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LUBRICANT

Eugene Lieber, West New Brighton, Staten Island, N. Y., and Aloysius F. Cashman, Bayonne, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

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This invention relates to improved lubricants, and more particularly to the addition of a corrosion preventer to lubricating oils which are normally corrosive to metals coming in contact therewith.

In the manufacture of lubricating oils, it is often desirable to incorporate small amounts or even substantially large amounts of materials which have some special beneficial effect, such as increasing the oiliness or load-carrying capacity of the lubricating oil base stocks, even though such materials may impart thereto a tendency to corrode metals coming in contact with the lubricants. Thus, for imparting high film strength to oils to be used for lubricating bearings in engines, gears and other moving metal parts which contact each other under high pressures, as well as for cutting oils as used for machining various metals, these lubricants are often compounded by adding to a mineral lubricating oil base stock substantial amounts of chlorinated materials, either alone or in combination with sulfur compounds and sometimes phosphorous compounds. Such lubricants tend to rust the gear surfaces which are being lubricated and also cause corrosion and staining ferrous, copper-bearing alloys used in bearings, bushings, pistons, etc. Also, sulfur alone or in the presence of chlorine, especially cutting fluids, usually causes a black stain such as copper sulfide, on copper alloys. Other industrial oils such as turbine oils generally cause or permit a certain amount of corrosion of the metal parts.

It has now been found that these corrosive tendencies of the lubricant can be substantially reduced, without substantially interfering with the other more desirable characteristics of the lubricant. The invention is particularly applicable to lubricants containing active halogen and/or sulfur, and especially to such lubricants containing more than 1½% of chlorine, based on the total weight of lubricants.

Broadly, the invention comprises adding to a lubricant which is normally corrosive to metals, a small amount of an oil-soluble amide. Although amides containing an unsubstituted amino group are considered to come within the scope of the invention, it is preferred to use amides in which one or both of the hydrogen atoms attached to the nitrogen in the amino

group, are substituted, i. e. replaced, by an organic group which may be a simple hydrocarbon group such as an alkyl group or may be a complex group such as that derived from a polyolefin poly-amine. The amide may therefore broadly be considered as a compound containing at least one group Ac-N, in which Ac represents an acyl group or an acid radical, such as fatty acids, naphthenic acids, or various dibasic or other polybasic acids. The amides or N-substituted amides to be used should ordinarily contain more than 10 carbon atoms and preferably more than 15 carbon atoms.

The simpler amides coming within the scope of the invention may be considered to have the general formula Ac-NRR' in which Ac represents the acid radical and R and R' represent either hydrogen or an organic group. Preferably, at least one of either R and R' is either an alkyl group or contains a substantial amount of aliphatic carbon atoms. Examples of some of these amides are the following: N-octyl stearamide having the formula $C_{17}H_{35}CONHC_8H_{17}$, N,N,diamyl stearamide, N diamyl oleyl amide, N,N',diamyl sebacamide, N-octyl amide of petroleum naphthenic acids, N diamyl amide of petroleum naphthenic acids.

An example of a more complex amide suitable for the present invention and, in fact a preferred type of amide is the naphthenamide of triethylene tetramine and of tetraethylene pentamine. By the term "naphthenamide" is meant the naphthenic acid amide. Since the poly-olefin poly-amines such as the triethylene tetramine and tetraethylene pentamine, having an amino group at each end of the molecule, each of these terminal amino groups would normally tend to react when added to a carboxylic acid chloride, and therefore the resultant acid amide would have two acid radicals linked together by a polyolefin polyamine group.

The amides of this invention, having the amino nitrogen atom linked directly to the carbonyl carbon atom of the acid, are not to be confused with plain amines or amine salts or soaps, in which latter cases the nitrogen atom is linked to an oxygen atom and not to a carbon atom in the acid radical.

In preparing lubricants according to this invention, any of the commonly used mineral oil

base stocks can be used such as distillate or residual fractions derived from paraffinic, naphthenic, or other typed crudes, and these various fractions may have been subjected to any of the known refining or treating processes such as acid treating, clay treating, solvent extraction, etc.

Generally, the amount of the amide to be used will depend to a substantial extent upon the amount of constituents present which have corrosive tendencies, but normally the amount of amide should be about 0.1%–5.0%, and generally, or preferably, about 0.3%–2.0%. For instance, 0.5% has been found very suitable for most purposes.

The invention is particularly applicable to extreme pressure lubricants containing corrosive chlorine compounds, for instance, chlorinated derivatives of aliphatic or aromatic hydrocarbons such as paraffin wax, kerosene, aromatic petroleum fractions or coal tar solvents, and such derivatives which also contain sulfur. The amount of chlorine, especially 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% and 50% in the chlorinated organic compounds, or between the approximate limits of 0.05% and 10% based on the total weight of lubricant (exclusive of any water which may be used in the preparation of special types of lubricant such as of the water-soluble type, e. g. cutting oil).

In preparing extreme pressure lubricants of the active 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-sulfide, xanthate, xanthogen sulfides, thiocarbonates, etc., may be used, in which generally from about 1% to 30% of sulfur is incorporated in the active or combined state. Based on the total weight of lubricants, 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 with a sulfur halide or by reacting the halogen compound with an inorganic sulfide, polysulfide, thiocarbonate, or xanthate.

One example of an extreme pressure lubricant is one composed of 83% of mineral oil, 10% of sulfurized non-corrosive fatty oil base such as sulfurized sperm oil containing 10% sulfur, and 7% of chlorinated paraffin wax containing about 40% of chlorine. Another extreme pressure lubricant may be made by reacting sodium polysulfide with a chlorinated hydrocarbon such as chlorinated kerosene, and blending the resultant products with mineral oil. A cutting oil may be prepared by incorporating a small amount, such as 0.8%, of elementary sulfur into a mineral oil such as one having a viscosity of about 100 seconds Saybolt at 100° F.

The amides of the present invention are intended to be incorporated in any of these lubricants which are normally corrosive to metals by reason of the presence of active chlorine and/or sulfur.

In preparing lubricants according to this invention, it is also possible and in certain cases may be desirable to incorporate other known addition agents such as, for instance, fatty oils,

fatty acids, soaps of fatty acids or naphthenic acids, esters, thickeners of various types such as polyisobutylene having a molecular weight above 1,000, V. I. improvers, pour depressors such as the ones made by Friedel-Crafts condensation of chlorinated paraffin wax with naphthalene, antioxidants, oil-soluble metal soaps, dyes, etc.

The following description gives the details of preparation of one kind of extreme pressure agent, namely, a sulfurized chlorinated kerosene:

Water white kerosene was chlorinated in a glass vessel (nickel could be used) to 41.5% Cl., temperature of reaction being regulated in such a manner, as to keep it below the flash point at all times. Thus in the early stages of chlorination, the temperature was held at 120° F., whereas the flash of the feed kerosene was 123° F. When the percentage of chlorine added reached approximately 20% by weight, the reaction temperature was allowed to rise to 175° F. and was maintained at this point until the desired amount of chlorine (41.5% by weight) had been added.

The following reactants were then used to prepare an extreme pressure agent:

25	Chlorinated kerosene (41.5% Cl)-----gms--	800
	91% isopropyl alcohol-----cc--	850
	Aqueous NaSH (32% NaSH)-----gms--	212
	Aqueous caustic (25% NaOH)-----gms--	98
30	Elementary sulfur-----gms--	20

The above materials were placed in a glass (nickel could be used) reactor equipped with reflux condenser, gas outlet, thermometer and electrical stirrer. Agitation was started and the temperature of the mix was gradually raised to reflux (178° F.). Small samples were withdrawn at regular intervals and allowed to settle, then were returned to the reactor. After refluxing for 1¼ hrs. the sample withdrawn separated immediately into three distinct layers, as follows:

Top layer—alcohol+small amount E. P. agent—yellow color.

Middle layer—E. P. agent+small amount alcohol—black.

45 Bottom layer—brine+solid NaCl—water white.

This type of separation has come to be regarded as indicative of the end point of the reaction, for tests have shown that the brine is acidic and consequently contains no sodium sulfide.

The reaction was continued at reflux for an additional 30 minutes and then cooled and settled. The brine was withdrawn and discarded; the top layer of alcohol was retained for recycling purposes.

The middle layer of crude extreme pressure agent was stripped of residual alcohol under high vacuum over an oil bath at 230° F. and filtered under suction to remove any solid materials, e. g. NaCl. The yield was 731 gms. of extreme pressure agent which analyzed at 7.0% sulfur and 32.6% chlorine.

The following data will illustrate several modifications of the invention and will make the advantages of the invention clearly apparent.

An extreme pressure lubricant was prepared by blending with 90% of a mineral oil base stock having a viscosity of about 200 seconds Saybolt at 210° F. and derived from a Panhandle crude, 10° of a sulfurized chlorinated kerosene made by the method just described above but containing 7.2% of sulfur and 33.1% of chlorine. This lubricant was considered as the control blend. Four other blends were made just like the control except that 0.5% of the extreme pressure

lubricating agents, namely, the sulfurized chlorinated kerosene, was replaced by 0.5% of a corrosion-preventing amide of this invention. These five blends were then subjected to a load-carrying test on the S. A. E. machine and to the Chrysler Almen corrosion test with the results indicated in the following table:

Test	Corrosion-preventing amide	Per cent added	Tests on blends	
			Chrysler Almen corrosion test	S. A. E. machine at 1,000 R. P. M.
1			Failed	425
2	N, N, diamyl stearamide	0.5	Slight corrosion.	365-590
3	Naphthenamide of triethylene tetramine.	0.5	No corrosion.	395
4	Naphthenamide of tetraethylene pentamine.	0.5	do	410
5	N-octyl stearamide	0.5	do	400-580

The above table shows that the various amides tested either substantially or completely eliminated the corrosive tendencies of the extreme pressure lubricants, yet without materially affecting the load-carrying capacity.

The naphthenamide of tetraethylene pentamine used in test 4 was made as follows:

Naphthenic acids (approx. M. W.=266) were treated with slight excess of phosphorus trichloride at 200° F. for 2 hours with occasional vigorous shaking. The mixture was allowed to settle and the phosphorus hydroxide went to the bottom of the flask.

95 gms. of the naphthenyl chloride was decanted into 200 ccs. of benzene, 90 gms. of tetraethylene pentamine was slowly added to the solution with vigorous shaking. Considerable heat was evolved. The mix was then slowly raised to reflux and held there for 1 hour with occasional vigorous shaking. After cooling water was added and the mass was extracted with ethyl ether to remove the amide, the amine hydrochloride being left behind in the water. The ether solution was washed with water to remove last traces of the amine hydrochloride, dried over anhydrous sodium sulfate and stripped of solvent under high vacuum to a bottoms temperature of 400° F. The yield consisted of 95 gms. of a pale red resin with a green cast. This product is the naphthenamide of tetraethylene pentamine.

The naphthenamide of triethylene tetramine used in test 3 was prepared by using exactly the same procedure and quantities of materials as above, except that 70 gms. of triethylene tetramine were used instead of 90 gms. of tetraethylene pentamine. The yield consisted of 95 gms. of pale red resin with a green cast.

Similarly, this method may be used to prepare other substituted naphthenamides generally.

It is not intended that this invention be limited to any of the particular examples which have been given merely for the sake of illustration, nor unnecessarily by any theory as to the mechanism of

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 well as other modifications coming within the scope and spirit of the invention.

We claim:

1. An extreme pressure lubricant comprising a mineral oil having dissolved therein an organic material containing metal-corroding constituents selected from the group consisting of halogen and sulfur, and an oil-soluble N-alkyl substituted carboxylic acid amide in which the carboxylic acid radical contains at least 7 carbon atoms.

2. An extreme pressure lubricant comprising a mineral oil having dissolved therein an organic material containing metal-corroding constituents selected from the group consisting of halogen and sulfur and an oil-soluble N-alkyl substituted compound having at least one group of $\text{Ac}-\text{N}=\text{}$, wherein Ac is a carboxylic acid radical of at least 7 carbon atoms.

3. An extreme pressure lubricant according to claim 1, containing an oil-soluble acid amide of a poly-olefin poly-amine in which the carboxylic acid radical contains at least 7 carbon atoms.

4. An extreme pressure lubricant according to claim 1 containing an oil soluble naphthenamide of a poly-olefin poly-amine.

5. An extreme pressure lubricant according to claim 1 containing an oil soluble naphthenamide of tetraethylene pentamine.

6. An extreme pressure lubricant according to claim 1 containing an oil soluble N-alkyl substituted amide of petroleum naphthenic acid.

7. An extreme pressure lubricant according to claim 1 containing an oil soluble N-alkyl substituted amide of a fatty acid containing at least 10 carbon atoms.

8. An extreme pressure lubricant according to claim 1 in which the carboxylic acid amide contains more than 10 carbon atoms.

9. An extreme pressure lubricant comprising a mineral oil having dissolved therein an organic material containing at least 1.5% of halogen and a corrosion-preventing amount of an oil-soluble N-alkyl substituted carboxylic acid amide in which the carboxylic acid contains at least 7 carbon atoms.

10. An extreme pressure lubricant according to claim 9 containing chlorinated kerosene and about 0.3 to 2.0% of an oil-soluble naphthenamide of tetraethylene pentamine.

11. An extreme pressure lubricant according to claim 9 containing in addition at least 0.2% of sulfur.

12. An extreme pressure lubricant comprising a mineral oil having dissolved therein an organic material containing at least 0.3% of sulfur and about 0.3 to 2.0% of an oil-soluble N-alkyl substituted carboxylic acid amide in which the carboxylic acid radical contains at least 7 carbon atoms.

EUGENE LIEBER.
ALOYSIUS F. CASHMAN.