Patented May 21, 1946 2,400,611

UNITED STATES PATENT OFFICE

2,400,611

TURBINE OILS

Herschel G. Smith, Wallingford, and Troy L. Cantrell, Lansdowne, Pa., and John G. Peters, Audubon, N. J., assignors to Gulf Oil Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

No Drawing. Application March 19, 1945, Serial No. 583,657

12 Claims. (Cl. 252—32.5)

This invention relates to turbine oils, and it comprises improved anti-rust turbine oils having outstanding rust preventive qualities, in addition to a plurality of other advantageous properties, said improved turbine oils containing small amounts of a composite improvement agent dissolved therein; and it further comprises a homogeneous, oil-soluble, composite improvement agent which is readily soluble in turbine oils and is capable of imparting marked rust preventive qualities thereto, in addition to a plurality of other advantageous properties; all as more fully hereinafter described and claimed.

In the lubrication of turbines, it is essential that the lubricating oil protect the metal parts, particularly from rust and corrosion, as well as satisfactorily lubricate the moving parts thereof. Further, under service conditions, turbine oils are subjected to various conditions, some of which are rather drastic.

Accordingly, commercial turbine oils are subjected to various drastic tests, such as accelerated corrosion tests, emulsion tests, oxidation tests, and Falex wear test, as well as various other tests as to lubricating qualities. To be acceptable commercially, turbine oils must satisfactorily pass all of such tests.

Therefore, commercial turbine oils generally are highly refined, high grade mineral lubricating oils having the desired physical properties. Usually, commercial turbine oils are of viscosities ranging from 150 to 600 seconds, SUV at 100° F., and are substantially free of non-hydrocarbon compounds. Also, they usually are quite resistant to oxidation.

However, such highly refined mineral lubricating oils or turbine oils do not give satisfactory protection to metals against rust and corrosion, especially in the presence of water and steam, such as encountered in the lubrication of turbines.

Accordingly, various addition agents have been proposed for incorporation in turbine oils as improvement agents, to modify or improve various properties of the oil. In general, the improvement agents or additive compounds previously used or proposed have not been commercially satisfactory in all respects.

We have now discovered a new, oil-soluble composite improvement agent which is readily soluble in turbine oils, and which is capable of imparting marked rust preventive qualities and a plurality of other advantageous properties to turbine oils when dissolved therein in small amounts. For instance, turbine oils containing between 0.01 and 1.0 per cent by weight on the oil of our new composite improvement agent dissolved therein have given markedly superior results in turbines, the metal parts of the turbine and of the oil system being maintained bright and free of rust for long periods. Further, such improved turbine oils also gave improved lubrication under service conditions for long periods.

Our new oil-soluble, composite improvement agents comprise a blended mixture of polyvalent metal salts of N-substituted phthalamidic acids and amine salts of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid with cyclohexyl amines and primary fatty amines, respectively; these salts being blended together into a homogeneous oil-soluble composite improvement agent. Usually, the two amine salts and the said polyvalent metal salt are blended together in equal proportions. However, the respective proportions thereof may be varied in our composite improvement agents. For instance, they may vary, depending upon the particular amine salts and particular polyvalent metal salts used in preparing the same. Further, in blending the said salts into a homogeneous composite agent, varying amounts of mineral oil may be employed as a blending agent.

The following example illustrates one useful composite improvement agent and an advantageous method of preparing same within the scope of this invention; this example being a typical embodiment thereof.

Example I.—In preparing this composite improvement agent, the procedure was as follows:

Into a suitable kettle, equipped with means for heating, cooling, and agitating the charge, there were charged 2,000 pounds of the dodecyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid. Next, 2,000 pounds of the di-cyclohexyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid were gradually added with stirring. Then, while continuing the stirring, this mixture of liquid amine salts was heated to 180° F. to form a uniform blend thereof. Then, 6,000 pounds of a hot solution of the substantially neutral calcium salt of N-dodecyl phthalamidic acid in a light mineral oil were gradually added while continuing the stirring. This mineral oil solution of said calcium salt contained the said salt and oil in a ratio of 1:3 by weight. Finally, this mixture, containing said calcium salt and amine salts admixed with a minor amount of oil, was further heated and stirred until a uniform, homogeneous blend was obtained.

After a homogeneous blend had been obtained, the composite improvement agent was cooled to

room temperature. The improvement agent so obtained was a heavy, viscous liquid which is readily soluble in mineral oils in the proportions required for the present purposes.

The composite improvement agent obtained by the above procedure had the following composition:

Ingredient	Per cent by weight
Dodecyl amine salt	20
Di-cyclohexyl amine salt	20
Calcium salt	20
Oil	40
Total	100

The above composite agent may be incorporated in any suitable mineral turbine oil in producing improved, superior turbine oils in accordance with this invention.

For instance, by incorporating from 0.16 to 16.7 pounds of the above composite agent in 1,000 pounds of turbine oil, superior anti-rust turbine oils can be readily obtained. The improved turbine oils so prepared contain from 0.0033 to 0.3333 per cent of each of the said salts; the total amount of said salts in the turbine oil being 0.01 to 1.0 per cent by weight on the oil; a marked improvement in anti-rust qualities and other properties being greatly in excess of that obtainable with the corresponding amine of each of these salts involved. That is, the outstanding improvements so obtained are due to the general correlated action of the several salts present in our composite agent.

The outstanding improvements obtained by the present invention are illustrated in the following example, which is typical of our improved turbine oils and our simple method of making the same.

Example II.—In this example, a superior, improved turbine oil was prepared from a commercial turbine oil having a viscosity of 150 seconds, SUV at 100° F. and the other properties set forth post.

In doing so, 66.7 pounds of the composite improved agent obtained in Example I, ante, were mixed with 100,000 pounds of the commercial turbine oil, and the mixture agitated by air blowing until the composite agent had dissolved in the turbine oil and a homogeneous blend was obtained.

The properties of said commercial turbine oil and the improved turbine oil prepared therefrom as above, were as follows:

	Uninhibited oil	Inhibited oil
Gravity, °API	32.7	32.7
Viscosity, SUV:		
70° F	345	344
100° F	152.9	152.5
130° F	87.4	87.2
210° F	43.8	43.9
Viscosity index	107	109
Flash, OC, °F	390	395
Fire, OC, °F	455	450
Pour, °F	+5	+5
Color, NPA	1.25	1.25
Carbon residue, percent	Trace	Trace
Copper strip test, 212° F., 3 hr	Passes	Passes
Neutralization No.	0.01	0.02
Iodine No., mod. Hanus	7.1	7.4

As shown by the above tabulation of properties, the incorporation of this improvement agent in the commercial turbine oil, in the amounts necessary to impart marked rust preventive qualities thereto, did not substantially change any of the above properties thereof.

However, the markedly improved rust-preventive qualities of the improved oil so obtained is clearly shown by the results obtained when our improved turbine oil was subjected to the following standard corrosion test. The data obtained in such test were as follows:

	Uninhibited oil	Inhibited oil
Corrosion test, ASTM D665-42T:		
Distilled water 10%; 140° F., 48 hr.; steel strip:		
Appearance	Rusted	Bright.
Area rusted, per cent	100	0.
Corrosion test, method 412, Gulf:		
Distilled water; 122° F., 12 days; steel strip:		
Appearance	Rusted	Bright.
Area rusted, per cent	100	0.

As shown by the above data, rusting of steel is entirely prevented with the improved oil.

This improved turbine oil also had other advantageous qualities which render it particularly useful and advantageous as a lubricant in various types of turbines. When subjected to the various standard tests used in evaluating commercial turbine oils, it successfully passed all of them, even the most drastic ones.

For instance, this improved turbine oil is very resistant to emulsification. Further, when emulsions are formed they readily break. This is clearly shown by the data obtained in standard emulsion tests; the results obtained being as follows:

	Uninhibited oil	Inhibited oil
Emulsion test, 130° F.:		
Method 320.13, Gov't—		
Distilled water	40—40—0 (1)	40—40—0 (10)
1% salt solution	40—40—0 (1)	40—40—0 (8)
N caustic soda solution	40—40—0 (1)	40—40—0 (7)
Emulsion test, 180° F.:		
Method 320.13, Gov't—		
Distilled water	40—40—0 (1)	40—40—0 (4)
1% salt solution	40—40—0 (1)	40—40—0 (3)
N caustic soda solution	40—40—0 (1)	40—40—0 (5)

The above clearly shows the superior qualities of our improved turbine oils in this respect; these qualities being important in the satisfactory lubrication of turbines.

Further, in addition to the above advantageous properties, namely, the marked resistance to emulsification, and marked anti-corrosion qualities, our improved turbine oils have other superior properties advantageous in lubricating turbines. For instance, they have excellent lubricating qualities as evaluated by the standard "Falex wear test." When so evaluated, the test data obtained are as follows:

	Uninhibited oil	Inhibited oil
Falex wear test:		
500 lb. gauge load, 15 min. wear, No. of teeth	0	0
Gauge load at seizure, lb	750	1,150

Also, in addition to their excellent lubricating qualities, our improved turbine oils are markedly resistant to oxidation and deterioration.

In other words, a plurality of advantageous properties can be imparted to turbine oils by incorporating our new composite improvement agent therein.

Likewise, similar improvements can be obtained by incorporating our composite improvement agent in other commercial grades of turbine oils. For instance, in Example II ante, other commercial turbine oils having viscosities ranging from 150 to 600 seconds, SUV at 100° F., can be employed and similarly improved.

The following example illustrates the preparation of another such improved turbine oil, prepared with the composite improvement agent disclosed in Example I ante, in accordance with the present invention.

Example III.—In this example, another superior, improved turbine oil was prepared from a commercial turbine oil having a viscosity of 430 seconds, SUV at 100° F. and the other properties set forth post.

In doing so, 167 pounds of the composite improvement agent obtained in Example I ante were mixed with 100,000 pounds of the commercial turbine oil, and the mixture agitated by air blowing until the composite improvement agent had dissolved in the oil and a homogeneous blend was obtained. The properties of said commercial turbine oil and the improved turbine oil prepared therefrom, as above, were as follows:

	Uninhibited oil	Inhibited oil
Gravity, °API	28.2	28.1
Viscosity, SUV:		
100° F	428	429
210° F	58.0	57.3
Color, NPA	2.75	2.75
Neutralization No	0.02	0.08

As shown by the above tabulation of properties, the incorporation of such a very small amount of our new composite improvement agent in the turbine oil did not substantially change any of these ordinary physical properties. However, this small amount of composite agent did markedly improve the rust-preventative qualities of the turbine oil, as clearly shown by the data obtained in standard corrosion tests, as follows:

	Uninhibited oil	Inhibited oil
Corrosion test, ASTM D665-42T:		
Distilled water 10%; 140° F., 48 hr.; steel strip:		
Appearance	Rusted	Bright.
Area rusted, per cent	100	0.
Corrosion test, method 412, Gulf:		
Distilled water; 122° F., 12 days; steel strip:		
Appearance	Rusted	Bright.
Area rusted, per cent	100	0.

In other words, the improved turbine oil obtained in Example III also had a plurality of advantageous properties, as did the other improved turbine oils shown in Example II ante.

That is, Examples I, II, and III ante are typical embodiments of the present invention. Of course, in the commercial practice thereof, various other embodiments thereof may be employed.

In general, our composite improvement agents, comprising a blended mixture of polyvalent metal salts of N-alkyl phthalamidic acids and amine salts of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid with secondary cyclohexyl amines and primary fatty amines, respectively, may be employed in preparing a wide variety of improved mineral oil compositions, as well as improved turbine oils. In preparing such improved mineral oil compositions, various blends of the said salts may be employed within the scope of this invention.

In particular, we have found it advantageous to employ composite improvement agents comprising homogeneous, blended mixtures of the said salts in certain proportions, as follows:

Rust inhibitor salt	Parts by weight
Primary fatty amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid.	45 to 10
Secondary cyclohexyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid.	45 to 10
Polyvalent metal salt of N-alkyl substituted phthalamidic acid.	10 to 45
Mineral oil	0 to 400

In preparing our new composite improvement agents, using said salts in the proportions given above, we have found it advantageous to employ the particular salts given in Example I ante.

In particular, the di-cyclohexyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid, itself, is an advantageous rust inhibitor. This amine salt and methods of making the same are described in our companion application Serial No. 583,651, filed March 19, 1945, now U. S. Patent No. 2,387,538. In turn, that application is a continuation-in-part of our prior application Serial No. 420,439, filed November 25, 1941, now U. S. Patent No. 2,371,852, wherein we have described and claimed improved mineral oil compositions containing di-cyclohexyl amine salts of 3-methyl-butyl, 2-ethyl-hexyl acid phosphate, as a rust inhibitor.

Likewise, the dodecyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid is also a good rust inhibitor, as shown in our companion application Serial No. 583,650, filed March 19, 1945, now U. S. Patent No. 2,387,537. In that application, we have described methods of making oil-soluble, amine salts from said acid and primary fatty amines containing 8 to 18 carbon atoms. As a class, the primary fatty amine salts thereof are useful rust inhibitors, as described in that application. Any of the primary fatty amine salts or rust inhibitors there disclosed may be employed in the practice of the present invention. In particular, the fatty amine salts of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid, with primary fatty amines having the formula

$$H_2N—CH_2—(CH_2)_n—CH_3$$

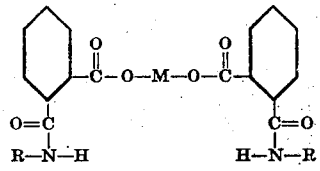
wherein n represents a number between 8 and 18, are useful and advantageous in preparing our composite improvement agents.

In turn, our said application Serial No. 538,650 is a continuation-in-part of our prior application Serial No. 420,438, filed November 25, 1941, now U. S. Patent No. 2,378,442, wherein we have described and claimed improved mineral oil compositions containing primary fatty amine salts of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid as a rust inhibitor.

Further, the neutral calcium salt of N-dodecyl phthalamidic acid, employed in Example I ante, is itself an excellent improvement agent for mineral oils. For instance, as disclosed in our prior application Serial No. 516,968, filed January 4, 1942, now U. S. Patent No. 2,378,442, improved mineral oil compositions containing said calcium salt alone have improved anti-rust qualities. Further, as described in that application, a wide variety of oil-soluble improvement agents or calcium salts of this type can be readily prepared from lime, phthalic anhydride, and primary alkyl amines by the methods described therein. Indeed, the oil solution of the calcium salt employed in Example I ante was obtained by the method

described in Example II of said Patent No 2,378,-442. Also, other oil soluble polyvalent metal salts of N-alkyl phthalamidic acids can be prepared by such methods, as described in our said prior application. The various oil-soluble, rust-preventive compounds or polyvalent metals described in that application may be employed in the practice of the present invention.

Indeed, in the generic practice of the present invention, we may broadly employ oil-solvent polyvalent metal salts of N-alkyl substituted phthalamidic acids; such metal salts being excellent rust-preventive compounds and readily soluble in mineral oils and compatible with the amine salts employed in making our composite improvement agents. For the present purposes, we find that the salts of divalent metals having the following formula are particularly advantageous:



wherein M represents a divalent metal and R represents an alkyl group containing 8 to 18 carbon atoms. However, other polyvalent metal salts of such N-alkyl substituted phthalamidic acids are also useful in certain embodiments of our invention, such as the substantially neutral aluminum salts thereof disclosed in our prior copending application Serial No. 566,402, filed December 2, 1944, now U. S. Patent No. 2,378,443; that application being a continuation-in-part of our earlier application Serial No. 516,968 mentioned ante.

In particular, the present invention is directed to a new, composite improvement agent for turbine oils, comprising a blended mixture of the salts set forth ante. It also includes improved turbine oil containing small amounts of the new composite improvement agent described in the present specification.

What we claim is:

1. An improved, anti-rust turbine oil comprising a mineral lubricating oil and an amount sufficient to retard corrosion of metal of an oil-soluble composite improvement agent capable of imparting excellent anti-rust properties thereto, said composite improvement agent being a homogeneous blended mixture of a polyvalent metal salt of N-alkyl phthalamidic acid and amine addition salts of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid with primary fatty amines and secondary cyclohexyl amines, respectively.

2. The improved turbine oil of claim 1 wherein said mineral oil is a lubricating oil having a viscosity of 150 to 600 seconds, SUV at 100° F.

3. The improved turbine oil of claim 1 wherein said mineral oil contains from 0.01 to 1.0 per cent by weight of said composite improvement agent dissolved therein, said improved turbine oil having outstanding anti-rust properties.

4. An improved anti-rust turbine oil comprising a mineral lubricating oil containing amounts sufficient to retard corrosion of metal of a neutral calcium salt of N-dodecyl ortho phthalamidic acid, of the di-cyclohexyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid and the primary dodecyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid dissolved therein.

5. The improved turbine oil of claim 4 wherein said mineral oil contains 0.0033 to 0.3333 per cent by weight of the said calcium salt, 0.0033 to 0.3333 per cent by weight of said di-cyclohexyl amine salt and 0.0033 to 0.3333 per cent of dodecyl amine salt dissolved therein.

6. As new compositions of matter, useful as improvement agents for turbine oils and other mineral oil compositions, the oil-soluble, composite improvement agents comprising a homogeneous blended mixture of a polyvalent metal salt of an N-alkyl substituted phthalamidic acid and amine addition salts of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid with secondary cyclohexyl amines and primary fatty amines, respectively, said composite improvement agent being capable of imparting marked anti-rust qualities and resistance to emulsification to turbine oils when dissolved therein in small amounts.

7. The composite improvement agents of claim 6 wherein said polyvalent metal salt is a neutral calcium salt of N-dodecyl ortho phthalamidic acid.

8. The composite improvement agents of claim 6 wherein said secondary cyclohexyl amine salt is the di-cyclohexyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid.

9. The composite improvement agents of claim 6 wherein said primary fatty amine salt is a primary dodecyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid.

10. The composite improvement agents of claim 6 wherein the blended mixture of said salts comprises 10 to 45 parts by weight of said polyvalent metal salt, 45 to 10 parts by weight of said secondary cyclohexyl amine salt, 45 to 10 parts by weight of said primary fatty amine salt and 0 to 400 parts by weight of mineral oil.

11. As an oil-soluble, composite improvement agent for turbine oils capable of imparting anti-rust properties thereto, the composite improvement agent comprising a homogeneous blended mixture containing 20 parts by weight of the di-cyclohexyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid, 20 parts by weight of the primary dodecyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid, 20 parts by weight of a neutral calcium salt of N-dodecyl phthalamidic acid and 40 parts by weight of mineral oil.

12. An improved anti-rust turbine oil comprising a mineral lubricating oil containing 0.01 to 1.0 per cent by weight of the composite improvement agent of claim 11 dissolved therein.

HERSCHEL G. SMITH.
TROY L. CANTRELL.
JOHN G. PETERS.