army Specification 2-105B which describes a multipurpose gear oil suitable as a lubricant for automotive hypoid gears under conditions of service ranging from high speed shock loading to low speed, high torque operation. These tests designated as L-19-645 and L-20-545 were developed by the Coordinating Lubricants Research Committee at the request of the Army Ordnance Department for the purpose of testing gear oils suitable as lubricants for automotive hypoid gears. As is well known, many lubricating compositions are satisfactory under one type of operation, such as high speed passenger car service, but are not satisfactory under others, such as low speed, high torque heavy truck operation. The L-19-645 test measures the high speed performance of a lubricant, while the L-20-545 test measures the low speed, high torque performance of a lubricant. A detailed description of each of these test procedures may now be found in the "CRC Handbook 1946" published by J. J. Little and Ives Company, New York, N. Y. Both of these tests employ actual gears operating under conditions simulating extremely severe service. Those familiar with the art will appreciate that these tests constitute the most satisfactory laboratory method of evaluating a gear lubricant.

ACTUAL SERVICE TESTS

The actual service tests were conducted in a Dodge truck operating under heavy load over mountainous terrain and in a Buick passenger

car operating under very high speed conditions. The procedures followed in these tests were as follows:

HIGH SPEED BUICK TEST

A Buick passenger car (1948) is used for this test. This is essentially a test to determine the performance of the rear axle lubricant under high speed road conditions. The Pennsylvania turnpike between the Carlisle and Bedford toll gates serves as the test course. The round trip distance is 160 miles.

The course is traversed for the most part at a speed of 90-92 miles per hour, with occasional bursts of speed to 100-105 M. P. H. Rapid deceleration and acceleration are practiced when entering and leaving the 35 M. P. H. speed zones at the five tunnels and two toll houses. The average running speed for the course is 77 M. P. H.

The turnpike run of 5,000 miles under the above conditions constitutes the test on a new

must perform satisfactorily under these diverse conditions. During the mountain test the tooth loading reaches 10,000 inch pounds during ascent of the mountain, while in excess of 40,000 inch pounds is absorbed during descent in low gear. In the case of the CRC L-20-545 Test, 32,311 inch pounds of torque constitutes the load conditions of the gears.

Summarized in the accompanying table are the results obtained using the above-described tests on oil blends of the three component additives of the invention, as compared to blends of only one or two of the component additives in the oil. It will be noted that only the three component additive blends satisfactorily pass all tests.

The base oil used in the tests was a Mid-Continent SAE 90 grade oil. The additive concentrations are expressed in weight percentages based on the oil-free product. RX in the table signifies "reaction product."

Additive No.	Original Oil Plus Additive	High Speed Test CRC-L-19-645	High Torque Low Speed Test CRC-L-20-545	Buick High Speed Road Test	Dodge Truck Mountain Axle Test
I	(A) 5% RX Chlorinated Kerosene Plus K-Ethyl Xanthate. (B) 1% Dihydroabietyl Malate. (C) 0.5% RX Ditertiaryamyl Phenol Plus P ₂ O ₅ .	Pass	Pass	Pass	Good (Slight Surface Distress Gears).
II	10% Chlorinated Kerosene Plus K-Ethyl Xanthate.	do	Fail (Surface Fatigue Ripple and Ridge)		Very Poor (Heavy Wear and Surface Fatigue).
III	(A) 5% RX Chlorinated Kerosene Plus K-Ethyl Xanthate. (B) 1% Dihydroabietyl Malate. (C) 0.5% Monotertiaryoctyl Phenol Plus P ₂ O ₅ , RX.	do	Pass		Excellent (Negligible Surface Distress of Gears).
IV	(A) 5% RX Chlorinated Kerosene Plus K-Ethyl Xanthate. (B) 0.5% Monotertiaryoctyl Phenol Plus P ₂ O ₅ , RX.	do			Fair (Appreciable Surface Distress of Gears).
V	(A) 5% RX Chlorinated Kerosene Plus K-Ethyl Xanthate. (B) 1% Dihydroabietyl Malate. (C) 0.5% RX Wax Phenol Plus P ₂ O ₅ .	do			Good.
VI	(A) 5% RX Chlorinated Kerosene Plus K-Ethyl Xanthate. (B) 1% Dihydroabietyl Malate. (C) 0.5% RX Di-Secondary Amyl Phenol Plus P ₂ O ₅ .	do			Do.

rear axle differential carrier assembly. A subsequent examination of the hypoid gear tooth surfaces for signs of surface distress, such as wear, corrosion, discoloration, scratching, etc., furnishes the basis for rating the experimental lubricant. The lubricant is given a "pass" rating only if the surfaces are entirely free of any signs of distress.

DODGE TRUCK MOUNTAIN PROCEDURE

A 1½-ton Dodge tractor-trailer unit, loaded to 22,500 pounds gross vehicle weight, is used for this test. The vehicle operates over mountainous terrain on a prescribed test course between Hagerstown, Md. and Cumberland, Md. (Route U. S. 40). Much severe low speed, high torque service is imposed on both the coast side and drive side of the axle gear teeth throughout this test, mixed with some high speed, low torque running. A new differential assembly is installed in the truck for each run. A 3,000-mile test is sufficient to reveal the lubricating qualities of the gear oil, as deduced from gear tooth surface examination, conditions of bearings and other parts and used oil analysis.

The mountain test is considerably more severe than the CRC L-20-545 High Torque Test not only with respect to higher tooth pressures under low speed conditions, but also because a considerable amount of the operation is under relatively high speed conditions and the lubricant

The component additives of the invention may be blended in the lubricating oil either individually or they may be first mixed together to form the composite additive and then blended, as such, with the oil. We have found that the effective ranges of concentration (in weight per cent) for the individual additives are the following: (a) from about (1) per cent to about 10 per cent, preferably 5 per cent, of the chlorinated aliphatic compound-thiocarbonate products; (b) from about 0.1 per cent to about 3 per cent of dihydroabietyl malate; and (c) from about 0.1 per cent to about 1.5 per cent of the alkylated phenol-phosphorus pentoxide product. The total amount of additives within these ranges which we may use, therefore, is from about 1.2 per cent to about 14.5 per cent, with the preferred amounts giving a total concentration of 6.5 per cent. The composite mixture for addition to the oil in the latter concentration will, therefore, contain the individual additive in the following proportions:

	Per cent
(a) Chlorinated aliphatic compound-thiocarbonate product	76.9
(b) Dihydroabietyl malate	15.4
(c) Alkylated phenol-P ₂ O ₅ product	7.7

It is to be understood that the composite additive of this invention may also be added to the oil in concentrations greater than the range

given above, i. e. upwards of about 15 per cent by weight of the composite additive, to form oil "concentrates" suitable for marketing, such concentrates providing a readily soluble form of the composite additive for dilution with a suitable quantity of lubricating oil prior to actual use.

As hereinbefore indicated, it is contemplated that other additives may be added to the oil compositions and "concentrates" herein described for the purpose of improving the character of the oil in respects other than its E. P. quality, such as resistance to corrosion, detergency, viscosity index, pour point, etc.

Having now fully described our invention, what we claim as new and patentable is:

1. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon material having from 2 to about 24 carbon atoms with a thiocarbonate group, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product formed by reacting 3 moles of an alkylated phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

2. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon material having from 2 to about 24 carbon atoms with a xanthate group, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product formed by reacting 3 moles of an alkylated phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

3. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon having from about 5 to about 15 carbon atoms with a thiocarbonate group, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product formed by reacting 3 moles of an alkylated phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

4. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon having from about 5 to about 15 carbon atoms with a xanthate group, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product formed by reacting 3 moles of an alkylated phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

5. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition

agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated petroleum naphtha with a thiocarbonate group, such product having a chlorine content of from about 25% to about 40% and a characterizing thiocarbonate group content of from about 7% to about 22%, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product formed by reacting 3 moles of an alkylated phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

6. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follow: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated petroleum naphtha with an alkyl xanthate group, said product having a chlorine content of from about 25% to about 40% and a characterizing xanthate group content of from about 10% to about 22%, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product formed by reacting 3 moles of an alkylated phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

7. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon material having from 2 to about 24 carbon atoms with a thiocarbonate group, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of ditertiary amyl phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

8. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon material having from 2 to about 24 carbon atoms with a thiocarbonate group, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of monotertiary octyl phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

9. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon material having from 2 to about 24 carbon atoms with a thiocarbonate group, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of wax phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

10. An extreme pressure lubricating composition comprising a major proportion of a mineral

lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon having from about 5 to about 15 carbon atoms with a thiocarbonate group, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of ditertiary amyl phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

11. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon having from about 5 to about 15 carbon atoms with a thiocarbonate group, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of mono-tertiary octyl phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

12. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon having from about 5 to about 15 carbon atoms with a xanthate group, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of ditertiary amyl phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

13. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon having from about 5 to about 15 carbon atoms with a xanthate group, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of mono-tertiary octyl phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

14. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated petroleum naphtha with a thiocarbonate, said product having a chlorine content of from about 25% to about 40% and a characterizing thiocarbonate group content of from about 7% to about 22%, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of ditertiary amyl phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

15. An extreme pressure lubricating compo-

sition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated petroleum naphtha with a thiocarbonate, said product having a chlorine content of from about 25% to about 40% and a characterizing thiocarbonate group content of from about 7% to about 22%, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of mono-tertiary amyl phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

16. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated petroleum naphtha with an alkyl xanthate group, said product having a chlorine content of from about 25% to about 40% and a characterizing xanthate group content of from about 10% to about 22%, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of ditertiary amyl phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

17. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated petroleum naphtha with an alkyl xanthate group, said product having a chlorine content of from about 25% to about 40% and a characterizing xanthate group content of from about 10% to about 22%, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of mono-tertiary octyl phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

18. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil and minor proportions of addition agents as follows: (a) from about 1% to about 10% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated petroleum naphtha with an alkyl xanthate group, said product having a chlorine content of from about 25% to about 40% and a characterizing xanthate group content of from about 10% to about 22%, (b) from about 0.1% to about 3% of dihydroabietyl malate and (c) from about 0.1% to about 1.5% of the reaction product produced by reacting 3 moles of wax phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.

19. A mineral lubricating oil concentrate including a major proportion of a mineral lubricating oil and a minor proportion, upwards of about 15% by weight, of a composite mixture of the following materials: (a) about 76.9% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated aliphatic hydrocarbon material having from 2 to

15

about 24 carbon atoms with a thiocarbonate group, (b) about 15.4% of dihydroabietyl malate and (c) about 7.7% of the reaction product formed by reacting 3 moles of an alkylated phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.; said minor proportion being of such magnitude that when said concentrate is blended with mineral lubricating oil, the resulting mineral lubricating oil will contain between about 1% and about 15% by weight of said composite mixture.

20. A mineral lubricating oil concentrate including a major proportion of a mineral lubricating oil and a minor proportion, upwards of about 15% by weight, of a composite mixture of the following materials: (a) about 76.9% of a product obtained by chemically substituting a part only of the chlorine in a chlorinated petroleum naphtha with an alkyl xanthate group; said product having a chlorine content of from about 25% to about 40% and a characterizing xanthate group content of about 10% to about

16

22%, (b) about 15.4% of dihydroabietyl malate and (c) about 7.7% of the reaction product produced by reacting 3 moles of mono-tertiary octyl phenol with about 1 mole of phosphorus pentoxide, at a temperature of from about 75° C. to about 125° C.; said minor proportion being of such magnitude that when said concentrate is blended with mineral lubricating oil, the resulting mineral lubricating oil will contain between about 1% and about 15% by weight of said composite mixture.

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