Patented Jan. 25, 1944

2,340,036

UNITED STATES PATENT OFFICE

2,340,036

LUBRICANT COMPOSITION

John C. Zimmer and George M. McNulty, Union, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application December 30, 1941, Serial No. 424,927

14 Claims. (Cl. 252—51)

This invention relates to improved lubricants such as lubricating oil and grease compositions intended for the lubrication of moving metal parts which come into contact at high pressures. It relates especially to the preparation of improved lubricant compositions of high film strength for bearing and engine lubrication, to the preparation of improved extreme pressure lubricants for use especially for hypoid gears, and to the preparation of improved cutting oils for use in machining metals.

In the lubrication of hypoid and other gears, various materials containing chlorine or other halogens are used alone or in combination with other metals effective in increasing the extreme pressure lubricant characteristics of the composition, such as sulfur or phosphorus compounds. These compositions have a serious disadvantage, however, in that they tend to rust the metal surfaces which are being lubricated. They also cause corrosion and staining of ferrous and copper-bearing alloys used in bearings, bushings, pistons, etc. Also, the use in cutting fluids of sulfur or sulfur compounds, alone or in the presence of chlorine compounds, usually causes a black stain of copper sulfide on copper alloys.

It has now been found, and is a primary object of the present invention, that this undesirable corrosion and staining of metals can be prevented by adding to the high film strength or extreme pressure lubricant a small proportion of an oil-soluble salt, preferably a metallic, ammonium or other onium base salt, of an auto-condensation product of a hydroxyarylalkyl amine.

A preferred type of condensation product for use in making the salts of this invention is prepared as an ammonium derivative of an alkyl phenol-formaldehyde-hydrogen halide condensation product. These compounds are obtained with satisfactory oil solubility and effectiveness for the purpose of this invention by condensing an alkyl phenol with formaldehyde in the presence of a hydrogen halide, then reacting the resulting phenolic condensation product with ammonia or other strong base, e. g., an amino compound or other organic nitrogen base. Ammonia is the preferred base reactant. Next in order come the aliphatic and aromatic amines, especially the primary and secondary amines. The solubility of salts of these products in hydrocarbon oils varies with the degree of auto-condensation or resinification of the reaction products, the salts of the simplest products of reaction often being very slightly soluble. Their solubility and effectiveness are readily increased by subjecting the hydroxy compounds to auto-condensation conditions during their preparation, or the simple reaction products may be prepared and thereafter subjected to auto-condensation treatment.

Another very important factor in the preparation and use of these agents is that their oil-solubility increases with the length of the alkyl substituent in the phenol nucleus.

Even though the initial phenolic compound may contain a long alkyl or aliphatic substituent group, which in ordinary types of reaction lowers the reactivity of the phenolic compounds, the reaction for preparing the desired hydroxyarylalkyl amine goes with great ease. The complete reaction may be considered as involving two stages: first, the introduction of a halogenated aliphatic radical in the phenolic compound; and second, a splitting out of the halogen by condensation of the substituted phenolic compound with the base. Very little halogen, and preferably none, is left in the final product. The preparation of a typical product is illustrated by the following:

EXAMPLE 1

900 grams of paraformaldehyde (30 mols of formaldehyde) and 5,000 grams of concentrated hydrochloric acid were placed in a 12-liter flask provided with a stirrer, a reflux condenser and a thermometer. A solution of 2,060 grams (10 mols) of paraisooctylphenol (para-tetramethyl butyl phenol) in an equal weight of benzene was then added to the flask over a period of 20 to 25 minutes, while passing hydrochloric acid gas continuously through the solution throughout the reaction in order to keep the reaction mixture saturated. The stirrer was also operated continuously to provide efficient contact between the two liquid phases present during the reaction. The temperature of the initial mixture of paraformaldehyde and hydrochloric acid was 15° C. It increased to 45–50° C. upon addition of the phenol and this temperature was thereafter maintained for 1½ hours while constantly stirring and passing in hydrochloric acid gas. At the end of this time the stirring was stopped, whereupon an upper phenolic benzene layer separated from a lower fuming hydrochloric acid layer and was separately withdrawn from the reaction vessel. The upper layer was washed several times with water. Analysis of a small sample of the oil from which the benzol was removed showed it to contain 14.2% chlorine.

To 600 grams of this benzene solution there were slowly added (with thorough stirring) 50 grams of anhydrous ammonia dissolved in 300 grams of 98% isopropyl alcohol. This reaction takes place with great evolution of heat and, on a larger scale, cooling or pressure is necessary to prevent loss of solvent and ammonia. After complete addition of the ammonia, the mixture consisted of a thick, tacky, yellow slurry containing an excess (about 10%) of ammonia. This mixture was then placed in a stainless steel bomb of one liter capacity which was sealed and then heated for 20 hours at a temperature of 110 to 120° C. It is possible to pass in gaseous ammonia

at such a rate as to control the temperature, rather than use the ammonia in alcoholic solution.

After heating, the reaction product was obtained as a material completely soluble in the benzene-alcohol solvent present which also contained a fine suspension of insoluble ammonium chloride. This mixture was washed with water several times to remove the suspended salt and the alcohol. 500 grams of a refined paraffinic lubricating oil having a viscosity Saybolt at 210° F. of 43 seconds were added and the mixture was blown with nitrogen at 120° to 130° C. for two hours to remove the benzene. After this, more oil was added to provide a concentrate of relatively low viscosity and clear red color containing 25% of the reaction product.

A small portion of the benzene solution was withdrawn for analysis prior to addition of the lubricating oil. Evaporation of the benzene produced a brittle, resinous material containing 2.8% nitrogen.

The heating of the ammonia condensation product is effective in obtaining a completely oil-soluble final product. The extent of heating which produces the desired result varies with the chlorine content of the intermediate product, materials containing 11% combined chlorine requiring only four to six hours heating, while materials containing 14.2% chlorine require 15 to 20 hours. Materials of still higher chlorine content did not yield completely oil-soluble products by this heat treatment, the degree of insolubility increasing with increase in chlorine content. The preparation of intermediate products containing about 12 to 14% chlorine is preferred, as the metallic salts of these products are very effective lubricating oil improving agents.

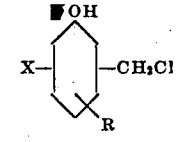
The chlorine content of the intermediate product may be controlled by the ratio of the formaldehyde and phenol used in the initial reaction. For example, when conducting the process as described in Example 1 with several different proportions of formaldehyde and para-iso-octylphenol, the chlorine content of the intermediate product, and the nitrogen content of the final product, were observed to be as follows:

Formaldehyde, octyl phenol mols	Intermediate product, per cent Cl	Final product, per cent
1.0	2.7	0.5
1.5	8.7	1.7
2.0	11.9	2.4
2.5	13.5	2.9
3.0 (Example 1)	14.2	2.8

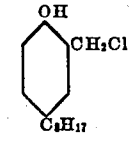
Instead of washing the heat treated reaction product with water as described above, the suspended ammonium chloride salt may be removed by filtration, preferably by filter pressing the suspension with the addition of a filter aid such as Hyflow. A suitable lubricating oil may then be added to the filtrate (if it is desired to produce directly an oil solution of the final product) and the alcohol-benzene solvent may then be removed by distillation.

Although a very satisfactory procedure for preparing the hydroxyarylalkyl amine product has been described with reference to the condensation of a nitrogen base with a condensation product of an alkyl phenol, formaldehyde, and hydrogen chloride, and the further auto-condensation of the resulting product, it is to be understood that other procedures may be employed for obtaining products of similar character, though the described procedure is preferred. In these procedures the order of the reaction steps may be changed and similar reactants may be used. For example, the formaldehyde or other aldehyde may be first reacted with ammonia or amines to form alkylolamines for condensation with the phenol or alkyl phenol; or it may be desired to alkylate the base or the base derivatives of the phenol condensation product, e. g., with an alkylating agent such as diethyl sulfate, an alkyl halide, an alcohol, ketone, or olefin, by known alkylating methods, and with reduction by hydrogen, if needed or desired.

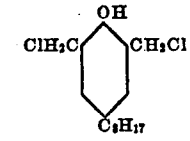
As in the case of many resin preparations, the exact mechanism of the reaction is not entirely understood. In the first stage the alkyl phenol may be regarded as condensing with the reaction product of the hydrogen halide and aldehyde, or as condensing with formaldehyde, the condensation product thereof being condensed with the hydrogen halide. The resulting product of this reaction is a complex mixture of various chlormethyl derivatives, having the following general formula:



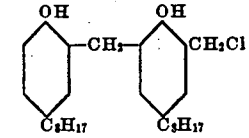
in which the substituent groups may be attached to any position of the aryl nucleus indicated diagrammatically by the hexagon, R represents a hydrocarbon group of at least two and preferably an alkyl group of four or more carbon atoms, and X represents hydrogen or an organic radical, especially an alkyl, aryl or aralkyl radical which may in turn contain substituent groups. Among the compounds which have been found to be present in the products from such reaction are the following:



Chlormethyl diisobutyl phenol

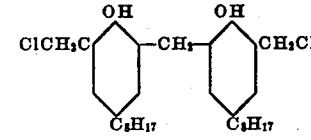


Bis chlormethyl diisobutyl phenol



Chlormethyl bis (diisobutyl hydroxy phenyl) methane

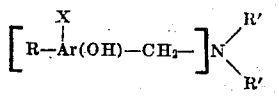
and



Bis (diisobutyl chlormethyl hydroxy phenyl) methane

In the second stage of reaction, the condensation products of the alkyl phenol, the formalde-

hyde, and the hydrogen halide split off halogen in undergoing a further condensation with the nitrogen base, and thus, the alkyl phenol radical becomes united with the base radical through the methylene (—CH_2—) group, thereby forming compounds containing the following characteristic group:



wherein, as before, R—Ar(OH)— represents the alkyl phenol group, X represents H or an organic group and the nitrogen atom N has valences which may be satisfied by hydrogen or organic radicals, (R'), which may represent alkyl, cycloalkyl, aryl or a hydroxy alkyl benzyl radical, and which may represent similar or different radicals in the molecule, as, for example, in the following types of compounds:

R—(X)Ar(OH)—CH_2—NH_2
[R—(X)Ar(OH)—CH_2—]$_2$NH
[R—(X)Ar(OH)—CH_2—]$_3$N
R—(X)Ar(OH)—CH_2—N(R')$_2$
[R—(X)Ar(OH)—CH_2—]$_2$NR'

The salts of the simplest non-resinous compounds containing a single hydroxy benzyl group are not very effective, while the salts of compounds containing at least two hydroxy benzyl radicals in the molecule are more desirable, and the still more complex resinous type of the agents herein disclosed have been found particularly effective for forming improving agents for lubricating oils. In the case of products prepared from ammonia, this condensation and resinification to form the preferred resinous type of products may take place even on standing at room temperature for a long period of time. It is greatly hastened by heating, and such heating is generally necessary to resinify and to render effective the products prepared from amines. During the auto-condensation ammonia or amines are liberated, so that the nitrogen content of the final resinous product will correspondingly be decreased.

While the products described above are preferred for the preparation of addition agents of this invention, it is also possible to prepare suitable hydroxyarylalkyl amines by a number of other methods, of which the following are illustrative:

The hydrogen chloride and formaldehyde may first be reacted to form bis-chlormethyl ethers such as $ClCH_2OCH_2Cl$ and $ClCH_2(OCH_2)_nOCH_2Cl$, in which n is an integer, and these chlorethers may then be caused to react with the phenol. This may be done by passing dry HCl through a suspension of paraformaldehyde in a solvent such as benzene until most of the formaldehyde has reacted with the HCl to give a soluble reaction product. The entire reaction mixture is then mixed with the alkyl phenol to give the —CH_2Cl derivative, the reagents being used preferably in a ratio of about 2.5 mol equivalents of formaldehyde per mol of phenol. This intermediate product is reacted with ammonia and heated as in Example 1 to give an oil-soluble product. The bis-chlormethyl ethers may also be prepared by any other suitable method; the mixed ether products may be fractionated to separate substantially pure single ethers, any one of which may be reacted with the phenol. The phenol may also be added to the formaldehyde-benzene mixture and dry HCl passed through this mixture to obtain the desired reaction product in a single stage reaction. This product is then reacted with ammonia and heated as before to give a resinous product.

The reaction of hydrogen chloride and formaldehyde may also be conducted in the presence of an alcohol, for example, methyl alcohol, to give an alphachlor alkyl ether. This may be done by passing dry HCl into a suspension of paraformaldehyde in the alcohol. This ether may be reacted with the alkyl phenol by heating with or without a catalyst such as zinc chloride, to give the alkyl hydroxy benzyl chloride, the original alcohol being formed as a by-product.

Also, the alkyl phenol may be converted to the sodium salt and this salt, with no excess alkali present, may then be caused to react with an aldehyde to give a dialkylol derivative. This may be converted to the chloride by reaction with hydrogen chloride. Either the alkylol derivative or the resulting halide derivative may then be reacted with ammonia and heated as in Example 1 to give an oil-soluble product suitable for use in this invention. This is illustrated in the following example:

EXAMPLE 2

A molal ratio of iso-octyl phenol (tetramethyl butyl phenol) and of sodium hydroxide are dissolved in water containing sufficient alcohol to dissolve the resulting sodium phenolate. The use of about two volumes of water and two-thirds volume of methyl alcohol per volume of phenol is sufficient for this purpose. Three mols of formaldehyde (in the form of formalin containing 37% CH_2O) is added to this solution and the mixture allowed to stand for about 48 hours at room temperature, the reaction proceeding with the formation of the dimethylol derivative. The reaction mixture is then neutralized with acetic acid or any suitable mineral acid and the liberated bis-hydroxy methyl iso-octyl phenol separates as an upper layer and may be used directly as such or after purification. To form the dichloride, the bis-hydroxy methyl iso-octyl phenol is contacted with concentrated aqueous hydrogen chloride, or dry HCl may be passed through a solution of the compound in a suitable solvent such as benzene, carbon tetrachloride, chloroform, etc.

The reaction with ammonia may be carried out by adding an excess of ammonia, dissolved in isopropyl alcohol, to a solution of the hydroxy methyl iso-octyl phenol or of the corresponding chloride in a solvent such as benzene. This reaction with ammonia, which is quite violent at first, is conducted in the same manner as described in Example 1. When the addition of ammonia is completed, the reaction mixture is sealed in a bomb and heated at 110 to 120° C. for about 18 to 24 hours. The mixture is then washed with water to remove iso-propyl alcohol and ammonium chloride and the benzene solvent is then evaporated to recover the complex reaction product. The latter is a brittle solid resin, readily soluble in asphaltic and mixed base lubricating oils and soluble in turbine oils of high viscosity index at temperatures above about 60 to 70° C.

It is also possible to conduct the reaction of the phenol-formaldehyde and ammonia directly in a single stage by placing a mixture of suitable proportions of these reagents in a bomb and

heating it, for example, at about 110° to 140° C. for about 15 to 20 hours. The proportions of reagents are preferably similar to those used in the processes described above, at least a molal equivalent of formaldehyde and of ammonia being used per mol of phenol. The ammonia is preferably in excess, some remaining at the end of the reaction. This is illustrated in the following example:

EXAMPLE 3

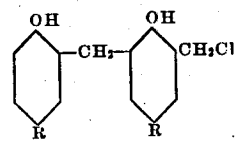
A stainless steel bomb was charged with 51.5 grams of iso-octylphenol. Then 20 grams of 37% strength aqeuous formaldehyde and 25 cc. of concentrated aqueous ammonia were added and the bomb was quickly sealed. It was then heated to 120° C. and held at this temperature for 16 hours. The bomb was then cooled, opened and the reaction mixture poured into water and extracted with ether. The ether extract was washed free of ammonia and was dried over sodium sulfate. Ether was then evaporated, leaving 50.5 grams of a soft red resin which contained 1.3% nitrogen.

EXAMPLE 4

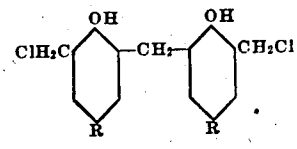
A stainless steel bomb was charged with 150 cc. of absolute ethyl alcohol and 7.5 grams of trioxymethylene. The solution was then saturated with ammonia gas at 0° C. and the trioxymethylene dissolved during the process of saturation, 17.5 grams of ammonia being absorbed. 55.5 grams of iso-octylphenol were then added, the bomb was quickly closed and then heated at 110° C. for 20 hours. The bomb was then cooled, opened and the reaction mixture poured into water and extracted with ether. The ether extract was washed free of ammonia with water and then dried over sodium sulfate. On evaporation of the ether, 62 grams of a soft light colored resin were obtained, which upon analysis was found to contain 2.52% nitrogen. This material was then heated at 200° C. for one-half hour under 3 mm. absolute pressure. Upon cooling the heated product, a brittle resin was obtained which had a nitrogen content of 0.56%.

Primary and secondary amines such as diethyl amine, diamyl amine, piperidine, aniline, diphenyl amine, substituted amines such as ethanol amine, and the like may be substituted for the ammonia in any of the above described processes to prepare similar amine condensation products. These upon heating also undergo further condensation and polymerization.

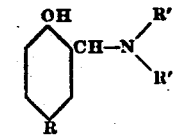
Similarly, more complex derivatives of hydroxy benzyl chloride may be prepared by any suitable methods and may be reacted with ammonia or a primary or secondary amine and heated to secure resinous condensation and polymerization products suitable for use in this invention. Examples of such hydroxy benzyl chlorides are



and



Hydroxy benzyl amines such as those having the characteristic structure



may also be heated to produce resinous auto-condensation products suitable for use in forming the lubricant improvement agents of this invention. In the above formulae the substituents may be linked to any position of the aryl nucleous, and the radicals R and R' have the same significance as in the formulae previously described. This is illustrated by the following example:

EXAMPLE 5

Diethyl amino methyl-isooctyl phenyl,

$(C_2H_5)_2NCH_2.C_8H_{17}C_6H_3OH$

was prepared by reaction of equimolal amounts of ethoxy methyl diethyl amine

$(C_2H_5)_2NCH_2OC_2H_5$

with isooctyl phenol at the temperature of the steam bath for 24 hours. The product was distilled under 3 mm. mercury absolute pressure, obtaining about equal amounts of a clear liquid distillate fraction at 163° to 165° C. and a residue which was a yellow, transparent, hard resin.

The phenols used in any of the above described processes include generally all nuclearly hydroxylated aromatic compounds having phenolic properties and a readily replaceable nuclear hydrogen atom which is preferably either ortho or para to the hydroxyl group. Phenols extracted from petroleum oils may also be used as obtained or after alkylation. Also, other naturally occurring phenols such as those found in vegetable oils, for example, cardinol, obtained from cashew nut shells, may be used. As indicated above, it is preferred that the phenols contain an alkyl group of at least 2, and preferably 4 or more carbon atoms attached to the nucleus. This may be accomplished by alkylating any of the above-described phenols which do not already contain suitable alkyl groups. The alkyl phenols may be prepared by alkylation of phenols with olefins, including mixtures of olefins such as are obtained in cracked petroleum fractions, and by alkylation of phenols with alkyl halides, including chlorinated paraffin wax and chlorinated petrolatums derived from petroleum. Such chlorinated waxes may contain dichlorides and polychlorides and may be used in alkylating phenols by the customary Friedel-Crafts type of synthesis to give complex alkylated phenols of high molecular weight in which several phenol radicals are linked by alkyl radicals in a single molecule. These high molecular weight complex alkyl phenolic products, when reacted with an aldehyde and a nitrogen base as described herein, and then converted into metallic salts, give products which are effective in reducing the pour point of waxy oils and in raising the viscosity index of lubricating oils as well as in improving their lubricating properties, such as film strength, and their stability and resistance to oxidation.

The foregoing description has related to methods of preparing the resinous auto-condensation products of hydroxyarylalkyl amines. The metallic salts of these products, which are the addi-

tion agents of the present invention, may be readily prepared by reacting the products with metallic bases, alcoholates, etc. For example, the octylphenol-formaldehyde-hydrogen chloride-ammonia product of Example 1 may be reacted with barium hydroxide hydrate by heating with a dispersion of the latter in mineral oil or benzene to form a barium salt in which the metal replaces a hydroxy group. The same material may be reacted with an alcoholate, such as magnesium methylate or ethylate; or it may be reacted with caustic alkali, and the alkali salt so formed may be converted into other metallic salts by double decomposition, as in reacting with a salt of another metal. Chlorides of polyvalent metals, such as magnesium, zinc and the like, work satisfactorily in the double decomposition except in the case of barium, which is preferably used in the form of the bromide to secure sufficient solubility in absolute alcohol, which is the preferred medium for these reactions.

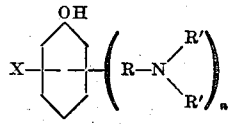
The onium salts of the resinous products of hydroxyarylalkyl amines may be prepared by reacting a halide of an onium base, e. g., a tetraalkyl ammonium chloride, a sulfonium chloride, or the like, with an alkali metal salt of the resinous hydroxyarylalkyl amine, preferably in an alcoholic solution. The alkali halide formed in the reaction is insoluble and may be conveniently removed.

The preparation of the salts from the compounds containing free hydroxy groups is illustrated by the following example of the preparation of a barium salt:

EXAMPLE 6

145 grams of the ammonia derivative of chloromethyl diisobutyl phenol, obtained, for example, as in Example 1, was refluxed with 145 grams of C. P. benzene and 215 grams of $Ba(OH)_2.8H_2O$ for 60 hours, water being removed from the reaction mixture through a trap in the reflux condenser. The mixture was filtered to give an approximately 50% solution of the barium salt in benzene. Analysis showed that the product, on a benzene-free basis, contained 11.13% barium. A product containing 10.87% of barium on a solvent free basis may, however, be obtained after only eight hours of refluxing. On removal of the solvent the dry material was a brown powdery mass.

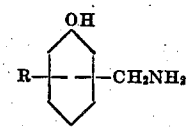
The invention thus contemplates the use as improving agents for extreme pressure lubricants of metal salts of high molecular weight resinous auto-condensation products of hydroxyarylalkyl amines containing the characteristic structure



in which R is an alkyl linkage such as



in which R' represents either H or alkyl or aryl groups or substituted alkyl or aryl groups and may represent similar or different groups in the same molecule, n represents a small whole number, and X represents hydrogen or one or more organic radicals attached to the aryl nucleus, especially an alkyl, aryl or aralkyl radical which may in turn contain substituent groups, such as a hydroxy alkyl benzyl radical. The desired compounds are also characterized by having at least four carbon atoms in alkyl groups joined to the aryl nucleus and/or to the amine radical (N=) and are further characterized in having undergone an auto-condensation reaction to produce a resinous, viscous liquid to solid product of high molecular weight which is soluble in hydrocarbon oils. In this, as in all the other structural formulae given in this application, the location of the substituent radicals in regard to the aryl nucleus is given merely as an illustration, and the various substituent radicals may be attached to any positions of the aryl nucleus, ortho, meta and/or para to the hydroxyl group and to each other. The preferred compounds for use according to this invention come within the above definition and are salts of resinous auto-condensation products of materials having the characteristic structure



in which R is an alkyl group of at least four and preferably five to twenty or more carbon atoms, the compounds having undergone an auto-condensation reaction as described above. Although the alkaline earth metal salts of these resinous products are especially useful, other divalent metal salts, such as the salts of zinc, tin, cadmium and lead, as well as the alkali metal salts, should be particularly mentioned. In place of the metallic salts the corresponding salts containing basic radicals instead of metals, such as onium salts, e. g., the ammonium, alkylammonium, sulfonium, phosphonium and pyridonium salts, may be used to advantage.

Illustrations of the use of the products described above as extreme pressure lubricant improving agents in accordance with this invention are presented in the following example:

EXAMPLE 7

An extreme pressure lubricant concentrate was prepared as described in U. S. Patent 2,124,598 by heating chlorinated kerosene (40% chlorine, prepared by chlorination of kerosene at 200° F. with chlorine gas) with a mixture of sulfur and aqueous alkaline sodium hydrosulfide, sodium hydroxide and isopropyl alcohol under reflux for several hours. The reaction mixture was then permitted to settle and a middle layer of the desired reaction product was separated from a lower aqueous layer of inorganic salts and an upper alcohol layer was then stripped free of alcohol. There was thus obtained a sulfurized chlorinated kerosene containing about 7% by weight of sulfur and 32% by weight of chlorine, both in effective form to increase extreme pressure lubricant properties of mineral oils, as evidenced by the ability of a 10% blend of this concentrate in a mineral lubricating oil to carry more than a 325 pound load on an S. A. E. Extreme Pressure Lubricant Testing Machine (S. A. E. Trans 1936, page 293).

This sulfur-chlorine extreme pressure concentrate was subjected to the Chrysler-Almen corrosion test (described below) as follows:

Ten parts by weight of this extreme pressure addition agent were blended with 90 parts by weight of a well refined straight mineral lubricating oil having a viscosity index of 100. A portion of this blend containing no addition

agent and other portions containing, respectively, 0.2% of the barium salt of the auto-condensation product of the ammonia derivative of chloromethyl diisobutyl phenol, prepared as in Example 6, 0.3% of the calcium salt of the same, 0.3% of the zinc salt of the same and a mixture of 0.2% of the auto-condensation product of the ammonia derivative of chloromethyl diisobutyl phenol and 0.1% of the barium salt of the same were subjected separately to the Chrysler-Almen corrosion test. The test pieces resulting from the test on the unblended lubricant were badly stained and showed considerable rust. The tests on blends of the lubricant with the various metal salts showed no evidence of corrosion, stain or rust in any case.

Chrysler-Almen corrosion test

The lubricant in question is run on the Almen machine with six weights for twenty minutes. The Almen test pieces and the lubricant is then placed in a bottle and stored in an oven at a temperature of 175° to 185° F. while air saturated with water vapor is blown through the lubricant for 24 hours. The test pieces are then washed with naphtha and examined.

The invention is particularly applicable to extreme pressure lubricants containing corrosive chlorine compounds, for instance, chlorinated aliphatic or aromatic hydrocarbons such as chlorinated paraffin wax, kerosene, aromatic, petroleum, or coal tar solvents and derivatives in which a portion of the chlorine has been replaced by sulfur. The amount of chlorine, especially the active chlorine, to be used will, of course, depend upon the severtiy of the conditions under which the lubricant is to be used but will generally vary between the approximate limits of 5% to 50% (preferably above about 32%) in the chlorinated organic compounds or between the approximate limits of .05% and 10% based on the total weight of lubricant (exclusive of any water which may be used as in the preparation of water-soluble type cutting oil).

In preparing extreme pressure lubricants of the halogen type, it is frequently desirable to incorporate sulfur compounds especially to increase the stability of the lubricant at high temperature and for this purpose a sulfurized fatty or mineral oil or a sulfur compound such as an organic sulfide, mercaptan, di- or polysulfides, xanthates, xanthogen sulfides, thio carbonates, etc., may be used in which generally from about 1% to 30% (and preferably about 7%) of sulfur is incorporated in the active or combined state. Based on the total weight of lubricant, the proportion of sulfur should normally be between the limits of about 0.2% and 10%.

Instead of using separate chlorine compounds and sulfur compounds, it is possible to use single materials in which both sulfur and halogen have been incorporated by treatment of suitable unsaturated organic compounds, such as cracked wax and fatty oils of the drying and semi-drying types, with a sulfur halide, or by reacting an organic halogen compound with an inorganic sulfide, poly-sulfide, thio carbonate or xanthate.

A further advantage of the improving agents of this invention is that they are soluble in highly paraffinic lubricating oils and may be used to prepare stable extreme pressure lubricants and cutting oils with highly refined petroleum base lubricants having a viscosity index of 80 to 103 and even higher. Such oils may be obtained directly as distillate and residual fractions of paraffin base lubricants or by suitable refining, such as solvent extraction, hydrogenation and the like of lower quality lubricating oil fractions such as those obtained from mixed base and asphaltic base crudes. Oils of viscosity indices below 80 may, of course, also be used. The viscosity and viscosity index of the base lubricating oils used in preparing the improved extreme pressure lubricants and cutting oils of the present invention should thus be selected in regard to the particular service for which the blended lubricant is intended.

Although the mechanism and the operation of the present invention are not thoroughly understood and it is not desired to be limited to any particular theory as to the operation thereof, it is believed that the active chlorine compounds present in the extreme pressure lubricant are capable of carrying very high loads between metal surfaces by means of the formation of microscopic films of metal halides such as ferrous or ferric chloride which prevent metal to metal contact and resultant welding and scoring. These films, particularly in the presence of moisture which is almost always present in gear cases tend to hydrolyze into metal oxides and hydrochloric acid. Also the chlorine compounds in the lubricant itself tend to hydrolyze with the liberation of hydrochloric acid (HCl) and this acid in turn attacks the metal surface because iron and steel and various alloys in general are quite susceptible to attack or corrosion by hydrochloric acid and other strong halogen acids. On the other hand, in lubricants containing a substantial amount of active sulfur, the latter, particularly in the presence of moisture and at elevated temperature and pressures produced between gear teeth or over a long period of time, tends to be converted into hydrogen sulfide and the latter tends to react with the metal to produce the corresponding metal sulfides which are generally black, such as iron and copper sulfides.

If desired, other known addition agents or lubricants may be incorporated in the lubricant prepared according to the present invention; for instance, fatty oils, fatty acid or naphthenic acid soaps, esters, thickeners such as polyisobutylene having a molecular weight above 1,000, pour depressants, antioxidants, oil-soluble metal soaps, dyes, etc., may be added.

It is not intended that this invention be limited to any of the particular examples which have been given for illustration only, nor by any of the theories as to the operation of the invention but only by the appended claims in which it is intended to claim all novelty inherent in the invention as broadly as the prior art permits.

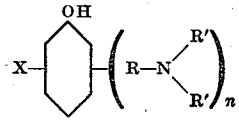
We claim:

1. A lubricant composition comprising a major proportion of a mineral lubricating oil, an oil-soluble halogen-containing compound of a kind and in sufficient quantity to substantially increase the load carrying capacity of the lubricant but tending to form a hydro-halogenic acid in the presence of said oil, and a small proportion of an oil-soluble salt of an auto-condensation product of a hydroxyarylalkylamine, said amine having alkyl groups which contain a total of at least 4 carbon atoms per molecule.

2. A lubricant composition comprising a major proportion of a mineral lubricating oil, an oil-soluble organic halide of a kind and in sufficient quantity to impart extreme pressure characteristics to said lubricant but tending to form a hydro-halogenic acid in the presence of said oil

and a small proportion of an oil-soluble metal salt of an auto-condensation product of an alkyl hydroxy benzyl amine having at least four carbon atoms in the alkyl group.

3. An extreme pressure lubricant comprising a major proportion of a mineral lubricating oil, a small proportion of an oil-soluble organic halide of a kind and in sufficient quantity to increase substantially the extreme pressure lubricant characteristics of said oil but tending to form a hydro-halogenic acid in the presence of said oil, and a small proportion of an oil-soluble salt of an auto-condensation product of an hydroxy-arylalkyl amine, the uncondensed amine having the characterizing structure



in which R is an alkyl linkage, R' is hydrogen or an alkyl or aryl radical or a substituted alkyl or aryl radical, n is a small whole number, and X is hydrogen or an organic radical.

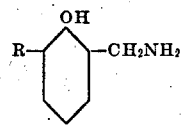
4. A lubricant composition comprising a mineral lubricating oil, a small proportion of an oil-soluble organic halide of a kind and in sufficient quantity to impart extreme pressure characteristics to said lubricant but tending to form a hydro-halogenic acid in the presence of said oil, and a small proportion of an oil-soluble metal salt of an auto-condensation product of an hydroxyarylalkyl amine, the uncondensed amine having the general composition formula

$$[R—Ar(OH)—CH_2—]_nX_m$$

wherein R represents at least one alkyl group substituent in the aromatic nucleus Ar, the subscripts m and n are integers to satisfy valence requirements, and X represents a nitrogen base radical in which the nitrogen is linked to the methylene group.

5. A composition as described in claim 4 in which the subscript n is an integer from one to three, and in which X is a nitrogen base radical in which the nitrogen is linked to the aryl nucleus, Ar, through or in a methylene group, $—CH_2—$.

6. An extreme pressure lubricant comprising a major proportion of a mineral lubricating oil, a substantial proportion of an oil-soluble organic halide of a kind and in sufficient quantity to impart extreme pressure characteristics to said lubricant but tending to form a hydro-halogenic acid in the presence of said oil, and a small proportion of an oil-soluble metal salt of a resinous auto-condensation product of an alkyl hydroxy benzyl amine having the characterizing structure



in which R represents an alkyl group of at least four carbon atoms.

7. A composition as described in claim 6 in which the salt is a salt of a divalent metal.

8. A composition as described in claim 6 in which the salt is a salt of an alkaline earth metal.

9. A composition as described in claim 6 in which the salt is a barium salt.

10. A composition as described in claim 6 in which the salt is a salt of an alkali metal.

11. A composition as described in claim 6 in which the salt is an onium base salt.

12. An extreme pressure lubricant comprising a major proportion of a mineral lubricating oil, a substantial proportion of an oil-soluble organic compound containing chlorine and sulfur and of a kind and in sufficient quantity to impart extreme pressure characteristics to said lubricant but tending to form hydrochloric acid in the presence of said oil, and a small proportion of a metal salt of an oil-soluble auto-condensation product of an ammonium derivative of an alkyl phenol - formaldehyde - hydrogen chloride condensation product, in which the alkyl substituent of the phenol contains at least four carbon atoms and in which a nitrogen base radical is linked through a methylene group to the aryl nucleus of the alkyl phenol.

13. A composition as described in claim 12 in which the alkyl phenol is a para-iso-octyl-phenol.

14. An extreme pressure lubricant comprising a major proportion of a mineral lubricating oil, a minor proportion, effective to increase substantially the extreme pressure lubrication characteristic of said oil, of a sulfurized chlorinated naphtha containing at least 7% by weight of sulfur and 32% by weight of chlorine and also containing as an anti-corrosion agent effective in suppressing the corrosive tendencies of said sulfurized halogenated naphtha, and a small proportion of an oil-soluble metal salt of a resinous condensation product of ammonia with an alkyl hydroxy benzyl chloride.

JOHN C. ZIMMER.
GEORGE M. McNULTY.