Patented Jan. 14, 1941 2,228,325

UNITED STATES PATENT OFFICE

2,228,325

LUBRICANT

John F. Olin, Grosse Ile, and Roland H. Goshorn, Wyandotte, Mich., assignors to The Sharples Solvents Corporation, Philadelphia, Pa., a corporation of Delaware

No Drawing. Application July 27, 1937, Serial No. 155,916

6 Claims. (Cl. 252—51)

The present invention pertains to the improvement of lubricating oils and greases and is particularly concerned with the addition of compounds to hydrocarbon lubricants for the purpose of enabling those lubricants to withstand very high pressures.

Modern advances in the art of automobile transmission design have resulted in the subjection of bearing surfaces to loads much higher than those heretofore encountered. This trend has resulted in a demand for lubricants capable of fulfilling their lubricating functions under the new conditions and of preventing scoring and seizure of lubricated parts. To this end, a large number of compounds have been synthesized and added to the lubricants.

These compounds include, for example, lead sulphide, sulphurized lubricating oils, chlorine derivatives of various organic compounds, phosphoric acid esters etc.

The object of the present invention has been to develop a new class of lubricants adapted for use as automobile engine and transmission lubricants or as cutting oils. The invention consists specifically in the addition to hydrocarbon lubricants of compounds of a class having the property of increasing the film strength of such lubricants greatly when added thereto in relatively small proportions.

The lubricants of the invention are synthetic products produced by blending a hydrocarbon lubricant with ammonium salts of the organic and inorganic acids. We have discovered that, when a small proportion of an ammonium salt of an organic or inorganic acid is added to a hydrocarbon lubricating oil, the ability of that oil to continue to perform its lubricating function under conditions of high pressure and temperature and low speeds is greatly increased. The compounds of this class which have been found to effect the most marked increase in the film strength of the lubricants with which they are blended are the ammonium salts in which one or more organic radicals are substituted for one or more hydrogen atoms of the ammonium radical. Thus, the amyl, di-amyl and tri-amyl ammonium chlorides have been found to enhance very substantially the film strength of the hydrocarbon lubricants with which they are blended. Similar results have been obtained by the addition of mono-, di- and tri-butyl ammonium chlorides. Indeed, the entire class of mono-, di- and tri-alkyl ammonium chlorides is useful in the practice of the invention. Similarly, mono-, di- and tri-alkyl ammonium thiophosphates, phosphates, sulphates, nitrates and the corresponding alkyl ammonium salts of other inorganic acids may be used in the practice of the invention for increasing the film strength of lubricants which are to be used under extreme pressure conditions.

The mono-, di- and tri-alkyl substituted ammonium salts of the organic acids may be used in a manner similar to the salts of the inorganic acids discussed above. Thus, the mono-alkyl ammonium salts of formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, caprylic acid, oleic acid, stearic acid, palmitic acid, oxalic acid, lauric acid, linoleic acid, sorbic acid, acrylic acid, hydracrylic acid, lactic acid, glyceric acid, ricinoleic acid, chlor-acetic acid, carbamic acid and substituents thereof, and other saturated and unsaturated substituted or unsubstituted mono- or poly-carboxylic aliphatic acids may be employed. The corresponding ammonium salts of the alicyclic acids, such as the naphthenic acids obtained from petroleum, quinic acid, hexhydrobenzoic acid, etc. may be similarly used.

The corresponding ammonium salts of the acids of the aromatic and heterocyclic series may also be used in the practice of the invention. Thus, the salts of aromatic sulphonic and phosphoric acids, benzoic acid, phthalic acid and anthranilic acid, salicylic acid, phenylacetic acid, cinnamic acid, furoic acid, pyridine sulphonic acid, pyridine mono- and di-carboxylic acid, etc., may be added to hydrocarbon lubricants to improve their film strength.

In short, the alkyl ammonium salts of the entire class of inorganic and organic acids fall within the scope of the invention. The organic acid salts employed may be the salts of aliphatic, alicyclic, aromatic or heterocyclic acids and these acids may be mono- or poly-carboxylic acids, amino acids, thio acids, hydroxy acids, acids substituted by carboxy radicals, etc. The ammonium radicals which form the positive ions of the salts of any of the above acids used in the practice of the invention may be substituted by alkyl radicals, by aryl radicals, by alicyclic radicals or by heterocyclic radicals. The invention thus comprehends within its broad scope the addition to hydrocarbon lubricants of ammonium salts of any acid provided such ammonium salts contain organic substituents for one or more of the hydrogen atoms attached to the nitrogen of the ammonium radical.

The ammonium salt added to the hydrocarbon lubricant to produce the lubricant composition

of the invention may be added in proportions varying widely depending upon the particular lubricant to be treated, the requirements of the use to which the lubricant is to be put and the particular ammonium salt added to improve the film strength of the lubricant. The proportion of ammonium salt added will usually fall within the range between 0.1% and 5%, depending upon these factors. Preliminary experimentation will indicate the best proportion of ammonium salt to add in each individual case.

In case the lubricating oil to be treated is not thoroughly miscible with the compound added to improve its film strength a common solvent for the oil and the added compound may be added in sufficient quantity to afford a clear solution.

While the entire class of ammonium salts having organic radicals substituted for hydrogen of the ammonium radical is useful in the practice of the invention, the salts in which three or four such radicals are substituted for such hydrogen have been found to be particularly useful, as will be seen from the following examples.

The following examples illustrate the practice of the invention:

Example 1

A sample of Mobiloil CW gear oil was tested in a Floyd split-bearing lubricant testing machine. The oil was found to have a film strength of 75 Floyd units (each Floyd unit is equal to 77 pounds per square inch pressure).

Example 2

1% of a mixture of tri-amyl ammonium chloroacetate and carboxy methylenetriamylammonium chloride formed by re-acting chloroacetic acid with triamylamine at 100° C. for about 10 minutes was added to a sample of oil similar to that of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of over 600 Floyd units. The same material, upon being tested with the Almen machine, withstood the full load of 15,000 pounds per square inch without damage to the bearing.

Example 3

1% of triamyl ammonium chloride was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of over 600 Floyd units.

Example 4

1% of monoamylammonium chloroacetate was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 5

1% of tributylammonium chloroacetate was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of over 600 Floyd units.

Example 6

3% of diamylammonium diamyldithiocarbamate was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 7

1% of monoamylammonium chloroacetate was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 8

0.5% of tributylammonium bromide was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 125 Floyd units.

Example 9

0.2% of tributylammonium sulphate was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 10

0.5% of triamylammonium nitrate was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 150 Floyd units.

Example 11

0.5% of tributylammonium valerate was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 175 Floyd units.

Example 12

0.5% of tributylammonium p-toluene sulfonate was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 13

0.5% of tributylammonium 2-5 dichlorobenzene sulfonate was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 525 Floyd units.

Example 14

0.2% octylammonium chloride was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 15

0.2% laurylammonium chloride was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 16

0.2% tributylbenzylammonium chloride was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 17

0.2% tributylhydroxyethyl ammonium chloride was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 18

0.5% of a substituted ammonium salt formed by reacting tributylamine and benzene sulfonyl chloride was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 19

0.2% of a substituted ammonium salt formed by reacting tributylamine and chloroacetic acid was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 20

0.5% tributylammonium alphachloropropionate was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of over 600 Floyd units.

Example 21

0.5% of an ammonium salt formed by reacting tri-butylamine and dichloroacetic acid was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of over 600 Floyd units.

Example 22

0.5% ammonium salt formed by reacting tributylamine and tri-chloroacetic acid was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 23

A substituted ammonium salt formed by reacting tri-butylamine and alpha chloropropionic acid was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of over 600 Floyd units.

Example 24

A substituted ammonium salt formed by reacting tri-butylamine and beta chloropropionic acid was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 100 Floyd units.

Example 25

0.5% of a substituted ammonium salt formed by reacting p-chloroaniline and alpha chloropropionic acid was added to the gear oil of Example 1. The lubricant resulting from the compounding of the ammonium salt with the gear oil, when tested in the Floyd machine, had a film strength of 400 Floyd units.

Example 26

A sample of D. T. E. oil, a highly refined paraffinic oil, was tested in the Floyd split bearing lubrication testing machine. This oil was also found to have a film strength of 75 Floyd units.

Example 27

A sample of the D. T. E. oil of Example 26 was treated with one percent of tri-amyl ammonium chloride and four percent of diamyl phenol added to give a perfectly clear solution. The resulting gear oil when tested gave a value of 325 Floyd units.

Example 28

One percent of the reaction mixture formed by reacting dioctyl hexyl amine and mono chloro acetic acid was dissolved in the D. T. E. oil. The resulting lubricant, upon being tested in the Floyd machine, was found to have a value of over 600 Floyd units. The same material, upon being tested with the Almen machine, withstood the full load of 15,000 pounds per square inch without damage to the bearing.

Example 29

One percent of the reaction mixture formed by reacting diamyl laurylamine and chloroacetic acid was dissolved in the D. T. E. oil. The lubricant so obtained had a value of over 600 Floyd units. The same material, upon being tested with the Almen machine, withstood the full load of 15,000 pounds per square inch without damage to the bearing.

Example 30

One percent of the reaction mixture formed by reacting dibutyl aniline and chloroacetic acid was dissolved in the D. T. E. oil. The resulting lubricant was found to have a value of over 600 Floyd units. The same material, upon being tested with the Almen machine, withstood the full load of 15,000 pounds per square inch without damage to the bearing.

Example 31

.5% of the reaction mixture formed by reacting tributylamine hydrochloride and cupric chloride was suspended in Mobiloil CW. Upon being tested, it was found that this material had a film strength of 100 Floyd units.

Modifications will be obvious to those skilled in the art and we do not wish to be limited except by the scope of the subjoined claims:

By the term "inorganic hydro-halogenic acid" in the appended claims it is intended to include those acids which result solely from the combination of halogen atoms and hydrogen atoms as, for example, hydrochloric acid and hydrobromic acid.

We claim:

1. A lubricating composition comprising a hydrocarbon oil and a small proportion of a trialkyl ammonium salt of an inorganic hydrohalogenic acid.

2. A lubricating composition comprising a hydrocarbon oil and a small proportion of a trialkyl ammonium salt of an inorganic hydrohalogenic acid, the alkyl radicals of said ammonium salt containing between three and seven carbon atoms.

3. A lubricating composition comprising a hydrocarbon oil and a small proportion of an unhydroxylated tri-alkyl ammonium salt of an inorganic hydrohalogenic acid.

4. A lubricating composition comprising a hydrocarbon oil and a small proportion of an alkyl ammonium salt of an inorganic hydrohalogenic acid.

5. A lubricating composition comprising a hydrocarbon oil and a small proportion of an unhydroxylated alkyl ammonium salt of an inorganic hydrohalogenic acid.

6. A lubricating composition comprising a hydrocarbon oil and a small proportion of a tetraalkyl ammonium salt of an inorganic hydrohalogenic acid.

JOHN F. OLIN.
ROLAND H. GOSHORN.