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TRANSAXLE LUBRICANT

Howard J. Matson, Harvey, Leonard E. Beare, Lansing, and Rodney J. McConnell, Palos Heights, Ill., assignors, by mesne assignments, to Sinclair Research Inc., New York, N.Y., a corporation of Delaware
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This invention relates to new and improved lubricant compositions capable of maintaining an effective lubricant film between gear surfaces, and also capable of acting as the fluid element in automotive automatic transmissions.

It is well-known that ordinary lubricants, e.g. motor oils, are not capable of withstanding the enormous pressures existing between gear surfaces, such as the hypoid gears used in motor vehicles. This situation has led to the development of chemical additives which will react with gear surfaces to form a lubricating film that is capable of withstanding these tremendous pressures. Such chemical ingredients are known in the art as extreme pressure, or EP, additives, and lubricating oil bases that incorporate these additives are known as extreme pressure lubricants. Among the various substances that have been employed for this purpose are: sulfur, both free and chemically combined; phosphorus, usually as acids and esters; chlorine, principally as chlorinated hydrocarbons; and metal derivatives of organic compounds such as lead soaps and zinc dialkyldithiophosphates. It is evident that by the very mechanism of EP additive action, that is, by reacting with metal surfaces, one can only expect that effective EP additives are essentially corrosive materials. It is perhaps less obvious, but equally true, that EP additives are not noted for resistance to oxidation and in fact frequently they are pro-oxidant, pro-sludging, provarnishing, etc. These disadvantages, however, are preferable to the gross catastrophic destruction that could result to gears in the absence of EP lubricant additives.

It is also well-known that special lubricants are required in the automatic transmissions used on modern automotive vehicles. In this case, the lubricant should not only have a selected base stock but must contain special chemical ingredients to insure maximum resistance against deterioration due to oxidative effects, and to minimize the effects of such oxidation as does occur on the complicated functional mechanism of the automatic transmission. These chemical ingredients are frequently referred to as oxidation inhibitors, metal deactivators, detergents-dispersants, and the like. The fluid should be able to pass a copper corrosion test and have no significant deleterious effect on seals and clutch plate materials.

It thus is apparent that hypoid gear lubricants and automatic transmission (AT) fluids are very dissimilar. Although both gear lubricants and automatic transmission fluids may employ certain additives in common, usually these are supplemental type materials such as foam inhibitors, pour depressors and, to some extent, viscosity index improvers. Similarity between the two fluids ceases, however, at about this point. Probably the fundamental difference between the two fluids can be stated in terms of the additives employed to impart the important properties that define the separate fluids: the typical AT fluid is a low pour, high viscosity index material that will withstand prolonged periods of high temperature operation with a high degree of oxidation resistance; it may contain some oiliness or anti-friction materials, but little or no extreme pressure additives. The typical hypoid gear lubricant has only moderate

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pour and viscosity index characteristics, and relatively little resistance to oxidation. It contains powerful extreme pressure additives as primary ingredients.

A given additive may be used in common by both lubricants; however, this use does not by itself make a gear lubricant out of a transmission fluid or make a transmission fluid out of a gear lubricant. For example, sulfurized materials which are usually considered to be mild EP and anti-friction additives, such as sulfurized sperm oil, have been added to AT fluids to increase oiliness in order to reduce chattering or "squawking"; but it is in no way pretended that this addition will convert the AT fluid into a gear lubricant suitable for use in high torque-high speed-shock load gear operation. Conversely, zinc dialkyl dithiophosphates which normally are considered to be oxidation inhibitors in AT fluids, can be added to gear lubricants to increase film strength; but again this additive by itself will not render the gear lubricant suitable for use in automatic transmissions.

A few such examples of additives that can be used in either type fluid therefore do exist. However, it can be said that in general the additive requirements of the two fluids not only are different, they are mutually antagonistic. To illustrate this antagonism, a small amount of detergent-dispersant added to an otherwise satisfactory extreme pressure gear lubricant can essentially negate the high torque performance of the gear lubricant as measured for example by the L-20 axle test that is described in the "CRC Handbook, 1946." To illustrate further, a small amount of conventional extreme pressure additive such as a sulfurized hydrocarbon, when added to an otherwise satisfactory AT fluid, will promote a manifold increase in sludge and varnish formation, deteriorate seal materials, and severely corrode copper alloy parts.

Aside from differences in additives there are other major points of dissimilarity that are well-known to those working with these fluids. Automatic transmission fluid generally is conceded to have less viscosity than a gear lubricant, particularly at low temperatures. The lowest viscosity hypoid gear lubricant defined by the Ordnance MIL-L-002105A specification dated December 1958, although only slightly more viscous than AT fluid at 210° F., has a maximum permissible 0° F. viscosity of about 50,000 SUS (10,850 cst.), whereas AT fluid at 0° F. has a maximum permissible viscosity of not more than 7000 SUS and at -10° F. it should not be more than about 5000 cst. (4500 cps.). There are of course many differences in performance requirements. For example an automotive gear lubricant is expected to pass gear performance tests, the more severe of which are the high speed-shock load type tests as illustrated by the Buick 10A and Oldsmobile Schedule 26 procedures. The automatic transmission fluid on the other hand is expected to pass transmission performance tests, some of the more important of which measure oxidation stability, and durability with respect to seals, clutch plates, etc.

60 Thus, it will be seen that whereas the well-designed extreme pressure gear lubricant will provide satisfactory lubrication under conditions experienced in gears, and a well-designed automatic transmission fluid will provide satisfactory performance in transmissions, the simple mixing of these fluids or a random interchange of the additive ingredients is not likely to provide a lubricant that will give adequate protection under both types of service conditions. It is in fact more likely that such mixing or additive interchange will result in a fluid that is neither an automatic transmission fluid nor an extreme pressure gear lubricant.

Although these two separate lubricant applications are not new, the problem of combining the individual properties in a single fluid involves an entirely unique development. In order to meet the unusual and diverse performance requirements of this combination transmission and differential fluid, it has been found that certain combinations of additive materials can be used. For example, it has been found that certain inhibitor-detergent combinations which usually are effective in preventing deterioration and corrosion in AT fluid service, are not capable of handling increased stability and corrosion due to an extreme pressure additive. At the same time, it has been found that certain extreme pressure combinations develop different levels of lubrication according to the automatic transmission fluid into which they are incorporated. Further, it has been found that some EP additives which are entirely satisfactory for use in hypoid gear lubricants cannot be used in automatic transmissions because of their relatively poor stability and high corrosivity. The problem therefore is not one of selecting known additives for their expected results.

It is the principal object of this invention to provide a fluid meeting the rigorous requirements for service in an automatic transmission and also in an automotive hypoid differential. That is, it is the object of this invention to provide, in a single fluid, high viscosity index, low pour point, resistance to oxidation and corrosion, oiliness characteristics to avoid squawk, compatibility with seal and clutch plate materials, and finally extreme pressure gear lubricating properties.

This invention, therefore, resides in the discovery of unique combinations of ingredients which give outstanding effectiveness as a transmission-differential fluid. The fluid has a high VI, e.g. of at least about 125 or 130, and a low pour point, as an example below about -40° F., preferably below about -50° F.

The ingredients of this product are:

I. A high viscosity index lubricating oil base,

II. An oil soluble component selected from the group consisting of A, B and C below and in a small amount effective to impart oxidative and thermal stability to the compositions:

A. A polyvalent metal dithiophosphate diester and a basic alkaline earth metal sulfonate or phenate,
 B. A basic alkaline earth metal sulfonate and an alkaline earth metal salt of a condensation product of an alkyl substituted phenol, a lower aldehyde and an alkylene polyamine,
 C. A basic alkaline earth metal alkyl phenol sulfide,

III. An oil-soluble dialkyl thiocarbonate in a small amount effective to impart extreme pressure properties to the composition.

When desired the composition of the present invention may also include an oil-soluble chlorinated cyclic hydrocarbon so as to endow the composition with maximum extreme pressure properties.

The term "basic" as employed in group II above means the utilization of an excess of alkaline earth metal over that required to neutralize the sulfonic acid, phenol or phenol sulfide, e.g. usually at least about 1.2 equivalents of metal and preferably at least about 1.5 equivalents of barium. Generally the products do not contain more than about 5 equivalents of alkaline earth metal.

In order that this invention may be more fully understood, the several components which make up this novel combination lubricant will be discussed separately as will the particular combinations of components that make up the finished fluid. For the purpose of this invention, group II above will be referred to as the automatic transmission fluid additive package.

I. LUBRICATING OIL BASE

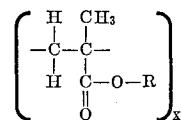
The lubricating oil base of the present invention has a minimum viscosity index of at least about 125 or 130

and forms the major proportion of the composition, say from about 70 to 98% by weight of the finished blend, often about 80 to 95%. The viscosity of the oil may vary, depending on the type and amount of additive content, but it will usually range from about 2 to 7 cst. (centistokes) at 210° F. Economically it is desirable to have a major portion of the oil be a refined mineral lubricating oil having a high viscosity index, e.g. at least about an 85 or 95 VI oil. Such oil may be a paraffinic base mineral oil or mixtures of paraffinic and naphthenic base mineral oils. These may be prepared by any of the usual methods such as solvent refining and solvent dewaxing, distillation and finishing; or pressing, distilling, acid treating, neutralizing, steaming and finishing; or combinations thereof. Since a base oil of very high viscosity index is needed this characteristic is usually obtained by providing the oil with a minor portion of a synthetic lubricant component.

The base oil may be entirely a synthetic lubricating oil of high viscosity index or more likely a blend of such an oil with a mineral oil lubricant, e.g. containing about 1 to 40% by volume of the synthetic oil. Suitable synthetic oils are known and include the ester based oils. The esters are often about 10 to 40% of the base oil and may be monoesters, diesters, complex esters, polymeric esters or mixtures thereof. Frequently the esters are aliphatic and are made from alkane mono- or dicarboxylic acids of 6 to 12 carbon atoms and mono- or polyhydric alkanols of 4 to 12 carbon atoms or the ether alcohols thereof. Preferably, at least one of the components reacted to give the esters, which may be substituted or unsubstituted, has only a single functional group, i.e. hydroxy or carboxylic, which takes part in the principal esterification reaction. Esters so derived are the mono-, di- and complex esters as distinguished from polymeric esters of a dicarboxylic acid and polyhydric alcohol. The latter products may be capped, i.e. the residual acid group reacted, with a monohydric alcohol but this is not the principal esterification reaction.

The base oil of the present compositions may include a synthetic oil component often identified as a viscosity index improver, and when present this component will generally be about 1 to 10% of the base oil. Among the viscosity index improvers that can be employed, for example, are polymers such as the methacrylate polymers, polyolefins of olefins of 3 to 5 carbon atoms, polyvinyl ethers, fumarate-vinyl acetate copolymers, polyalkylstyrenes, etc. and mixtures thereof.

The methacrylate polymers that can be used in our fluids include acrylic ester polymers usually having a molecular weight of about 5000 to 20,000. The series of commercially available polymers known as the "Acryloids" are particularly useful. Their chemical structure may be represented as:



where R is a fatty alcohol radical of 6 to 18 carbon atoms such as cetyl, lauryl or octyl and X is the number of molecules of similar structure condensed together to form a high molecular weight polymer. The "Acryloids" are clear viscous concentrates of methacrylic polymer in solvent refined neutral oil. The usual concentration is about 40 weight percent. "Acryloid 710" is particularly useful. "Acryloid 710," described in U.S. Patent No. 2,710,842, is a methacrylate polymer wherein R in the above formula is predominantly a mixture of lauryl and octyl groups and the molecular weight is about 10,000 to 20,000. Another commercial material of this type is "Acryloid 150," wherein R is predominantly a mixture of cetyl, lauryl and octyl groups and the molecular weight of the polymer is about 10,000 to 15,000.

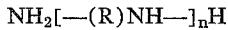
Among the other synthetic oils which may be employed are the higher molecular weight alkylene oxides, polycarbonates, methacrylate polymers, formals, polyformals, polyglyceryl ethers and other ethers, etc. Among the specific synthetic oils falling within the above classes are ethyl palmitate, ethyl stearate, di-2-ethylhexyl sebacate, di-2-ethylhexyl azelate, ethylene glycol dilaurate, etc.

II. AUTOMATIC TRANSMISSION-FLUID PACKAGE ADDITIVE

The polyvalent metal dithiophosphate diesters of combination A are the oil-soluble polyvalent metal salts derived from a wide variety of diester dithiophosphoric acids conventionally prepared by reacting a sulfide of phosphorus such as phosphorous pentasulfide, with an alcohol, phenol or mercaptan. The organic groups in the acid esters may be aryl, e.g., phenyl, alkyl, aralkyl, cycloalkyl or other monovalent hydrocarbon groups which contain from about 3 to 20 carbon atoms, preferably about 3 to 12 carbon atoms, and may be further substituted in the organic portion. Of the polyvalent metals, zinc is preferred but other metals of 28 to 30 atomic number, i.e. nickel and copper, are suitable. Alcohols which may be employed in preparing the acid esters include primary and secondary alcohols such as 2-methyl amyl alcohol, 4 - methylpentanol-2,2-methylpentanol-1,2-ethylhexanol, diisopropyl carbinol, cyclohexanol, butanol-1, isopropanol and octadecanol-1 or mixtures of high and low molecular weight alcohols. The preferred compounds are the zinc dialkyl dithiophosphates wherein the alkyl group contains about 3 to 12 carbon atoms, preferably about 3 to 8 carbon atoms. More specifically, the preferred compounds of this group include, for instance, dihexyl dithiophosphate, diheptyl dithiophosphate, di-2-methylamyl dithiophosphate, di-2-ethylhexyl dithiophosphate and the like.

The alkaline earth metal condensation products of combination B above are the oil-compatible, i.e. soluble, miscible or dispersible, alkaline earth metal salts of the condensation products obtained by reacting together an alkylene polyamine, a lower alkanol such as an aldehyde of 1 to 4 carbon atoms, and a substituted phenol, at an elevated temperature, such as a temperature of about 100 to 350° F. in the presence or absence of a solvent. The reactants are employed in a ratio of at least about 0.5 mole of each of phenol and aldehyde for every basic nitrogen present in the alkylene amine, with the upper limit being about two moles of each of phenol and aldehyde for each nitrogen atom in the amine. It is preferred that the reaction be carried out in a mineral oil so that on neutralization with an excess, for instance 50% excess, of an alkaline earth metal hydroxide, the alkaline earth metal salt of the condensation product is obtained as a concentrate in the oil. Preferred alkaline earth metal salts are those of calcium and barium.

The alkylene polyamines employed in the preparation of the condensation product are those amines represented by the general formula:



in which R is a divalent alkylene radical, substituted or unsubstituted and containing about 2 to 6 carbon atoms; and n is in integer of from 1 to 10, preferably 1 to 5. Typical amines included within the above formula are ethylenediamine, diethylene triamine, triethylenetriamine, tetraethylene pentamine, etc. The substituted phenols which are employed in the preparation of the condensation product are the monohydric phenols having at least one alkyl group and at least one ortho- or para-position which is available as a reaction site in the nucleus. Representative alkyl phenols are those in which the alkyl group contains 1 to 12 carbon atoms, for example, amyl phenol, p-diamyl phenol, octyl phenol, nonyl phenol, p-

tert-octyl phenol, cresol, a mixture of phenols and the like.

The basic sulfonates or basic phenates in combinations A and B of this group are aromatic including mahogany sulfonates and can be carbonated. The basic sulfonates can be prepared by neutralizing aromatic sulfonic acids with a theoretical excess of the hydroxides, chlorides, oxides or other inorganic compounds of the alkaline earth metals so as to obtain a product which contains an amount of alkaline earth metal in excess of that theoretically required to replace the acidic hydrogens of the sulfonic acids. The preferred alkaline earth metal is barium. Generally preferred aromatic sulfonic acids are the oil-soluble mahogany sulfonic acids which can be derived from the treatment of a suitable petroleum oil, such as a liquid petroleum distillate boiling in the range of about 600 to 1000° F., with fuming sulfuric acid or sulfur trioxide, separating the resulting acid sludge from the acid treated oil and recovering the mahogany acids contained in the acid treated oil. The useful mahogany acids generally have a molecular weight of from about 300 to 500 or more, and although their exact chemical structures may vary, it appears that such acids are composed to a large extent of sulfonated aromatic hydrocarbons having either one or two aromatic rings per molecule, possibly with one or more long chain alkyl groups containing from about 8 to 30 carbon atoms attached to the ring nuclei.

Other suitable aromatic sulfonic acids are the oil-soluble aryl sulfonic acids, which include the oil-soluble alkylated aryl sulfonic acids in which the alkyl chain contains from 8 to 18 carbon atoms, for instance, dinonyl naphthalene sulfonic acid, and those prepared by reaction of paraffin wax alkyl chains of 20 or more carbons with aromatic nuclei which are then sulfonated by fuming sulfuric acid, e.g. wax-substituted naphthalene. The aromatic oil-soluble sulfonic acids are conveniently employed as a concentrate in the hydrocarbon from which they are derived and are usually present in an approximate 10 to 30 weight percent concentration.

The basic sulfonates can be carbonated as for instance by contacting the basic alkaline earth metal sulfonate with carbon dioxide until the strong basicity of the sulfonate to phenolphthalein is reduced and a final pH of about 7 to 8.5 is obtained. This can be carried out, for example, by introducing the basic alkaline earth metal sulfonate to the top of a packed column and then feeding carbon dioxide to the bottom of the tower. The carbonated basic alkaline earth metal sulfonate is recovered and vacuum dried to obtain the final product. As an example, a typical carbonated basic barium sulfonate prepared from an oleum-treated West Texas gas oil fraction analyzed 2.86% barium and had a Base No. (to pH of 4) of 11.3.

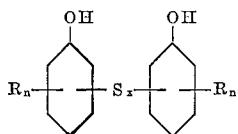
The basic phenate can be similarly obtained by neutralizing a phenol compound with a sufficient amount of a basic alkaline earth metal (Ca, Ba, Sr) compound so as to obtain an oil-soluble basic salt which contains at least about 1.2 times the theoretical amount of the metal required to form the normal or neutral alkaline earth metal salt. The preferred alkaline earth metal is barium. This type of reaction can be brought about by heating the metallic oxide or hydroxide with the phenol in the presence of a suitable solvent under conditions well-known in the art. The phenol compounds preferred are those which can have a hydrocarbon group attached to the ring structure. Such phenols may contain one or more alkyl groups which have from 8 to 24 carbon atoms such as dodecyl, n-decyl, tertiary decyl, tertiary octyl, cetyl and C₁₆ to C₂₄ branched chain groups. Other phenols which can be employed include aryl substituted phenols such as phenyl phenol, diphenyl phenol, etc. The basic phenates may also be carbonated. The ratios of the sulfonate or phenate to the salt of the condensation product of B or to the dithiophosphate salt of A as the case may

be, will generally be of about 1 to 10 parts by weight sulfonate or phenate, preferably about 1.5 to 6 parts, to 2 parts by weight of the other salt.

The basic, oil-soluble alkyl phenol sulfides (sub-group C of II above) are the oil-soluble basic alkaline earth metal salts of alkyl phenol sulfides, for instance, those in which the total number of carbon atoms in the alkyl group or alkyl groups is about 6 to 24, such as dodecyl, n-decyl, cetyl and the like. Suitable alkyl phenol sulfides are tertiary-octyl phenol sulfide, 2,4-diamyl phenol sulfide, 2-ethylhexyl phenol sulfide, C_{16} to C_{24} branched chain alkyl phenol sulfides and the like. Those having other alkyl substituents are also suitable so long as they are oil-soluble. The preferred alkaline earth metal is barium.

Suitable alkylated phenols for conversion to phenol sulfides may be prepared by alkylating phenol, cresol or other phenolic compounds, for example, by condensing phenols with simple alkyl halides or with chlorinated petroleum or chlorinated paraffin wax or with a chlorinated kerosene or gas oil. Naturally occurring phenols, such as those obtained by alkaline extraction of certain petroleum stocks or those obtained from cashew nut shell liquid or those obtained from other vegetable oil sources may likewise be used, so long as the final barium salt is oil-soluble.

For conversion of phenols to phenol sulfides the substituted phenol is reacted with sulfur dichloride to produce essentially a phenol monosulfide having a thioether linkage, while sulfur monochloride may be used to produce essentially the phenol disulfide. About one-half to one mol of sulfur halide is used with each mol of phenol. The phenol sulfides have, theoretically, the characterizing structure:



in which R is an alkyl group containing at least five carbon atoms, n and x are integers from 1 to 4, and the total carbon atoms in the R groups is 6 to 24. It is to be understood that when more than one R group is attached to a given aromatic nucleus, such groups may be alike or different. It should also be understood that the term "basic phenol sulfide" is meant to include not only the monosulfide but also the di-n-polysulfides and polymers of basic alkyl phenol sulfides as well.

In the preparation of the basic alkaline earth metal salts of the above-mentioned phenol sulfides the phenol radical is neutralized with a sufficient amount of a basic alkaline earth metal compound so as to attain an oil-soluble basic salt which contains at least about 1.2 times the stoichiometric amount of metal required to form the normal or neutral metal salt with the phenol group. It is possible to prepare basic alkaline earth metal salts having various ratios of metal to organic groups; such a salt may have a molar ratio of metal to phenol sulfide of 1.5:1, 2:1 or even 3:1. Intermediate ratios of alkaline earth metal to phenol sulfide such as 1.8:1 or 2.3:1, may occur in which mixtures of the types of basic compounds and complexes are obtained. The reaction can be brought about by heating the alkaline earth metal or hydroxide directly with the phenol in the presence of a suitable solvent under conditions well-known in the art.

It is convenient to carry out the reaction with the aid of solvents, particularly high boiling hydrocarbon solvents such as xylol of a petroleum fraction. A particularly preferred reaction medium is a lubricating oil fraction, since the final reaction product may thus be obtained as a mineral oil concentrate of the desired additive, which may be conveniently shipped or stored as such and then readily blended with the lubricating oil base. The basic

alkaline earth metal phenol sulfides may also be carbonated. It is preferable to carry out carbonation in the presence of or subsequent to a treatment with a controlled amount of water either in liquid form or as steam.

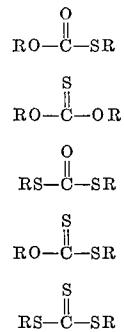
5 The CO_2 apparently renders the excess alkaline earth metal inaccessible in finishing operations. The exact amount or proportion of the oxide and steam required varied to some extent according to the way in which the metal salt was prepared. Ordinarily the amount of carbon dioxide should be less than about 25%, and preferably less than 5% by weight, based on the amount of basic phenol sulfide in the oil solution being treated. The amount of oil is usually sufficient to give a composition which is fluid and readily handled and blended at room temperature and is often in the range of 30 to 70%, based on the weight of the metal salt being treated. After the treatment with carbon dioxide and steam the entire mixture should be filtered, preferably with the use of a filter aid.

10 15 20 The amount of group II component employed in the novel composition of the present invention will generally fall within the range of about 1 to 10 weight percent (oil-free basis) depending somewhat upon the particular sub-component A, B or C selected. For more advantageous results the following amounts for each of the sub-components are usually employed:

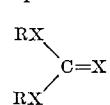
A—about 1 to 8 weight percent, preferably about 2 to 5%;
B—about 1 to 6 weight percent, preferably about 1.2 to 4%;
30 C—about 1 to 6 weight percent, preferably about 2 to 4%.

III. DIALKYL THIOCARBONATE

35 The dialkyl thiocarbonates of this invention can be a mono-, di- or trithiocarbonate but we prefer the dithiocarbonates having the divalent radical (OCS_2). Monomeric type thiocarbonates are exemplified by the following structures:

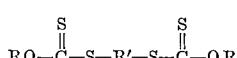


These formulae can be represented by the generic formula

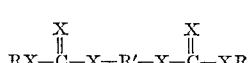


60 50 wherein X is oxygen or sulfur and on the average at least 1 X is sulfur, that is the X's may be up to 2 oxygens and 1 to 3 sulfurs. It is preferred that in the >C=X radical X be sulfur.

Also, two of these thiocarbonate molecules of like or 65 different configuration can be joined through an alkylene group. In this situation a dialkyl dithiocarbonate can be illustrated by the following formula:



These dimer-type structures have the generic formula:



In this formula X is again oxygen or sulfur and on the average at least 1 X on each side of R' is sulfur, that is the X's on a given side of R' may be up to 2 oxygens and 1 to 3 sulfurs. It is preferred in the >C=X radicals that X be sulfur, and that the X's on each side of R' be similarly chosen.

The R groups of these various formulae are alkyl, including cycloalkyl, radicals of about 1 to 15 or more carbon atoms, preferably of about 4 to 8 carbon atoms and these groups can be substituted as with hydroxyl. The R' group is an alkylene radical, including cycloalkylene, of about 1 to 15 carbon atoms, preferably of 4 to 8 carbon atoms and can also be substituted. Also the R and R' groups can have their carbon chains interrupted, for instance by an ether oxygen atom. However, the dialkyl thiocarbonates should contain little if any halogen attached to an aliphatic, i.e. noncyclic, carbon atom, for instance not more than about 5% of aliphatic halogen, preferably not more than about 2%.

The alkyl or R portion of the dialkyl thiocarbonates may be derived from any alcohol or any mixture of alcohols such as methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, oxoalcohols, etc., and polyhydric alcohols such as pentaerythritol and neopentyl glycol. In general, the C₄ to C₈ monoalcohols are preferred for reasons of solubility of the final product compared with the lower molecular weight alcohols and for reasons of cost compared to the higher molecular weight alcohols.

One generally used procedure for preparing the dialkyl dithiocarbonates consists of treating an excess of the desired alcohol with an alkali or alkaline earth metal compound. The alcoholate thus formed is treated with a slight excess of CS₂ while maintaining the reaction temperature below about 30° C. with vigorous stirring to form the alkali or alkaline earth metal xanthate. The salt is then reacted with a suitable halogenated material and under conditions such that substantially all of the aliphatic halogen of the halogenated material is replaced by the organic portion of the xanthate to form the additive of group III of the present invention.

When the halogenated material contains a single halogen, for instance chlorine, atom, the monomeric type thiocarbonates are formed, whereas when the halogenated material contains a plurality of halogen atoms the dimer type structure is afforded. Examples of suitable halogenated materials which may be used are those containing about 1 to 15 or more carbon atoms, preferably about 4 to 8 carbon atoms, for instance the aliphatic halides, such as methyl, ethyl, propyl, butyl, etc., chlorides, ethylene dichloride, trimethylene chlorobromide, 1,4-dichlorobutane, beta, beta'-dichloro-diethyl ether, amyl chlorides, hexyl chlorides, polychlorides having not more than 2 aliphatic chlorine atoms in the molecule, for instance 1,2,3,4,5,6-hexachlorocyclohexane. For reasons of solubility it is preferable that the chloride reacted be selected so that the resulting reaction product contains a minimum of about 6 carbon atoms.

The procedure generally used for this reaction is as follows: the halogenated material is added to the alkali xanthate and the reaction mixture heated to between about 50 and 110° C. The dialkyl thiocarbonate is formed by splitting out salt (NaCl or KCl) which is precipitated and removed by filtration and water washing; then concentrated by vacuum topping to remove excess alcohol and solvent, if any has been added. Solvents that may be used are ethers, alcohols, hydrocarbons, and mixtures thereof. As noted above, substantially all of the aliphatic halogen is removed from the halogenated material, that is the resulting dialkyl thiocarbonate contains little if any aliphatic halogen.

This preparation may be illustrated in more detail by reference to the following examples.

445 grams of isobutyl alcohol (6 moles), 170 grams of 97% sodium hydroxide (4 moles), in 160 grams of benzene and 120 grams of water, were heated to reflux temperature. After cooling the resultant solution to 5 to 10° C. in an ice bath, 310 grams of carbon disulfide (4 moles) were gradually added in small portions with vigorous stirring. The reaction became pronounced with the evolution of heat, and reaction temperature was controlled to below 30° C. by means of the ice bath. To the sodium isobutyl xanthate thus formed, 200 grams of ethylene dichloride (2 moles), and 25 grams of pyridine were added and the reaction mass heated to reflux and maintained at reflux for several hours. The reaction product designated product W was isolated by filtering off the precipitated salt, water washing and vacuum topping. Product W was obtained in a yield of 454 grams.

Analysis.—Product W: Percent sulfur, 40.8; percent chlorine, .22. Theor. O,O'-bis isobutyl SS' ethylene xanthate: percent sulfur, 39.2; percent chlorine, 0.

110 grams of isoamyl potassium xanthate (0.544 mole) prepared as in Example A were dissolved in 300 grams of isopropyl alcohol. 32 grams of 1,4-dichlorobutane (0.25 mole) were added at room temperature and the reaction mixture refluxed for two hours. After water washing and vacuum topping a yield of 73 grams of product designated X was recovered.

Analysis.—Product X: Percent sulfur, 33.0; percent chlorine, trace. Theor. O,O'-bis isoamyl SS' butylene xanthate: Percent sulfur, 33.5; Percent chlorine, 0.

1790 grams of 97% sodium hydroxide (41.6 moles) in 770 grams of water were added to 9376 grams of isobutyl alcohol (12.6 moles) and 1000 grams benzene. After cooling in an ice bath to about 13° C., 3344 grams of carbon disulfide (44 moles) were added slowly and with constant vigorous stirring at about 16 to 27° C. 2860 grams of beta,beta'-dichlorodiethyl ether (20 moles) were then added and the temperature allowed to rise about 72° C. and the reaction mixture was refluxed under partial vacuum at this temperature for four hours. The reaction product designated Product Y was isolated by sodium chloride water washing, vacuum topping and filtering. Product Y was obtained in a yield of 6166 grams.

Analysis.—Product Y: Percent sulfur, 33.4; percent chlorine, 1.2. Theor. O,O'-bis isobutyl SS' diethyl ether xanthate: Percent sulfur, 34.65; Percent chlorine, 0.

A 77° C. solution of 1480 grams of 97% sodium hydroxide (35.6 moles) in 547 grams of water were added to 9353 grams of isobutyl alcohol (12.6 moles) and 1000 grams benzene at about 54° C. and the temperature allowed to increase to about 82° C. After cooling in an ice bath to 2° C. 2835 grams of carbon disulfide (37.1 moles) were added slowly and with constant stirring at about 15 to 20° C. Addition of 2016 grams of 1,4-dichlorobutane (16 moles) was started at a temperature of 54° C. and the temperature allowed to rise to about 70° C. The reaction mixture was then allowed to reflux at this temperature under partial vacuum for 3 hours. The reaction product, designated Product Z, was isolated by washing with a dilute salt water solution, vacuum topping and filtering. Yield of Product Z was 5141 grams.

Analysis.—Product Z: Percent sulfur, 35.1; percent chlorine, .56. Theor. O,O'-bis isobutyl SS' butylene xanthate: Percent sulfur, 36.2; percent chlorine, 0.

According to the methods of the preceding examples

with minor variations in proportions, temperatures, recovery methods, etc., the following xanthate reaction products have been prepared.

As aforementioned, the composition of the present invention may include, if so desired, an oil-soluble chlorinated cyclic hydrocarbon in a small amount effective

TABLE I

| Product | Alcohol reactant | Chlorine reactant | Percent sulfur | | Percent chlorine | |
|---------|---------------------|---------------------------------------|----------------|-------|------------------|-------|
| | | | Theory | Found | Theory | Found |
| E. | Isopropyl | β,β' -Dichloroethyl ether | 37.4 | 37.2 | 0 | .48 |
| W. | do | Ethylene dichloride | 30.2 | 40.8 | 0 | .22 |
| Y. | do | β,β' -Dichlorodiethyl ether | 34.6 | 33.4 | 0 | 1.2 |
| Z. | do | 1,4-dichlorobutane | 36.2 | 35.1 | 0 | .56 |
| F. | do | 3-chloropropene | 33.7 | 32.4 | 0 | .29 |
| H. | do | Trimethylene chlorobromide | 37.6 | 38.0 | 0 | 1.36 |
| I. | Amyl | Ethylene dichloride | 36.2 | 34.2 | 0 | ----- |
| J. | Isoamyl | 1-chlorobutane | 29.1 | 29.4 | 0 | .07 |
| K. | do | 2-ethylhexyl chloride | 23.2 | 23.9 | 0 | .26 |
| X. | do | 1,4-dichlorobutane | 33.5 | 33.0 | 0 | Nil |
| L. | do | Ethylene dichloride | 36.2 | 39.1 | 0 | .28 |
| M. | do | β,β' -Dichlorodiethyl ether | 32.1 | 29.1 | 0 | 1.68 |
| O. | do | 1,2,3,4,5,6-hexachlorocyclohexane | 23.5 | 24.0 | 26.2 | 12.2 |
| P. | 4-methyl-2-pentanol | Ethylene dichloride | 33.6 | 39.6 | 0 | .05 |
| Q. | 2,2-dimethyl | 1-chlorobutane | 34.5 | 31.2 | 0 | .27 |
| S. | Pentaerythritol | do | 38.3 | 36.3 | 0 | Nil |
| T. | do | 3-chloropropene | 36.1 | 39.6 | 0 | .57 |
| U. | do | 3-chloropropene | 42.3 | 41.3 | 0 | .06 |

It sometimes may be advantageous to effect more purification of the xanthate reaction product than indicated by these examples; for example, by solvent extraction or distillation at very low pressures.

As stated, the proportions of reactants and conditions used in this reaction should be such as to hold the aliphatic chlorine content of the final product to a low value. By this means the possibility of any corrosion resulting from the hydrolysis of aliphatic chlorine will be minimized. Moreover, it also has been found that the dialkylthiocarbonate additives contemplated by this invention are more useful than a partially xanthated chloride, for example a chloronaphtha xanthate such as manufactured by Monsanto Chemical Co. as Santopoid S. For example, in a given automatic transmission fluid (described in following sections) one of the additives of this invention and chloronaphtha xanthate, i.e. a partially xanthated chloride containing approximately 30 to 35% chlorine, are compared.

TABLE II

| | Blends in AFT Base No. 1 | | 55 |
|-----------------------------------|--|---|----|
| | 3% Product W (ethylene diisobutyl xanthate) | 3% Santopoid S (chloronaphtha xanthate) | |
| Cst. at 100° F. | 42.38 | 45.10 | |
| Cst. at 210° F. | 7.67 | 7.82 | |
| Viscosity index | 142 | 138 | |
| SAE safe load at 1,000 r.p.m. | 165 | 0 | |
| Cu activity at 300° F.: 8 hrs. | 1A | 1A | |
| 24 hrs. | 1A | 2C | |

It is quite apparent that the blend containing an additive of this invention is superior in several respects: it maintains a higher viscosity index, it develops a greater amount of EP, and it is less corrosive to copper. The SAE machine is described in the CRC Handbook, 1946, CRC designation L-17-545.

The amount of the dithiocarbonate component (group III) employed in the present invention will fall in the range of about 2 to 12 weight percent based on the composition, preferably about 4 to 8 %.

to endow the composition with improved extreme pressure properties. Since the composition should contain little if any halogen attached to a non-cyclic carbon atom, the cyclic chlorinated additive contains its essential chlorine content in the form of chlorine atoms attached to ring carbon atoms. The chlorinated materials useful in this invention are derived from carbocyclic materials such as aromatic or alicyclic structures rather than aliphatics because of the fundamentally less stable and resultant pro-corrosive nature of the latter. The chlorinated carbocyclic materials can be mono- or polynuclear cyclic structures having about 6 to 18 carbon atoms and a chlorine content generally in the range of about 20 to 75% based on the mole weight of the material. They may be present in the composition of the present invention in an amount of about 0 to 12%. When the additive is present it will usually be at least about 1 weight percent, preferably about 4 to 9 weight percent. The chlorine compounds are useful primarily because of their effect on increasing the film strength or load capacity of a fluid when used in conjunction with the sulfur additives of this invention. This effect is shown by the following data on SAE film strength.

TABLE III
[Blends in ATF Base No. 1]

| | | | |
|-------------------------------------|------|-----|------|
| Percent chlorinated biphenyl | 7 | 0 | 7 |
| Percent Product W | 0 | 3 | 3 |
| SAE safe load at 1,000 r.p.m., lbs. | Zero | 165 | 450+ |

[Blends in ATF Base No. 2]

| | | | | | | | | | | |
|------------------------------|---|---|----|----|-----|-----|-----|------|-----|-----|
| Percent chlorinated biphenyl | 7 | 0 | 0 | 4 | 5 | 6 | 6 | 7 | 3 | 5 |
| Percent Product Z | 0 | 4 | 6 | 4 | 4 | 5 | 6 | 6 | 6 | 6 |
| SAE, lbs., 1,000 r.p.m. | 0 | 0 | 87 | 76 | 232 | 271 | 356 | 450+ | 164 | 328 |

A variety of chlorine additives other than chlorinated biphenyl can be used to accomplish this effect, as illustrated by the following data obtained in ATF Base No. 1.

TABLE IV

| | Percent chlorine additive | Dialkyl thiocarbonate | | | SAE, lbs., 1,000 r.p.m. |
|--|---------------------------|-----------------------|-------------------|-------------------|----------------------------|
| | | Percent Product Z | Percent Product Q | Percent Product O | |
| | | | | | |
| ATF Base No. 1 Neat | | | | | 0 |
| ATF Base plus dialkyl thiocarbonate | | 3 | | | 0 |
| Do | | 6 | | | 170 |
| Do | | | 3 | | 94 |
| Do | | | | 3 | 0 |
| ATF Base plus chlorinated biphenyl 1280 | 4 | 3 | | | 71 |
| Do | 7 | 3 | | | 229 |
| Do | 4 | | 3 | | 199 |
| Do | 4 | | | 3 | 145 |
| Do | 7 | 6 | | | 255 |
| ATF Base plus chlorinated diphenyl oxide | 4 | 3 | | | 86 |
| Do | 7 | 6 | | | 450+ |
| ATF Base plus chlorinated naphthalene | 4 | 3 | | | 108 |
| Do | 7 | 3 | | | 223 |
| Do | 4 | | 3 | | 188 |
| ATF Base plus dibutyl chlorendate | 7 | 3 | | | 225 |
| ATF Base plus pentachloro benzene | 4 | 3 | | | 115 |
| Do | 7 | 3 | | | 238 |
| Do | 7 | 6 | | | 450+ |
| Do | 4 | | 3 | | 201 |
| ATF Base plus 1,2,4-trichlorobenzene | 4 | 3 | | | 87 |
| Do | 7 | 6 | | | 450 |
| ATF Base plus 1,2,3,4-tetrachlorobenzene | 4 | 3 | | | 117 |
| Do | 7 | 6 | | | 450+ |
| ATF Base plus pentachloronitrobenzene | 4 | 3 | | | 191 |
| Do | 7 | 6 | | | 450 |

The present composition also preferably includes effective amounts of a suitable anti-foam agent since the fluid of the present invention is circulated rapidly in operation and air may be entrapped. For this purpose, a silicone polymer of high viscosity, such as dimethyl silicone polymer having a kinematic viscosity at 25° C. of about 1000 centistokes and above, is advantageously employed. A silicone polymer is conveniently employed in the form of a concentrate in a hydrocarbon solvent, such as kerosene. For example, a very satisfactory anti-foam agent for this purpose is prepared by diluting 10 grams of a dimethyl silicone polymer (1000 cts. at 25° C.) with kerosene to bring the volume to 100 cc. A pro-

portion of the order of about 0.0001 to .02 part by weight to this concentrate is ordinarily employed.

Should the base oil not be sufficiently low in pour point a pour depressor can be included in the composition. For example, the polymethacrylates described above can be used, usually in an amount of about 1 to 5% of the composition.

To demonstrate the effectiveness of the composition of the present invention, laboratory and actual performance tests were conducted on oil blends of the automatic transmission fluid (ATF) and differential gear lubricant (EP) additives. This may be illustrated by reference to the following examples.

TABLE V

| | AT Fluid No. 1 | AT Fluid No. 2 | AT Fluid No. 3 | AT Fluid No. 4 | AT Fluid No. 5 |
|---|----------------|----------------|----------------|----------------|----------------|
| Percent by volume: | | | | | |
| 80 SUS at 100° F.—Solvent refined MC neutral | | 30 | 55 | | |
| 160 SUS at 100° F.—Solvent refined MC neutral | 70 | 70 | 35 | 70 | 70 |
| 60 SUS at 100° F.—Conventional refined coastal neutral | | 15 | | 15 | 15 |
| 100 SUS at 100° F.—Conventional refined coastal neutral | | 15 | 10 | 15 | 15 |
| Percent by weight: | | | | | |
| Base oil | 88.88 | 91.0 | 89.0 | 87.65 | 84.25 |
| Zn methyl amyl, isopropyl dithiophosphate-basic Ba C ₁₂ alkyl phenate (approx. 1-2 weight ratio mixture as 45% conc. in mineral oil) | 6.37 | | | | |
| Basis barium C ₁₂ alkyl phenol sulfide (about 45% conc. in mineral oil) | | | | 7.6 | |
| Calcium salt of octylphenol, formaldehyde, diethylene triamine condensation product, 40% conc. in mineral oil | | 2.0 | 2.0 | | |
| Carbonated basic barium mahogany sulfonate, 25% conc. in mineral oil | | 3.2 | 3.2 | | 8.0 |
| Methacrylate polymer ¹ | 4.50 | 3.8 | 3.8 | 4.5 | 4.5 |
| Methacrylate polymer ² | 0.25 | | | 0.25 | 0.25 |
| Polyisobutylene (10,000 to 12,000 molecular weight, 40% conc. in mineral oil) | | .001 | 2.0 | | |
| Dimethyl silicone ³ | | | .001 | .001 | .001 |
| Zn di(methyl amyl) dithiophosphate (45% conc. in mineral oil) | | | | | 3.0 |

¹ "Acryloid 710," 40% concentrate in mineral oil solution.

² "Acryloid 150," 40% concentrate in mineral oil solution.

³ 10% concentrate of dimethyl silicone polymer (1,000 cts. at 25° C.) in kerosene.

TABLE VI

| ATF-EP Fluid Identity | I | II | III | IV | V | VI | VII | VIII | IX | X | XI |
|-----------------------|------|------|------|------|------|------|------|------|------|------|----|
| Percent by Weight: | | | | | | | | | | | |
| ATF Base No. 1 | 89.5 | 87.0 | 87.0 | 87.0 | 87.0 | 87.0 | 84.0 | 88.0 | 92.0 | | |
| ATF Base No. 2 | | | | | | | | | | | |
| ATF Base No. 3 | | | | | | | | | | | |
| ATF Base No. 4 | | | | | | | | | | | |
| ATF Base No. 5 | | | | | | | | | | | |
| Product W | 3.0 | | 6.0 | 6.0 | 6.0 | | 7.0 | 12.0 | 8.0 | 10.0 | |
| Product Z | | | | | | | | | | | |
| Product Y | | | | | | | | | | | |
| Chlorinated diphenyl | 7.5 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 9.0 | | | | |

Tests that have been obtained with the compounded automatic transmission-differential fluids include the following:

transmission Corvair car equipped with a combination differential-transmission. Although these units were separately sealed, Fluid III was run in each and drain sam-

TABLE VII

| ATF-EP Identity | I | II | III | IV | V | VI | VII | VIII |
|--------------------------|--------|--------|--------|--------|--------|-------|-------|-------|
| Gravity, °API | 20.3 | 19.7 | 23.4 | | | 23.3 | | |
| Flash, °F. COC | 370 | 375 | 410 | | | 415 | | |
| Fire, °F. COC | 400 | 405 | 455 | | | 460 | | |
| Vis. at— | | | | | | | | |
| 100° F., cps | 47.38 | 45.83 | 42.93 | 40.44 | 57.64 | 42.30 | 43.04 | 41.11 |
| 210° F., cps | 7,914 | 7,628 | 7,256 | 7,209 | 9,137 | 7,263 | 7,329 | 7,282 |
| Viscosity index | 135 | 133 | 133 | 139 | 134 | 135 | 134 | 139 |
| Brookfield vis. at— | | | | | | | | |
| 10° F., cps | | 5,500 | 4,070 | 3,700 | | 4,415 | | |
| 20° F., cps | 12,085 | 13,350 | 10,630 | 67,600 | 17,200 | 5,450 | 5,250 | 8,310 |
| 40° F., cps | | | 87,400 | | | | | |
| Pour, ° F. | —50 | —55 | | | —50 | —55 | —55 | —55 |
| SAE at 1,000 r.p.m., lbs | 375 | 345 | 292 | | 279 | 280 | 450+ | 450+ |

To demonstrate the utility of the fluids in the above examples as combination lubricants for automatic transmissions and hypoid differentials, a number of in-use performance tests have been run. For example:

Fluids I, II, III and VI have been run in a full-sized Chevrolet Powerglide transmission to determine oxidation resistance and thermal stability. In this test the fluid is driven at 1750 r.p.m. under no load, at 275 to 300° F., and dry air is metered into the test fluid at a rate of about 100 ml. per minute. At the conclusion of the test times, ranging from about 165 to 192 hours, inspection of the transmission and the used oil indicated the combination fluids had oxidative and thermal stability approximately equal to the AT fluids on which they were based. The parent AT fluids are designed for the rigorous oxidative and thermal conditions encountered in passenger car automatic transmissions.

Fluid I was tested by the Oldsmobile No. 26 differential scoring test. This test involves wide open throttle accelerations, and accelerations to 50, 60 and 70 m.p.h. with downshifting to Lo range at the peak of each acceleration. The gears from the test on Fluid I were rated very good to perfect.

Fluids II and III were run in an accelerated cycling test designed to indicate transmission clutch plate life. In this test, a Powerglide transmission system was loaded by inertia weights and dynamometer, and accelerated at full throttle through the shift sequences, three times per minute. Fluid II completed 3500 cycles by this test, and Fluid III left the clutch plates in very good condition after 5000 cycles.

Fluids I and III have been evaluated under standard or normal driving conditions. Fluid I was tested for over 16,000 miles in both the differential and transmission of a 1959 Oldsmobile equipped with Hydramatic. Operation during this time was satisfactory, and inspection of the units and the conclusion of this test confirmed a satisfactory condition. Fluid I gave a negative result when tested for "squawk."

Fluid III was tested in a new 1960 Chevrolet automatic

samples from the separate units were interchanged at regular intervals. About 22,000 road miles were accumulated with satisfactory performance, as further confirmed by inspection of the units at this mileage.

It is claimed:

1. A lubricating fluid composition suitable for use in both automotive automatic transmissions and automotive hypoid differentials and characterized by a viscosity index of at least about 125 and a pour point below about —40° F. consisting essentially of:

(I) a major amount of base lubricating oil,
(II) about 1 to 10 weight percent of an oil-soluble component selected from the group consisting of A, B and C below:

A. metal dialkyl dithiophosphate wherein the metal has an atomic number of 28 to 30 and the alkyl group contains about 3 to 12 carbon atoms and an oil soluble basic compound selected from the group consisting of basic alkaline earth metal aromatic sulfonate and basic alkaline earth metal alkyl phenate, the proportions in parts by weight of said sulfonate or phenate to said dithiophosphate being about 1 to 10/2,

B. a basic alkaline earth metal aromatic sulfonate and the alkaline earth metal condensation product of an alkyl-substituted phenol, said alkyl group having about 1 to 12 carbon atoms, an alkanol of 1 to 4 carbon atoms and an alkylene polyamine represented by the structural formula:



in which R is a divalent alkylene radical containing about 2 to 6 carbon atoms and n is 1 to 5, the proportions in parts by weight of said sulfonate to said condensation product being about 1 to 10/2,

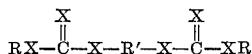
C. a basic alkaline earth metal alkyl phenol sulfide, said alkyl group containing about 6 to 24 carbon atoms; and

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(III) about 2 to 12 percent of a dialkylthiocarbonate selected from the group having the structural formulas:



wherein R is an alkyl group of about 1 to 15 carbon atoms, X is selected from the group consisting of oxygen and sulfur and at least one X is sulfur, and

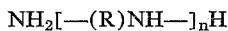


wherein R is an alkyl group of about 1 to 15 carbon atoms, X is selected from the group consisting of oxygen and sulfur and at least one X on each side of R' is sulfur and R' is an alkylene radical of about 1 to 15 carbon atoms.

2. A lubricating fluid composition consisting essentially of the composition of claim 1 and a small amount effective to endow the composition with improved extreme pressure properties of an oil-soluble ring-chlorinated carbocyclic hydrocarbon of about 6 to 18 carbon atoms.

3. The composition of claim 1 wherein component II is a metal dialkyl dithiophosphate wherein the metal has an atomic number of 28 to 30 and the alkyl group contains about 3 to 12 carbon atoms and an oil soluble basic compound selected from the group consisting of basic alkaline earth metal aromatic sulfonate and basic alkaline earth metal alkyl phenate, the proportions in parts by weight of said sulfonate or phenate to said dithiophosphate being about 1 to 10/2.

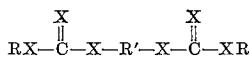
4. The composition of claim 1 wherein component II is a basic alkaline earth metal aromatic sulfonate and the alkaline earth metal condensation product of an alkyl-substituted phenol, said alkyl group having about 1 to 12 carbon atoms, an alkanal of 1 to 4 carbon atoms and an alkylene polyamine represented by the structural formula:



in which R is a divalent alkylene radical containing about 2 to 6 carbon atoms and n is 1 to 5, the proportions in parts by weight of said sulfonate to said condensation product being about 1 to 10/2.

5. The composition of claim 1 wherein component II is a basic alkaline earth metal alkyl phenol sulfide, said alkyl group containing about 6 to 24 carbon atoms.

6. The composition of claim 1 wherein the component of group III is

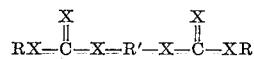


wherein R is an alkyl group of about 1 to 15 carbon atoms, X is selected from the group consisting of oxygen and sulfur and at least one X on each side of R' is sulfur and R' is an alkylene radical of about 1 to 15 carbon atoms.

7. A lubricating fluid composition suitable for use in both automotive automatic transmissions and automotive hypoid differentials and characterized by a viscosity index of at least about 125 and a pour point below about -40° F. consisting essentially of a major amount of base mineral lubricating oil, about 1 to 8 weight percent of an oil-soluble composition consisting essentially of zinc dialkylthiophosphate, wherein the alkyl group contains about 3 to 12 carbon atoms and an oil soluble basic compound selected from the group consisting of basic alkaline earth metal aromatic sulfonate and basic alkaline earth metal alkyl phenate, the proportions in parts by weight of said sulfonate or phenate to said dithiophos-

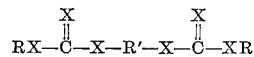
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phate being about 1 to 10/2; about 4 to 8 percent of a dialkyl thiocarbonate having the structural formula:



wherein R is an alkyl group of about 1 to 15 carbon atoms, X is selected from the group consisting of oxygen and sulfur and at least one X on each side of R' is sulfur and R' is an alkylene radical of about 1 to 15 carbon atoms, and about 4 to 9 weight percent of an oil-soluble, ring-chlorinated carbocyclic hydrocarbon of about 6 to 18 carbon atoms.

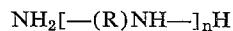
8. The composition of claim 7 wherein the dialkylthiocarbonate has the structural formula:



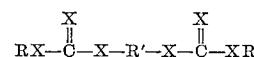
wherein R is an alkyl group of about 4 to 8 carbon atoms, X is oxygen or sulfur and two X's on each side of R' are sulfur and R' is an alkylene radical of about 4 to 8 carbon atoms.

9. The composition of claim 8 wherein the basic compound is basic barium alkyl phenate.

10. A lubricating fluid composition suitable for use in both automotive automatic transmission and automotive hypoid differentials and characterized by a viscosity index of at least about 125 and a pour point below about -40° F. consisting essentially of a major amount of base mineral lubricating oil, about 1 to 6 weight percent of an oil-soluble composition consisting essentially of a basic alkaline earth metal aromatic sulfonate and the alkaline earth metal condensation product of an alkyl substituted phenol, said alkyl group having about 1 to 12 carbon atoms, an alkanal of 1 to 4 carbon atoms, and an alkylene polyamine reported by the structural formula

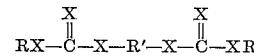


in which R is a divalent alkylene radical containing about 2 to 6 carbon atoms and n is 1 to 5, the proportions in parts by weight of said sulfonate to said condensation product being about 1 to 10/2; about 4 to 8 percent of a dialkyl thiocarbonate having the structural formula:



wherein R is an alkyl group of about 1 to 15 carbon atoms, X is selected from the group consisting of oxygen and sulfur and at least one X on each side of R' is sulfur and R' is an alkylene radical of about 1 to 15 carbon atoms, and about 4 to 9 weight percent of an oil-soluble, ring-chlorinated carbocyclic hydrocarbon of about 6 to 18 carbon atoms.

11. The composition of claim 10 wherein the dialkylthiocarbonate has the structural formula:



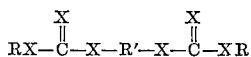
60 wherein R is an alkyl group of about 4 to 8 carbon atoms, X is selected from the group consisting of oxygen and sulfur and two X's on each side of R' are sulfur and R' is an alkylene radical of about 4 to 8 carbon atoms.

12. The composition of claim 11 wherein the alkaline earth metal of the sulfonate is barium.

13. A lubricating fluid composition suitable for use in both automotive automatic transmission and automotive hypoid differentials and characterized by a viscosity index of at least about 125 and a pour point below about -40° F. consisting essentially of a major amount of base mineral lubricating oil, about 1 to 6 weight percent of an oil-soluble composition consisting essentially of a basic alkaline earth metal alkyl phenol sulfide, said alkyl group containing about 6 to 24 carbon atoms; about

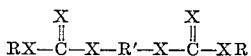
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4 to 8 percent of a dialkyl thiocarbonate having the structural formula:



wherein R is an alkyl group of about 1 to 15 carbon atoms, X is selected from the group consisting of oxygen and sulfur and at least one X on each side of R' is sulfur and R' is an alkylene radical of about 1 to 15 carbon atoms, and about 4 to 9 weight percent of an oil-soluble, ring-chlorinated carbocyclic hydrocarbon of about 6 to 18 carbon atoms.

14. The composition of claim **13** wherein the dialkyl thiocarbonate has the structural formula:



wherein R is an alkyl group of about 4 to 8 carbon atoms, X is selected from the group consisting of oxygen and sulfur and two X's on each side of R' are sulfur and R' is an alkylene radical of about 4 to 8 carbon atoms.

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15. The composition of claim **13** wherein the alkaline earth metal is barium.

16. The composition of claim **1** wherein the reactants of the alkaline earth metal condensation products of combination B are employed in a ratio of about 0.5 to 2 moles of each of the phenol and the aldehyde for every basic nitrogen present in the alkylene polyamine.

References Cited by the Examiner

UNITED STATES PATENTS

| | | | | |
|----|-----------|---------|----------------------|------------|
| 10 | 2,178,513 | 10/1939 | Prutton et al. _____ | 252—48.8 X |
| | 2,353,491 | 7/1944 | Oberright _____ | 252—42.7 |
| | 2,606,872 | 8/1952 | Gasser et al. _____ | 252—33.4 X |
| 15 | 2,691,632 | 10/1954 | Harle _____ | 252—48.2 X |
| | 2,713,557 | 7/1955 | Lowe _____ | 252—32.7 |
| | 2,723,234 | 11/1955 | Asseff et al. _____ | 252—32.7 |
| | 3,036,003 | 5/1962 | Verdol _____ | 252—33.4 |
| | 3,049,494 | 8/1962 | Palmer et al. _____ | 252—32.7 X |

20 DANIEL E. WYMAN, *Primary Examiner.*

JULIUS GREENWALD, JOSEPH R. LIBERMAN,
Examiners.