Patented May 30, 1939

2,160,273

UNITED STATES PATENT OFFICE

2,160,273

LUBRICANT

Clarence M. Loane and Bernard H. Shoemaker, Hammond, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

No Drawing. Application September 10, 1937, Serial No. 163,245

34 Claims. (Cl. 87—9)

This invention relates to improvements in lubricants, and in particular to lubricants having improved extreme pressure characteristics and having corrosion inhibiting properties when employed in the presence of hard metal alloy bearings.

The development of internal combustion engines having higher compression ratios, increased acceleration, and increased speed characteristics has made it desirable to use motor oils which possess extreme pressure properties. The improvements in the internal combustion engines have also necessitated the replacement of soft metal bearings, such as babbitt, by hard metal alloy bearings of the cadmium-silver type. The improved oil refining methods, such as the drastic acid treatment and/or the solvent extraction processes, to produce oils of improved viscosity indices, which have been developed almost contemporaneously with the introduction of the hard metal alloy bearings, resulted in a new problem in the lubrication of bearings of these types in that these highly refined oils have been found to be corrosive to bearings of the hard metal alloy type. An effective motor oil should therefore possess extreme pressure characteristics and be non-corrosive to bearings of the hard metal alloys.

Most of the so-called corrosive inhibitors of hard metal alloys do not possess extreme pressure lubricating properties, and vice versa, the known compounds which impart extreme pressure lubricating properties to lubricants do not necessarily inhibit corrosion of hard metal alloys. It is therefore one of the principal objects of the present invention to provide a material which when added to lubricants will inhibit the corrosion of hard metal alloys and impart extreme pressure lubricating characteristics to the lubricant.

We have found that extreme pressure lubricating properties and the property of inhibiting corrosion of alloy bearings of the cadmium-silver type can be imparted to lubricating oils by adding thereto up to 5% but preferably from about 0.05% to about 2% of an organic titanate selected from the group of compounds having the general formulas:

$$Ti(XR)_4,\ XTi(XR)_2,\ Ti(XR')_4,\ XTi(XR')_2,\ (XR)_nTiY_{4-n} \text{ and } (XR')_nTiY_{4-n}$$

in which R is a radical selected from the group consisting of alkyl, aryl, hydroaryl and aralkyl radicals, R' is a radical selected from the group consisting of halogenated alkyl, halogenated aryl, and halogenated aralkyl radicals, X is an element selected from the group consisting of oxygen and sulfur, Y is a halogen and n is an integer selected from the group of whole numbers consisting of 1, 2 and 3. The compounds illustrated by the foregoing general formulas are also known as the hydrocarbon titanates, hydrocarbon thiotitanates, hydrocarbon meta titanates, hydrocarbon meta thiotitanates, halo-hydrocarbon titanates, halo-hydrocarbon thiotitanates, halo-hydrocarbon meta titanates, halo-hydrocarbon meta thiotitanates, hydrocarbon halo-titanates, hydrocarbon halo-thiotitanates, halo-hydrocarbon halo-thiotitanates, halo-hydrocarbon halo-titanates.

As examples of specific compounds coming within the foregoing general classifications may be mentioned:

Butyl titanante	$Ti(OC_4H_9)_4$
Propyl titanate	$Ti(OC_3H_7)_4$
Phenyl titanate	$Ti(OC_6H_5)_4$
Amyl thiotitanate	$Ti(SC_5H_{11})_4$
Phenyl meta titanate	$OTi(OC_6H_5)_2$
Tolyl meta mono thiotitanate	$STi(OC_6H_4CH_3)_2$
Propyl meta dithiotitanate	$STi(SC_3H_7)_2$
Chlorbutyl titanate	$Ti(OC_4H_8Cl)_4$
Chlorpropyl titanate	$Ti(OC_3H_6Cl)_4$
Dichlorpropyltitanate	$Ti(OC_3H_5Cl_2)_4$
Chlorphenyl metatitanate	$OTi(OC_6H_4Cl)_2$
Dichlor butyl meta thiotitanate	$STi(SC_4H_7Cl_2)_2$
Diamyl dichlor titanate	$(C_5H_{11}O)_2TiCl_2$
Diphenyl dichlor titanate	$(C_6H_5O)_2TiCl_2$
Dicyclohexyldichlor titanate	$(Cyclo\ C_6H_{11}O)_2TiCl_2$
Amyl trichlor titanate	$C_5H_{11}OTiCl_3$
Amyl trichlor thiotitanate	$C_5H_{11}STiCl_3$
Chlorpropyl titanate	$(ClC_3H_6O)_4Ti$
Dichlor butyl titanate	$(Cl_2C_4H_7O)_4Ti$
Chlorpropyl chlortitanate	$(ClC_3H_6O)_3TiCl$
Chlorpropyl thiotitanate	$(ClC_3H_6S)_4Ti$
Chlorphenyl titanate	$(ClC_6H_4O)_4Ti$

The load carrying capacity of these organic titanates was determined on the Almen testing machine which is described by Wolf and Mougey in their paper on "Extreme pressure lubricants" given at the 13th annual meeting of the A. P. I. at Houston, Texas, November 17, 1932. Briefly, it consists of a test pin or journal made of ¼ inch diameter drill rod which can be rotated in a ½ inch long split bushing with provisions for loading the bearing thus formed by clamping together the two halves of the split bushing. Provision is also made to measure the torque required to rotate the journal in the loaded bearing.

The standard method of making a test on the Almen machine consits in immersing the test pin and bushings in the lubricant to be tested and then rotating the test pin at 600 R. P. M. The load, which clamps the two halves of the split bushing, is increased at the rate of 2 lbs. added every 10 seconds. A record is made of the torque required to rotate the pin at each load increment and the test is completed either when 30 lbs. have been added to the loading device or when seizure occurs, whichever happens first.

A sample of an S. A. E. 20 lubricating oil and another sample of the same oil containing 0.5% butyl titanate were submitted to tests on the Almen machine with the following results:

Almen test

Oil	Almen test
	Pounds
Control	6 to 8
Control +0.5% butyl titanate	20 to 24

The load carrying capacity of extreme pressure lubricants may be also determined on the so-called Timken testing machine described in the S. A. E. Journal, vol. 28, No. 1 (January, 1931) Page 53, and in U. S. Patent 1,990,771. Testing samples of the same oils used on the Almen machine, on the Timken machine the following results were obtained:

Timken test

Oil	Load at which seizure occurred
	Pounds
Control	8
Control +0.5% butyl titanate	40

The data obtained by these tests demonstrate that the extreme pressure properties of a lubricant containing a small amount of an organic titanate is from about 300% to about 500% better than the same lubricant containing no organic titanate.

The effectiveness of the organic titanates as corrosion inhibitors is demonstrated by the data in Table I which were obtained under the following conditions: Test strips of cadmium-silver alloy were submerged in a sample of highly refined motor oil which was normally corrosive to alloy bearings of the cadmium-silver type and a sample of the same motor oil containing 0.25% butyl titanate, which were heated and maintained at a temperature of about 341° F. At regular intervals the test strips were removed from the oils, washed with a solvent, dried and weighed, and the time in which the bearings lost 5 mg/cm.^{2} noted. The test strips in the sample containing no butyl titanate lost 5 mg/cm.^{2} in less than one day while the test strip in the sample of oil containing 0.25% butyl titanate lost 5 mg/cm.^{2} in about two days.

Table I

Oil	Corrosion, time (in days) for test strips to lose 5 mg/cm.^{2}
Control (highly refined S. A. E. 20 motor oil)	Less than 1 day.
Control+0.25% butyl titanate	2 days.

As used herein "highly refined" lubricating oil means viscous oils which have a minimum viscosity of S. A. E. 10 oils, or higher, and which have been subjected to such refining processes that the paraffinicity of the oil is markedly increased. It has been found that "highly refined" lubricating oils cause corrosion to alloy bearings of the hard metal type, such as cadmium-silver alloy bearings to the extent of about 5 mg/cm.^{2} and even greater when such bearings are submerged for 25 hours or less in an air agitated oil which has been preoxidized at about 340° F. for 25 to 50 hours. The motor oil may be "highly refined" lubricating oils as such or mixtures of highly refined lubricating oils with less highly refined lubricating oils, or stated in another way, mixtures of corrosive oils and non-corrosive oils, examples of the latter being lubricating oil fractions from Winkler crude or crudes of the Winkler type.

In addition to their use as E. P. lubricants in motor oils these organic titanates may be employed in lubricants such as oils and soft greases adapted for use on bearing surfaces which are subjected to high pressures and high rubbing velocities, such as are encountered in devices employed for the transmission of power such as hypoid gears, worm gears, heavy duty bearings, planetary automatic shifts and the like. The lubricating oils are preferably those ranging in viscosity from about 90 to 200 seconds Saybolt at 210° F. If desired, calcium, lead, aluminum or other soaps of high molecular weight organic acids may be added to the composition to increase the viscosity or the consistency of the lubricant. The organic titanates may also be used in combination with other compounds which impart extreme pressure characteristics to lubricants such as for example, lead soaps, chlorine compounds, sulfurized oils, etc. These compounds are likewise suitable for lubricants used in cutting and drawing operations where the oil must withstand the high pressures encountered under those conditions of use.

While we have described our invention by reference to preferred embodiments thereof we do not wish to be limited to the specific examples which are merely set forth to illustrate our invention and are not intended to be a limitation thereof except insofar as defined in the appended claims.

We claim:

1. A new composition of matter comprising a lubricant and a small amount of an alkyl titanate.

2. A new composition of matter comprising a lubricant and a small amount of an aryl titanate.

3. A new composition of matter comprising a lubricant and a small amount of butyl titanate.

4. An extreme pressure lubricant containing 0.05% to 5% of an alkyl titanate.

5. An extreme pressure lubricant comprising a lubricating oil and from 0.05% to 5% of butyl titanate.

6. A corrosion inhibited lubricant adapted for lubricating bearings of the cadmium-silver alloy type which comprises a lubricant normally corrosive to bearings of the cadmium-silver alloy type and from about 0.05% to about 5% of an alkyl titanate.

7. A corrosion inhibited motor oil adapted for lubricating hard metal alloy bearings of the cadmium-silver alloy type which comprises a highly refined mineral lubricating oil normally corrosive to hard metal alloys and from about 0.05% to 5% of butyl titanate.

8. A new composition of matter comprising a

lubricant and a small amount of an organic titanate.

9. A new composition of matter comprising a lubricant and a small amount of a hydrocarbon titanate in which the hydrocarbon radical is attached directly to the oxygen of the titanate nucleus.

10. A new composition of matter comprising a lubricant and a small amount of an organic thiotitanate.

11. A new composition of matter comprising a lubricant and a small amount of a hydrocarbon thiotitanate in which the hydrocarbon radical is attached directly to the sulfur of the titanate nucleus.

12. A new composition of matter as described in claim 11 in which the hydrocarbon radical is an aryl radical.

13. A new composition of matter as described in claim 11 in which the hydrocarbon radical is an alkyl radical.

14. A new composition of matter as described in claim 11 in which the hydrocarbon is a butyl radical.

15. A new composition of matter comprising a lubricant and a small amount of an organic halo-thiotitanate.

16. A new composition of matter comprising a lubricant and a small amount of a hydrocarbon halo-thiotitanate.

17. A new composition of matter as described in claim 16 in which the hydrocarbon is an aryl radical.

18. A new composition of matter as described in claim 16 in which the hydrocarbon is an alkyl radical.

19. An extreme pressure lubricant comprising a lubricant and an organic titanate, said organic titanate being used in an amount sufficient to impart to said lubricant extreme pressure properties.

20. An extreme pressure lubricant comprising a lubricant normally having no extreme pressure properties and a hydrocarbon titanate in an amount sufficient to impart to said lubricant extreme pressure properties.

21. An extreme pressure lubricant as described in claim 20 in which the hydrocarbon is an aryl radical.

22. An extreme pressure lubricant comprising a lubricant normally having no extreme pressure properties and an organic thio-titanate in an amount sufficient to impart to said lubricant extreme pressure properties.

23. An extreme pressure lubricant comprising a lubricant normally having no extreme pressure properties and a hydrocarbon thio-titanate in amounts sufficient to impart to said lubricant extreme pressure properties.

24. An extreme pressure lubricant as described in claim 23 in which the hydrocarbon is an aryl radical.

25. An extreme pressure lubricant as described in claim 23 in which the hydrocarbon is an alkyl radical.

26. An extreme pressure lubricant as described in claim 23 in which the hydrocarbon is a butyl radical.

27. An extreme pressure lubricant comprising a lubricant having substantially no extreme pressure properties and an organic halo-thiotitanate in an amount sufficient to impart to said lubricant extreme pressure properties.

28. An extreme pressure lubricant comprising a lubricant having substantially no extreme pressure properties and a hydrocarbon halo-thiotitanate in an amount sufficient to impart to said lubricant extreme pressure properties.

29. An extreme pressure lubricant as described in claim 28 in which the hydrocarbon is an aryl radical.

30. An extreme pressure lubricant as described in claim 28 in which the hydrocarbon is an alkyl radical.

31. A corrosion inhibited motor oil adapted for use in internal combustion engines equipped with hard metal alloy bearings of the cadmium-silver type comprising a highly refined mineral lubricating oil normally corrosive to said bearings and an organic halo-thiotitanate in a small but sufficient quantity to inhibit the corrosion of said hard metal alloy bearings.

32. A corrosion inhibited motor oil adapted for use in internal combustion engines equipped with hard metal alloy bearings of the cadmium-silver type comprising a highly refined mineral lubricating oil normally corrosive to said bearings and a hydrocarbon halo-thiotitanate in a small but sufficient quantity to inhibit the corrosion of said hard metal alloy bearings.

33. A corrosion inhibited motor oil described in claim 32 in which the hydrocarbon halo-thiotitanate is an aryl halo-thiotitante.

34. A corrosion inhibited motor oil described in claim 32 in which the hydrocarbon halo-thiotitanate is an alkyl halo-thiotitanate.

CLARENCE M. LOANE.
BERNARD H. SHOEMAKER.