

UNITED STATES PATENT OFFICE

2,334,594

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 January 29, 1941,
Serial No. 376,478

11 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 materials 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 alkyl hydroxy benzyl amine.

The materials effective in increasing the film strength of oils are often prepared as concentrates which are later blended with relatively large amounts of lubricating oils to prepare high film strength lubricant compositions for the particular purpose desired. It is often desirable to add other blending agents to the concentrates, both in order to simplify the later blending operations and to offset any tendency of the concentrates to corrode metals which may be evidenced during transportation and storage. It has also been found that the alkyl hydroxy benzyl amines described herein are soluble in such concentrates and are effective in reducing their corrosive action on metals. It is a further object of this invention to prepare improved highly stable concentrate solutions of high film strength lubricant additives.

The preferred type of agent utilized for the purpose of this invention is characterized by ammonium derivatives of alkyl phenol-formaldehyde-hydrogen halide condensation products. These compounds are obtained with satisfactory oil-solubility and effectiveness for the objects 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 liquid ammonia or an equivalent strong base, e. g., an amino compound, an organic nitrogen base, or other organic bases, which may contain other metalloids, such as phosphorus. Liquid ammonia is the highly preferred base reactant. Next in order of importance come the aliphatic amines and aromatic amines, primary, secondary, and tertiary.

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

Even though the initial phenolic compound contains 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 agent goes with great ease. The complete reaction may be considered as involving two stages: first, a substitution 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 the preferred agents is illustrated by the following:

EXAMPLE 1

Into a solution of 18 parts by weight of para-formaldehyde and 100 parts by weight of strong hydrochloric acid, hydrogen chloride gas was introduced until the solution was saturated. To this mixture, 41 parts by weight of para-iso-octyl phenol (para tetramethylbutyl phenol) in benzol solution (50% by weight) were added in the course of one-half hour, while stirring well, the temperature increasing from about 15° C. to 50° C. The stirring was continued at 50° C. for an hour after the phenol had been added, and during this time a feeble current of hydrogen chloride was conducted into the solution. The alkyl phenol-formaldehyde-hydrogen chloride condensation product formed remained in solution in the benzol and was separated from the aqueous hydrochloric acid mother liquid. For the second stage of treatment, the separated benzol solution of the condensation product was placed in a beaker, and a dilute liquid ammonia solution in isopropyl alcohol was added to this solution while stirring until a fair excess, about 10%, of ammonia was present. The mixture was then transferred to a bomb and heated therein for 16 to 20 hours at 110° C. without further agitation. The pressure developed during heating ranged from about 20 lbs. to 40 lbs. per square inch. The material in the bomb reacted vigorously with considerable evolution of heat. After the reaction was complete in the bomb, the reaction mixture comprising ammonium chloride, an ammonium derivative of the phenol-formaldehyde-hydrogen

chloride condensation product, and isopropyl alcohol, was transferred to an open vessel wherein it was diluted with naphtha and water, stirred until the ammonium derivative of the alkyl phenol-formaldehyde-hydrogen chloride condensation product went into solution in the naphtha, while ammonium chloride, excess ammonia, and the isopropyl alcohol were removed by the water. The naphtha solution was washed several times with water to free it of all soluble chlorides after which, to obtain a concentrate of the product, the naphtha solution was distilled to leave a brittle resinous material.

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, i. e., with chloromethyl alcohol; or, as condensing with formaldehyde, and the condensation product thereof being condensed with the hydrogen halide. Either way, the resulting product of this reaction may be considered as being a hydroxy alkyl benzyl chloride, or chloromethyl alkyl phenol, with the formula:

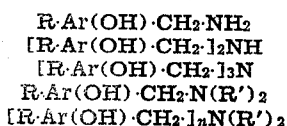


wherein the chlorine analysis of this product shows introduction of approximately one chloromethyl group into one alkaryl-hydroxy or alkyl phenol group, R.Ar(OH), R representing one and more alkyl substituents in the aromatic nucleus Ar.

In the second stage of reaction, the condensation product of the alkyl phenol, the formaldehyde, and the hydrogen halide acid, or the hydroxy alkyl benzyl chloride, splits off the halogen in undergoing a further condensation with the organic 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:

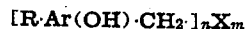


wherein, as before, R.Ar(OH) represents the alkyl phenol group and the nitrogen atom N has valences which may be satisfied by hydrogen or organic radicals, (R') e. g., alkyl, cyclo-alkyl, aryl, or by more than one hydroxy alkyl benzyl radical, as for example, in the following types of compounds:



In the simplest reaction with ammonia the primary amine would be formed, but from analysis of the components of the product, which is a resinous mixture of the amines, it is found that more complex compounds, i. e., the secondary and tertiary amines, are more probably present. Analysis of separated fractions of the product obtained by solvent extraction shows that one and more of the phenolic groups are combined with one nitrogen atom in the base radical, and principally the product is indicated to have the compositional formula corresponding to that of the secondary amines. However, fractionation is not necessary to obtain the desired effects of the product as a blending agent; but if so desired, the fractions may be separated to be used as blending agents for the objects set forth.

The base derivatives of the alkyl phenol-aldehyde-hydrogen halide condensation products, which in the broad sense are to be used as stabilizing agents in accordance with the present invention, may be represented by the generalized formula:



wherein n is an integer denoting the number of hydroxy alkyl benzyl groups attached to one or more (m) base radicals X, which is an amino group or an equivalent base radical.

The substances described as ammonium derivatives of a phenol-formaldehyde-hydrogen chloride condensation reaction are apparently formed in a manner which prevents the reactants from condensing to an infusible and insoluble stage, as occurs in ordinary phenol and formaldehyde condensation reactions. This may be accounted for by the action of hydrogen halide, which evidently prevents many phenol groups from becoming interlinked by methylene groups; and for the objects of this invention it has been found preferable to have the phenol groups contain alkyl or aliphatic substituents having at least 3 or 4 carbon atoms. The alkyl phenols having isoalkyl substituents containing from 4 to about 12 carbon atoms are more particularly preferred. Satisfactory products have been obtained with the aliphatic radical substituent ranging up to 18 or more carbon atoms, as with an octa-decyl group.

Although a very satisfactory procedure for preparing the stabilizing agent has been described with reference to the condensation of a base with a condensation product of an alkyl phenol, formaldehyde, and hydrogen chloride, it is to be understood that other procedures may be employed for obtaining blending agents of similar character though the described procedure is preferred. In these procedures the order of the reaction steps may be changed and equivalent reactants may be used. For example, it may be desired to alkylate the intermediate or final condensation product to introduce alkyl substituents into the phenol nucleus; it may be desired to first react the formaldehyde or other aldehyde with ammonia, or with a primary, secondary, or tertiary amine to form alkyl-alkylol amines 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 di-ethyl sulfate, an alkyl halide, an alcohol, or ketone, by known alkylating methods, and with reduction by hydrogen, if needed or desired.

As stated before, the more complex resinous type of the agents herein disclosed have been found more particularly effective. Hence to improve a monomeric agent having, for example, a compositional formula represented by $R.Ar(OH).CH_2.N(R')_2$, wherein R and R' represent hydrocarbon radicals, heat polymerization or condensation of such a monomer may be used to convert it into a more complex polymeric type compound, such as represented by the general compositional formula



wherein several of the units $[R.Ar(OH).CH_2]$ may be linked to one another and be terminally linked to one or more of the structural units $[N(R')_2]$. The amino radical, $N(R')_2$, in these compounds may be represented more generally by the formula $N(H)_\gamma(R')_{2-\gamma}$, wherein the γ hy-

drocarbon radicals R' and the x hydrogen atoms attached directly to the nitrogen add up to two, e. g., $\cdot\text{NH}_2$, $\cdot\text{N(H)}(\text{R}')$, or $\cdot\text{N(R}')_2$; and, of course, the hydrocarbon radicals in each instance may be similar or dissimilar.

The use of the blending agents described above in the preparation of high film strength lubricants is illustrated by the following examples:

EXAMPLE 2

An extreme pressure lubricant concentrate was prepared as described in U. S. P. 2,124,598 by heating chlorinated kerosene (40% chlorine, prepared by chlorination of kerosene at 200° F. temperature 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 and 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 a S. A. E. extreme pressure lubricant testing machine (S. A. E. Trans 1936, page 293).

This sulfur-chlorine E. P. (extreme pressure) concentrate was subjected to the Chrysler-Almen corrosion test (described below).

Ten parts by weight of this E. P. addition agent were blended with 90 parts by weight of a well-refined straight mineral lubricating oil having a viscosity index of 100. This blend was divided into two portions, (a) and (b). One-half percent by weight of the alkyl phenol methyl amine derivative described in Example 1 was added to portion (b). Both portions were then subjected separately to the Chrysler corrosion test. The test pieces resulting from the test on portion (a) were badly stained and showed considerable rust. The test pieces from the test on portion (b) showed no evidence of corrosion, stain or rust.

Chrysler-Almen corrosion test

The lubricant in question is run on the Almen machine with 4 weights for twenty minutes. The Almen test pieces and the lubricant are then placed in a bottle and stored in an oven at a temperature of 175° to 185° F. while moist air is blown through the lubricant for 24 hours. The test pieces are then washed in benzol and examined for rust.

EXAMPLE 3

A blend of 3% by weight of the alkyl hydroxy benzyl chloride-ammonia condensation product described in Example 1 and 97% by weight of the sulfur-chlorine E. P. concentrate, the preparation of which is described in Example 2, was held at a temperature of 120° F. for nine weeks. There was no evidence of any sedimentation at this time. Ten percent by weight of this concentrate was then blended with a straight mineral lubricating oil and the blend was subjected to the Chrysler-Almen corrosion test described above. The test pieces again showed no evidence of corrosion.

Similarly, mineral oil blends of the blended concentrate described above were subjected to

the same storage test, with no evidence of any tendency to separate or to deteriorate.

EXAMPLE 4

Blends (a) and (b) described in Example 2 were subjected to road tests, under conditions of high atmospheric humidity, in the lubrication of the rear axle of a current model Chevrolet passenger car equipped with new hypoid gears in each test. This is the test for hypoid gear lubricants described in "General Motor Standards," volume 2, page D-5, March, 1939. Blend (b) gave entirely satisfactory operation with no evidence of staining, rusting or scuffing of the gears, while the gears after the test with blend (a) were stained and reddened by rust.

Also, when gears have been stained by the use of corrosive extreme pressure lubricants to an extent insufficient to permanently harm the friction surfaces, it has been found that the substitution of the improved extreme pressure lubricants of this invention, such as the blend (b) described above, will remove these stains from the areas of contact of the gear surfaces and will thereafter prevent further staining or corrosion of such surfaces.

EXAMPLE 5

The blends (a) and (b) described in Example 2 were also subjected to copper corrosion tests in which a freshly polished copper strip was immersed in the test oil for one hour at a temperature of 212° F. The copper was stained and appreciably blackened by blend (a) but not by blend (b).

EXAMPLE 6

A light petroleum lubricating oil was blended with 10% of the sulfur-chlorine E. P. concentrate, the preparation of which is described in Example 2, and ½% by weight of flowers of sulfur. The resulting blend is an effective cutting oil, but stains copper and its alloys badly even under ordinary atmospheric conditions, by the formation of sulfide films.

One-half percent by weight of the alkyl hydroxy benzyl chloride-ammonia condensation product described in Example 1 was added to this cutting oil composition. The staining tendency of the blend was greatly reduced to such an extent that it was no longer objectionable in the use of this composition as a cutting oil, even in the presence of machine parts containing copper or its alloys.

Generally, the amount of the oil-soluble organic base to be used should be between the approximate limits of 0.01% and 1% or 2% depending upon the type and the amount of chlorine and sulfur or other active and corrosive load-carrying elements in the lubricant but generally an amount between the approximate limits of 0.05% and 0.5% will suffice. The improving agents of this invention may also be added to concentrates of materials of high film strength, intended for the preparation of E. P. lubricants or cutting oils, in suitable proportions of about 0.1% to 10% by weight, to secure the desired concentration in the finished lubricant.

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, espe-

cially the active chlorine, to be used will, of course, depend upon the severity 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 poly-sulfides, xanthates, xanthogen sulfides, thio carbonates, etc., may be used in which generally from about 1% to 30% (and preferably above 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.

The oil-soluble organic amines of this invention are believed to have some effect in preventing hydrolysis of the metal chloride films and they also apparently neutralize any nascent hydrochloric acid which may tend to form, and these organic amines act differently in oil than they do in aqueous media and have some unexpected ability to alter the chemical reactions which take place when the lubricant is subjected to extreme pressure conditions, permitting the desired film formation and lubrication under high pressures without substantial corrosion of the adjacent metal surfaces. As already indicated, an important characteristic of the improved extreme pressure lubricant improving agents of this invention is their ability to form stable compositions with extreme pressure lubricants and concentrates thereof containing chlorine in an active form, effective in increasing the film strength of the base oils. The ordinary amines form amine hydrochlorides in such E. P. lubricants, these precipitate out thereby reducing the concentration both of the E. P. agents and of the amine. The improving agents of this invention stay in solution over very extended periods with no precipitation or loss of effectiveness as corrosion preventatives. The superiority of the improving agents of this invention over the ordinary amines in this respect is indicated in the following example:

EXAMPLE 7

An extreme pressure lubricant was prepared by blending 10 parts by weight of the extreme pressure concentrate (7% sulfur and 32% chlorine in a chlorinated and sulfurized kerosene) described in Example 2 with 90 parts of a refined petroleum lubricating oil having a Saybolt viscosity of 100 seconds at 210° F. To separate portions of this blend were added 0.3% by weight of the alkyl hydroxy benzyl amine condensation product described in Example 1 and several other amines. One portion of each of the resulting blends was stored at room temperature and another portion at 120° F., the blends being examined daily for the appearance of any substantial amounts of separated matter. The results of these tests are given in the following table.

Stability tests

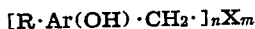
	Room temperature	120° F.
Sulfur-chlorine E. P. lubricant—		
+ triethanolamine.....	Sediment in 8 days..	Sed. in 3 days.
+ triamylamine.....	Sediment in 2 days..	Sed. in 1 day.
+ hexylamine.....	Sediment in 2 days..	Sed. in 1 day.
+ alkyl hydroxy benzyl amine.	No sediment in 90 days.	No sediment in 90 days.

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, anti-oxidants, 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 comprising a mineral lubricating oil, a small proportion of an organic halide containing halogen in an active form corrosive to metals and a proportion sufficient to function as an anti-corrosive agent of a resinous condensation product having the general compositional formula



wherein R represents at least one alkyl group substituent in the aromatic nucleus Ar, the subscripts n and m are integers, and X represents a base radical.

2. A composition as described in claim 1 in which the subscript n is an integer from 1 to 3, and in which X is a nitrogen base radical in which the nitrogen is linked to the aryl nucleus, Ar, through carbon in a methylene group, $\cdot CH_2$.

3. An extreme pressure lubricant comprising a major proportion of a mineral lubricating oil, a substantial proportion of an organic halide containing halogen in an active form and a proportion sufficient to function as an anti-corrosive agent of an ammonium derivative of an alkyl phenol-formaldehyde-hydrogen halide resinous condensation product containing a nitrogen base radical attached to the aryl nucleus of an alkyl phenol group through a methylene group.

4. An extreme pressure lubricant comprising a major proportion of a mineral lubricating oil, a substantial proportion of an organic compound containing chlorine and sulfur in an active condition and a proportion sufficient to function as an anti-corrosive agent of an ammonium derivative of an alkyl phenol-formaldehyde-hydrogen chloride resinous condensation product, in which the alkyl substituent of the phenol contains at least 4 carbon atoms and in which a nitrogen base radical is linked through a methylene group to the aryl nucleus of the alkyl phenol.

5. Composition as described in claim 4 in which the alkyl phenol is a para-iso-octyl-phenol.

6. 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 a proportion sufficient to function as an anti-corrosive agent of an oil-soluble resinous condensation product of ammonia with an alkyl hydroxy benzyl chloride.

7. An extreme pressure lubricant base concentrate comprising a major proportion of a sulfurized chlorinated naphtha containing at least 7% by weight of sulfur and 32% by weight of chlorine having dissolved therein about 0.1% to 10.0%

of an ammonia derivative of an alkyl phenol-formaldehyde-hydrogen halide resinous condensation product in which the alkyl substituent of the phenol contains at least 4 carbon atoms and in which nitrogen is linked through a methylene group to the aryl nucleus of the alkyl phenol group.

8. An extreme pressure lubricating composition comprising a major proportion of lubricating oil with the properties of such composition affecting its use as an extreme pressure lubricant improved by incorporating therein minor amounts based on the amount of lubricating oil of an organic compound which is substantially non-volatile, which is normally corrosive to bearings, which organic compounds contain an element in the active condition selected from the group consisting of chlorine, sulfur and phosphorus, and an amount sufficient to function as an anti-corrosive agent of a resinous mixture of an ammonia derivative of an alkyl phenol formaldehyde hydrogen halide condensation product containing a nitrogen base radical attached to the aryl nucleus of the alkyl phenol group through a methylene group.

9. An extreme pressure lubricating composition comprising a major proportion of lubricating oil with the properties of such composition affecting its use as an extreme pressure lubricant improved by incorporating therein minor amounts based on the amount of lubricating oil of a halogen compound in the active form which is substantially non-volatile and which is normally corrosive to bearings, and about 0.01 to 1% by weight of an ammonia derivative of an alkyl phenol formaldehyde hydrogen halide condensation product containing a nitrogen base radical attached to the aryl nucleus of the alkyl phenol group through a methylene group.

10. An extreme pressure lubricating composition comprising a major proportion of lubricating oil with the properties of such composition affecting its use as an extreme pressure lubricant improved by incorporating therein minor amounts based on the amount of lubricating oil of a halogen compound in active form and an amount sufficient to function as an anti-corrosive agent of a resinous mixture of amino derivatives of alkyl phenol formaldehyde hydrogen chloride condensation products containing a nitrogen base radical attached to the aromatic nucleus of a phenol radical through a methylene group.

11. An extreme pressure lubricating composition comprising a major proportion of lubricating oil with the properties of such composition affecting its use as an extreme pressure lubricant improved by incorporating therein minor amounts based on the amount of lubricating oil of a halogen compound in the active form and a proportion sufficient to function as an anti-corrosive agent of a resinous condensation product of ammonia with an alkyl phenol formaldehyde hydrogen chloride condensation product.

JOHN C. ZIMMER.
GEORGE M. McNULTY.