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MINERAL OIL COMPOSITION

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

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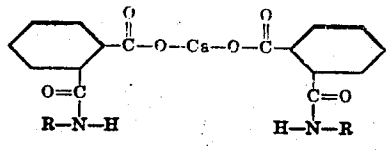
7 Claims. (Cl. 252—39)

This invention relates to improved mineral oil compositions, and, more particularly, to improved mineral oils and oil compositions, each comprising a major amount of a mineral oil and a minor amount of a new improvement agent, or mixture of agents, capable of imparting a plurality of useful, advantageous properties thereto; these new, improved oil compositions being useful and advantageous in protecting metals, both ferrous and non-ferrous, from rust, corrosion and wear. It also includes methods of making such agents and improved oil compositions containing the same.

As is well known, the simple, straight mineral oils usually are deficient, in one or more respects, for certain commercial uses, and it is common practice to incorporate one or more "additive" compounds in the oil to overcome the defect or defects thereof for certain uses. Likewise, various agents have been incorporated in oils, to improve certain of their properties for particular or special uses requiring a superior oil. In general, such agents or additive compounds are known as improvement agents.

We have now discovered certain new improvement agents for mineral oils which are particularly advantageous in the commercial preparation of various lubricants, protective coating compositions and other useful mineral oil compositions. Our agents can be readily incorporated in various mineral oils and oil compositions. When incorporated therein, even in very small amounts, these agents markedly improve the rust preventative qualities thereof. Further, they are also capable of imparting other useful and advantageous properties to mineral oils and oil compositions, as more fully described post.

Our new and advantageous improvement agents for mineral oils and the like are the products produced from the reaction or interaction of calcium hydroxide, phthalic anhydride, and primary alkyl amines, under conditions described post. These agents may be designated as calcium N-alkyl amido phthalates, or, as designated by us, calcium phthalyl alkyl amides. A generic formula for such a compound is,



wherein R represents an alkyl group containing 8 to 20 carbon atoms. As a class these compounds are usually solids at ordinary room temperatures, i. e. 75° F., but soften and melt at elevated temperatures; they being viscous liquids at elevated temperatures below their decomposition point. They can be readily fluxed and blended with mineral oils. In fact, they are sufficiently soluble in various mineral oils for the present purposes; they being readily soluble in naphthenic type oils. On the other hand, they are water-resistant compounds which are practically insoluble in water and aqueous solutions.

These compounds or agents can be readily prepared from lime, phthalic anhydride and primary alkyl amines, advantageously amines having the following generic formula,

$$H_2N—CH_2—(CH_2)_n—CH_3$$

wherein n is a number between 6 and 18. Some of the amines of this generic class are:

Mono-capryl amine,
Mono-lauryl amine,
Mono-myristyl amine,
Mono-palmityl amine,
Mono-stearyl amine,

and other primary alkyl amines having the above formula. Any of the above amines may be used with advantage in making our agents. For instance, mono-stearyl amine (primary octadecyl amine) may be used to prepare agents which are advantageous for certain purposes. Further, mixtures of such amines may also be employed; somewhat better products being obtained with mixed amines. For instance, one commercially available mixture of such amines is the so-called "cocoamine" prepared by converting the mixed acids of cocoanut oil into the corresponding amines by well known methods. The commercial "cocoamine" has an average molecular weight of about 200-210, and it may be employed with advantage in preparing our improvement agents.

In preparing cur agents from these primary alkyl amines, phthalic anhydride and lime, those chemicals are reacted together and converted into new compounds; they being chemically combined together in the molar ratios necessary to produce new compounds having substantially the generic structure given ante. In doing so, we usually re-

act the primary alkyl amine with phthalic anhydride in substantially equimolecular amounts to form a mono-alkyl amide of phthalic acid, and then neutralize the residual acidity of that compound by reaction with lime, sufficient lime being employed to form substantially neutral lime salts thereof. In lieu of lime, other polyvalent metal hydroxides may be employed, such as barium hydroxide, tin hydroxide, magnesium hydroxide, aluminum hydroxide, and the like. These reactions can be advantageously effected in the presence of sufficient mineral oil to dissolve the oil-soluble compounds so obtained; the new improvement agents being formed in situ in the oil.

The following examples illustrate various methods of preparing our improvement agents and improved mineral oil compositions containing the same.

Example 1.—In this example, the improvement agent was prepared from the following materials using the proportions by weight specified below:

Material	Weight
	Grams
Phthalic anhydride	74
Mono-octadecyl amine	135
Hydrated lime	19
Mineral oil	400

In preparing this agent, the phthalic anhydride and amine were heated together in the oil until dissolved therein. Then the dry lime was added, whereupon a violent reaction occurred. After this vigorous reaction subsided, the mixture was heated to 400° F. to complete the reaction and remove the water formed as a by-product of these reactions. The so dehydrated material, while still hot and fluid, was filtered to remove any insoluble matter. The substantially anhydrous oil solution of the calcium N-mono-octadecyl amido phthalate compounds so obtained was then cooled to room temperature.

This improvement agent had a good color and was substantially free of insoluble matter. It was readily miscible with various mineral oils and oil compositions and was directly soluble in most mineral oils in amounts effective for the present purposes. In particular, this improvement agent is useful and advantageous as an additive compound in preparing improved motor oils and like lubricants. It is also advantageous in preparing other improved oil compositions useful in protecting metals against abrasion and corrosion.

That is, the foregoing example is typical and illustrative of certain embodiments of this invention. In other embodiments thereof, other primary alkyl amines can also be employed in making our improvement agents. Further, our agents also can be readily prepared by other methods, such as those illustrated in the following examples:

Example 2.—In this example, our improvement agent was prepared from a commercial mixture of primary fatty amines, the specific materials and proportions thereof employed being as follows:

Material	Weight
	Grams
Cocoamine	105
Phthalic anhydride	74
Lime	19
Mineral oil	400

In preparing this agent, the lime and phthalic anhydride were admixed with the oil and the mixture stirred until they were dispersed and suspended in the oil. While continuing the stirring, the cocoamine was then gradually added whereupon an exothermic reaction occurred and the temperature rose to 120° F. After this reaction had subsided and the reaction mixture cooled to room temperature, the stirring was continued for one hour at room temperature. The viscous liquid product so obtained was then heated to 320° F. to complete the reaction and remove the water by-product. The dehydrated material, while still hot and fluid, was filtered to remove any insoluble matter and then cooled to room temperature.

The improvement agent so obtained was a clear, bright material substantially free of haze and had a good color. It can also be readily incorporated in mineral oils and oil compositions. This agent, like the one obtained in Example 1, is an advantageous additive compound in preparing improved motor oils and other lubricants for metals.

Example 3.—A typical procedure for preparation of a commercial batch of this material was as follows:

Ninety pounds of hydrated lime were added to 1800 pounds of coastal oil, testing 80 seconds viscosity at 100° F., at a temperature of 70° F., the mixture being stirred thoroly to disperse the lime in the oil; then 360 pounds of phthalic anhydride flakes were added and thoroly dispersed in the oil along with the lime. To this dispersion 540 pounds of commercial amines (Armour's AM—Coco—B) were added, while continuously stirring the mixture over a period of two hours; during this time the temperature rose to 125° F., cooling water being applied to the jacket of the mixing kettle to control the exothermic reaction temperature. The mixture was then heated by steam applied to the jacket, the temperature being slowly brought up to 180° F. and then held at this temperature for one hour. Then the temperature was gradually increased to 280° F. by further application of steam heat to the jacket; then a vacuum of about one-half atmosphere was applied to the contents of the kettle for one-half hour. The vacuum was released and the temperature was reduced to 180° F. by application of cooling water to the jacket, and the mixture was then drawn in the melted state into drums.

Improved motor oils useful and advantageous in lubricating Diesel engines, can be readily prepared by incorporating a few per cent of these improvement agents in a suitable mineral lubricating oil. The preparation of one improved Diesel oil is illustrated in the following example:

Example 4.—In preparing this Diesel oil, the lubricating base employed was a commercial mineral lubricating oil, known as Gulflube 20; this oil being employed at times in preparing lubricants for Diesel engines. This lubricating oil was blended with sufficient of the improvement agent obtained in Example 2 ante, to produce an improved oil composition containing approximately 3 per cent by weight of our new additive compound.

The compounded oil so obtained has improved detergent qualities as well as other advantageous properties.

Other improved motor oils can also be readily prepared by substituting various commercial mineral lubricating oils, such as SAE 30 coastal type

motor oil, SAE 60 motor oil and like, for the Gulflube 20 (SAE 20 paraffinic type motor oil) in Example 4 ante.

In general, such improved motor oils containing minor amounts of our improvement agents have a plurality of advantageous properties, all as more fully shown post. As there shown, they are superior lubricants for internal combustion engines, particularly aviation, automotive and Diesel engines, even under severe operating conditions.

For example, an improved motor oil containing 3.0 per cent by weight of a calcium phthalyl fatty amide dissolved in a commercial mineral lubricating oil, namely, SAE 60 motor oil, had improved detergent qualities and other advantageous properties when subjected to a standard test in a Waukesha-CFR test engine in comparison with the base oil.

In this test, 3 liters of the oil to be tested were placed in the crank case and the engine then run at 900 R. P. M. with the spark and the air-fuel ratio adjusted to give maximum power, the coolant being maintained at 350° F. during such test. At the end of 24 hours running, the engine was stopped and dismantled and the piston examined. Then the performance of the oil was rated according to the condition of the piston in keeping with the following scale in which the rating number increases as the piston condition becomes worse; the standard rating being as follows:

Rating No.	Condition of piston
1	No rings stuck, and no heavy hard deposits;
2	Top or oil ring (or both) stuck on a small part of circumference;
3	Top or oil ring (or both) completely stuck;
4	Top or oil ring (or both) completely stuck and 2nd ring partly stuck;
5	Top, 2nd, and oil rings completely stuck;
6	Condition No. 5 with 3rd and 4th rings partly stuck.

The above test (and rating numbers) is a standard test for rating motor oils for use in internal combustion engines. It is a direct measure under controlled conditions of the suitability of the motor oil for such purposes under service conditions; particularly its stability against deterioration by oxidation, the development and deposition of sludge and the various defects arising therefrom, such as ring sticking, formation of varnish on the cylinder walls, piston and piston rings and the like.

The test results obtained in the foregoing tests on the SAE 60 motor oil and our improved motor oil prepared therefrom clearly demonstrate the superiority of our improved motor oils for such purposes; the detailed test data being as follows:

	SAE 60 motor oil	Improved motor oil
Operating time.....hours	25	25
B. H. P. developed.....average	3.47	3.64
Fuel consumption, lb./B. H. P./hr.	0.714	0.641
Temperature, average °F., coolant.	350	350
Crankcase oil.....°F.	160	162
Oil consumption percent by weight	6.7	1.6
Piston condition No.	4	2
Carbon—Grams:		
On top of piston	0.190	0.130
Under top piston rings	1.080	0.574
Under other piston rings	1.200	0.621
Carbon: condition	Hard, coherent	Soft, friable

As shown by the above data, our improved motor oil had improved detergency and markedly reduced ring sticking, its piston rating being a No. 2 rating, whereas the base oil had a No. 4 rating. The superior stability of our improved motor oil in such test is clearly shown by the following properties of the respective oils before and after such service test:

	Motor service test			
	SAE 60 motor oil		Improved motor oil	
	Before	After	Before	After
Gravity.....°API	26.5	25.6	26.2	25.6
Viscosity, SUV:				
100° F.	1,819	2,230	1,736	2,000
210° F.	122.3	135.3	118.5	126.5
Flash, OC.....°F.	525	515	515	500
Fire, OC.....°F.	595	600	575	600
Color, NPA	5.5	7.5 dil.	5.5	4.75
Carbon residue.....percent	0.46	0.84	0.56	0.56

From the above data, it is evident that our improved motor oils are efficient and effective in lubricating internal combustion engines even under severe service conditions.

Furthermore, in addition to lubricating and cooling such engines effectively, our improved motor oils and like lubricants also effectively protect the metal parts thereof from rust and corrosion. That is, they are also effective rust preventive compositions even when the engine is not in operation. This is another important commercial advantageous embodiment of our improved mineral oil compositions.

For instance, it has been found in commercial practice that automotive Diesel engines and heavy duty gasoline engines are not always kept in continuous operation for excessively long periods. Accordingly, during the life of such motors, unavoidable lay-up periods normally occur. During such periods, rusting and corrosion frequently occur, particularly if the used oil is left in the engine. Therefore it is common practice in the art to drain off the used motor oil and replace it with protective coating compositions during such periods. Otherwise, rusting and corrosion usually occur. Even this precaution is not commercially satisfactory as the protective coating compositions so employed have to be removed and replaced with fresh motor oil when the engine is again placed in service.

With our new improved anti-rust motor oils, rusting and corrosion are effectively prevented during such idle periods, as well as when the engine is in operation, and it is not necessary to remove the motor oil during the idle periods. This is one of the many advantages of our improved motor oils and lubricants.

In fact, by the present invention a wide range of improved anti-rust lubricants can be prepared readily by incorporating minor amounts of our improvement agents in suitable mineral oils and oil compositions. In general, such improved anti-rust lubricants effectively protect ferrous and non-ferrous metals against rusting and corrosion, even when exposed to salt water and other severe service conditions. For example, one such advantageous anti-rust lubricant containing 0.1 per cent of our calcium phthalyl alkyl amide compounds dissolved in a light lubricating oil effectively protected steel strips when subjected to a drastic salt water corrosion test. The properties

of this improved oil and the corrosion test therewith, as compared with the base oil are as follows:

Composition	Base oil alone	Improved anti-rust oil
Properties		
Gravity °API	29.1	29.0
Viscosity, SUV, 100° F	107.5	105.2
Flash, OC °F	330	330
Fire, OC °F	370	365
Pour °F	Bel.−50	Bel.−50
Color, NPA	1.25	1.25
Neutralization No	0.02	Nil
Corrosion test rating:		
Steel strip, 122° F., 12 days—		
4 cc. water, 36 cc. oil	3	1
4 cc. sea water, 36 cc oil	4	1

The corrosion test ratings given in the above table were obtained on polished steel strips and are defined as follows:

Corrosion test rating	Condition of steel strip after test
1	No rust.
2	Moderate rust.
3	Heavy rust.
4	Disintegration.

The said corrosion tests employed were standard tests for determining the rust-preventive properties of our noncorrosive oils. In such tests the procedure is as follows:

Thirty-six cc. of the oil to be tested and 4 cc. of distilled water are placed in a 1" by 6" Pyrex test tube, a polished steel strip is inserted in the oil-water mixture, and 2000 cc. of humid air per hour are bubbled through the mixture from a point near the bottom of the tube, so as to provide aeration and mixing of the oil and water; the apparatus being set in a water bath maintained at 122° F. (50° C.) and the original water level in the tube maintained by additions of fresh water every 24 hours. This test is continued for 12 days after which the test strip is removed and inspected.

A like test is also employed, for which straight sea water (or synthetic sea water) is used instead of distilled water. This variation is a far more severe corrosion test, the corrosion effects being usually ten or more times those for fresh water, other testing conditions being the same.

As shown by the test data ante, our improved anti-rust oil had outstanding rust-preventive properties and satisfactorily passed said tests, particularly the drastic test with sea water. For instance, even in the latter test on our improved oil, the steel strip was bright and showed no evidence of rust or corrosion at the end of 12 days in contact with sea water under said conditions. On the other hand, the straight oil failed to pass this test, the steel test strip being partially disintegrated by the heavy corrosion thereof. In fact, with the straight oil, the steel test strip showed heavy rusting in less than 6 hours by the salt water test. Further, the straight oil also failed to pass even the milder distilled water test, the steel test strip showing heavy rust at the end of 12 days, and slight rusting even within 12 hours.

In view of their outstanding anti-rust properties and other advantageous properties shown ante, our improvement agents are useful and advantageous in a wide range of commercial oil compositions. They may also be incorporated in minor amounts in other types of oils, such as turbine oils, instrument oils, electric motor oils and other high quality lubricants where it is important to protect metal surfaces from rust and corrosion, as well as provide adequate lubrication thereof under service conditions. For example, an improved turbine oil was prepared by dissolving 0.01 per cent of our calcium phthalyl alkyl amide compounds, in a suitable, well-refined mineral lubricating oil, the final oil having the following tests:

Gravity: °API	32.3
Viscosity, SUV:	
100° F	151
Flash, OC: °F	400
Fire, OC: °F	455
Pour: °F	+5
Color, NPA	1.25
Neutralization No	Nil

This oil, with this remarkably low dosage of our highly effective corrosion preventive agent, and without the addition of any supplementary corrosion preventive agent, successfully passed, without any traces of rusting, the herein described steel strip corrosion tests for a test period of 12 days at 122° F.; furthermore, it also passed the tentative test of the American Society for Testing Materials, designated as ASTM D 655–42 T, which is a similar test, but involves continuous mechanical stirring of a mixture of 90% by volume of the oil and 10% of distilled water at 140° F. for 48 hours. At the termination of this test there was no trace of corrosion for the standard steel corrosion test strip. Before the addition of the small amount of the anti-corrosion agent, like tests by the two methods on the base oil both failed, with marked rusting, which began to appear in less than 12 hours from the start of each test.

These compounds have proven to be quite satisfactory addition agents for compounded turbine oils of higher viscosity types, such as are preferred for marine service, the preferred amount of the agent ranging from 0.01% to 0.04% according to our regular practice, altho somewhat larger amounts can be used without reducing the quality of the oil in other respects. For an actual marine service test, an improved turbine oil testing 300 viscosity at 100° F. containing 0.013% by weight of our improvement agent satisfactorily lubricated the turbines of an ocean going vessel under the severe operating conditions. After trial of 200 days, the lubricating system of the turbine and auxiliary equipment were all free of rust or like corrosion, the non-rusting quality of the improved turbine oil was found to be practically unchanged; a sample of the used oil, when tested for anti-rust and lubricating properties, was found to have retained its desired properties in all respects. The results from this run, along with others for similar operating conditions, demonstrate that the improved turbine oil is satisfactorily stable under service conditions and capable of operating satisfactorily for prolonged service in ocean going vessels; in particular, our improved turbine oils retain this important quality when exposed to oxidizing conditions or contact with water for long periods; that is, they retain this quality when exposed to oxidizing conditions of use, as well as the leaching effects of water for extended periods, due to the superior properties as regards resistance to oxidation and

practically insolubility in water. The properties of such an oil are:

Gravity: °API	31.6
Viscosity, SUV:	
100° F	299
Flash, OC: °F	435
Fire, OC: °F	485
Pour: °F	−5
Color, NPA	1.75
Neutralization No	0.04

In general, our improved anti-rust oil compositions containing minor amounts of the said calcium phthalyl alkyl amide compounds as an improvement agent, are excellent coating compositions for metals and effectively protect both ferrous and non-ferrous metals from corrosion, even when in contact with aqueous liquids or subjected to other drastic service conditions.

Accordingly, a wide range of protective coating compositions for metals can be prepared by the present invention. For instance, our new improvement agents can also be dissolved in volatile hydrocarbon liquids to obtain protective coating compositions for metals which can be applied by brushing, dipping or spraying the same on the metal. After evaporation of the volatile liquid the metal becomes coated with a tightly adherent protective film which is substantially impervious to water and aqueous solutions.

Further, our improvement agents can also be dissolved in substantial non-volatile hydrocarbon liquids, such as mineral lubricating oils and the like, to obtain still other excellent protective coating compositions for metal. In preparing such compositions, a mixture of mineral oils may be employed as a blended oil base to produce improved compositions useful for special purposes. For instance, a gel type rust preventive compound can be readily prepared by compounding together the following ingredients:

Ingredients	Percent by weight
Texas Red oil, 1900 viscosity/100° F	48
Reduced wax discharge, 95/105 viscosity/210° F	25
Asphaltum oil (a heavy Coastal residuum), 1400 vicosity/210° F	24
Calcium phthalyl alkyl amide (anti-rust compound)	3
Total	100

In the above improved composition, the anti-rust compound is the calcium phthalyl amide of cocoamine prepared by reacting calcium hydroxide, phthalic anhydride and cocoamine in stoichiometric proportions. This improved composition containing said anti-rust compound is an excellent rust-preventive coating composition for metals. It had the following properties:

Properties

Gravity, Liquid State	
°API, Theor	21.3
Melting Point: °F.	
Petrolatum, ASTM D 127-30	127.0
Penetration, ASTM D 217-33 T 77° F., 150 G., 5 Sec. Unworked	225
Viscosity, SUV	
210° F	129
Flash, OC: °F	465
Fire, OC: °F	540
Pour: °F	+117
Appearance	Smooth
Neutralization No	0.1
Mineral Acid Test: pH value	7.4

This composition when subjected to certain service tests successfully passed all of them as follows:

Drying test	Passes
Corrosion test:	
Steel plate	Passes
Brass plate	Passes
Copper plate	Passes
Aluminum plate	Passes
Adhesion and protection test, steel plate	Passes
Volatility; %	Nil
Stability on heating	Passes
Abrasive substance	Passes (nil)
Brushing consistency, 60° F	Passes
Rosin test	Passes (none)
Solubility test	Passes

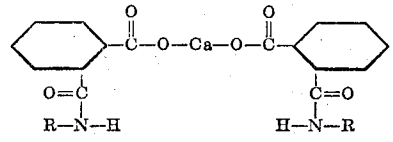
From the above table it is evident that this improved coating composition is an excellent commercial protective rust preventive coating for metals. In general, as shown ante, our improved mineral compositions effectively protect metals from rust and corrosion even under drastic conditions, as fully demonstrated by the illustrative examples given ante:

That is, our new improvement agents impart to mineral oil compositions a plurality of advantageous properties which render them particularly advantageous for such purposes. For instance, these improved oil compositions tightly adhere to the metal, forming protective films thereon which are substantially impervious to water and aqueous solutions and which are resistant to removal from the metal even when vigorously agitated with aqueous liquids. That is, our improved oil compositions are markedly resistant to water and aqueous solutions, as well as stable against oxidation.

Accordingly, in the broad practice of this invention, a wide range of improved mineral oil compositions can be readily prepared, including excellent protective coating compositions, as well as improved anti-rust lubricants. Thus, broadly, this invention relates to improved mineral oil compositions containing minor amounts of calcium phthalyl alkyl amide compounds as a new and advantageous improvement agent; the amount of such improvement agent being sufficient to impart thereto the advantageous properties desired. In general, our improved oil compositions usually contain from 0.002 to 10.0 per cent by weight of such improvement agents dissolved in the mineral oil.

What we claim is:

1. An improved mineral oil composition comprising a major amount of a mineral oil and a minor amount of an oil-soluble calcium phthalyl alkyl amide compound having the following formula:



wherein R represents an alkyl group containing 8 to 20 carbon atoms, the amount of said calcium phthalyl alkyl amide compound being sufficient to impart corrosion inhibiting properties to the improved composition.

2. The composition of claim 1 wherein the said improved mineral oil composition contains from 0.01 to 10.0 per cent by weight of said improvement agent dissolved in the mineral oil.

3. The improved composition of claim 1 where-

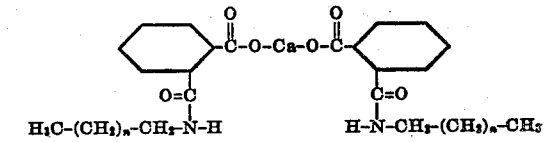
in the said oil-soluble improvement agent is calcium diphthalyl cocoamide.

4. The improved composition of claim 1 wherein the said oil-soluble improvement agent is calcium N-mono-octadecyl amido phthalate.

5. The improved composition of claim 1 wherein the said oil-soluble improvement agent is a substantially neutral calcium salt of mono-octadecyl amide of phthalic acid.

6. The composition of claim 1 wherein said improvement agent is an oil-soluble substantially neutral calcium salt of a mono-alkyl amide of phthalic acid.

7. An improved mineral oil composition comprising a major amount of a mineral lubricating oil containing dissolved therein from 0.01 to 10.0 per cent by weight of a calcium phthalyl alkyl amide compound having the following formula:



wherein n is a number between 6 and 18, said improvement agent being susbtantially neutral and readily soluble in mineral oils.

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