

1

## 3,224,969 NON-EMULSIFYING RUST INHIBITORS IN LUBRICANTS

Bruce W. Hotten, Orinda, Calif., assignor to Chevron Research Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Filed Feb. 5, 1963, Ser. No. 256,253

7 Claims. (Cl. 252—33.6)

This application is a continuation-in-part of patent application Serial No. 183,376, filed March 29, 1962.

This invention pertains to lubricating oil compositions having incorporated therein non-emulsible rust inhibitors. In particular this application is directed to new compounds which are useful in lubricating oil compositions as rust inhibitors where water vapor or water may be present.

The lubricating oil compositions described herein are markedly effective inhibitors against rust formation. Rust inhibitors which are presently available are used in lubricating oil compositions with varying degrees of success with regard to the effectiveness of reducing the rust formation. Such rust inhibitors are usually oil-soluble agents which also serve as emulsifying agents to form oil-in-water emulsions. For example, the numerous sulfonates and primary amines are oil-soluble rust inhibitors, but they are also effective emulsifying agents. Because these rust inhibitors are oil-soluble and readily emulsifiable in water, water readily washes the rust protective film from the metal which is to be protected. Furthermore, such agents are not only of doubtful value as rust inhibitors, but the separation of the water from the oil is made more difficult by their presence.

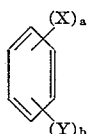
The non-emulsible rust inhibitors described herein are effectively used in steam cylinder oils, steam turbine oils, and particularly for other uses where water may be encountered during service.

It is a primary object of this invention to describe new compounds which are effective as rust inhibitors in lubricating oil compositions, rust inhibitors which are particularly effective where water is present.

Therefore, in accordance with this invention, it has been discovered that certain amides of benzene polycarboxylic acids are effective non-emulsible rust inhibitors in lubricating oil compositions. Thus, the lubricating oil compositions herein contain a base lubricating oil, and incorporated therein, an amide of benzene polycarboxylic acid; that is, the lubricating oil compositions described herein contain rust-inhibiting amounts of amides of benzene polycarboxylic acids.

The amides of benzene polycarboxylic acids used herein as non-emulsible rust inhibitors contain at least two free carboxyl groups and at least one amide group; the amide group being on the carbon atom adjacent to the carbon atom to which a carboxyl radical is attached.

The amides of benzene polycarboxylic acids, that is, benzene polycarboxylic acid amides are of the formula

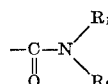


2

wherein X is a carboxyl radical (that is,



radical); Y is an amide radical such as



$a$  is a number having a value of at least 2;  $b$  is a number having a value of at least 1; the sum of  $a$  and  $b$  being from 3 to 6, that is,  $a+b=3$  to 6,  $R_1$  is an oil-soluble hydrocarbon radical having from 1 to 30 carbon atoms, preferably from 1 to 22 carbon atoms;  $R_2$  is hydrogen or an oil-soluble hydrocarbon radical having from 1 to 30 carbon atoms, preferably from 1 to 22 carbon atoms. When  $R_1$  is a hydrocarbon radical and  $R_2$  is hydrogen, the  $R_1$  radical has a minimum of 10 carbon atoms. When  $R_2$  is an oil-soluble hydrocarbon radical along with  $R_1$  being an oil-soluble hydrocarbon radical, the total number of carbon atoms in  $R_1$  and  $R_2$  is no greater than 44 and no less than 12. Preferably,  $a$  is 2,  $b$  is 1,  $R_1$  is an aliphatic radical, more preferably an alkyl radical, having from 8 to 18 carbon atoms, and  $R_2$  is hydrogen or an aliphatic radical, more preferably an alkyl radical, having from 8 to 18 carbon atoms.

The



radicals are derived from primary or secondary amines containing from 1 to 30 carbon atoms, preferably from 12–22 carbon atoms. Such primary and secondary amines are exemplified as follows: decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, eicosylamine, docosylamine, ethyl decylamine, ethyl dodecylamine, methyl dodecylamine, butyl hexylamine, butyl octylamine, butyl octadecylamine, tetracosylamine, hexacosylamine, triacontylamine, di(dodecyl)amine, di(decyl)amine, decyl dodecylamine, amines derived from soy bean fatty acids, amines derived from coco fatty acids, substituted piperazines having from 1 to 4 carbon atoms substituted thereon, etc.

Lubricating oils which can be used as base oils for the compositions described herein include a wide variety of lubricating oils, such as naphthenic base, paraffin base, and mixed base lubricating oils, other hydrocarbon lubricants, e.g. lubricating oils derived from coal products and the synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc. and the mixtures thereof), alkylene oxide type polymers, e.g. alkylene oxide type polymers prepared by polymerizing the alkylene oxides, e.g. propylene oxide, etc., in the presence of water or alcohols (e.g., ethyl alcohol), carboxylic acid esters (e.g. those which are prepared by esterifying such carboxylic acids as adipic acid, azelaic acid, subaric acid, sebacic acid, alkenyl succinic acid, fumaric acid, maleic acid, etc. with the alcohols (such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, pentaerythritol), liquid esters of acids of phosphorus, alkyl benzenes, polyphenyls (e.g. biphenyls and terphenyls), alkyl biphenyl ethers, polymers of silicon (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra(4-methyl-2-tetraethyl)silicate,

hexyl-(4-methyl-2-pentoxy)disiloxane, poly(methyl-2-pentoxy)disiloxane, poly(methyl)siloxane and poly(methylphenyl)siloxane).

The above base oils may be used individually or in combination thereof, whenever made miscible by the use of solvents.

The rust inhibitors described herein may be incorporated in thickened lubricating oil compositions, including lubricating oil compositions thickened to the consistency of greases. Such thickening agents include the metal soaps of fatty acids, such as lithium stearate, lithium 12-hydroxystearate, etc.; salts of dibasic acid-amine condensation product. Other thickening agents include polyethylene, the salts of monoamides of terephthalic acids, for example, N-octadecyl-lithium terephthalate, etc.

Amides of benzene polycarboxylic acids can be prepared by various methods. The methods by which these amides of polycarboxylic acids are prepared are not a part of this invention, since there are various means for preparing such amides of benzene polycarboxylic acids. For example, primary or secondary amines and the benzene carboxylic acid are blended together, using heat if necessary to melt the reactants. Usually the desired amine is added to a reaction vessel, and if necessary heat is applied thereto to melt the amine, after which the desired benzene polycarboxylic acid, or the anhydride

The anhydride used in these experiments was trimellitic anhydride.

Table I

Sample No.	1	2	3
Anhydride, grams	192	192	192
Soybean amine <sup>1</sup> , grams	269		
Sec.-coco amine <sup>2</sup> , grams		460	
Sec.-soy amine <sup>3</sup> , grams			530
Temperature, ° C	95	100	50-65
Time, hours	1	1	1
Appearance	( <sup>4</sup> )	( <sup>5</sup> )	
Melting point range, ° C	130-145	90-100	110-120
Acid No.:			
Actual	240	150	180
Theoretical	240	170	160

<sup>1</sup> The soybean amine was obtained from Armeen SD which is a product of the Armour Co. and consists of 10% by weight hexadecylamine, 10% octadecylamine, 85% octadecylamine, and 45% octadecylamine.

<sup>2</sup> This amine was obtained from Armeen 2C which consists of 8% octylamine, 9% decylamine, 47% dodecylamine, 18% tetradecylamine, 8% hexadecylamine, and 10% octadecylamine.

<sup>3</sup> This amine was obtained from Armeen 2S which consists of 20% dihexadecylamine, 20% dioctadecylamine, 25% dioctadecylamine, and 35% dioctadecylamine.

<sup>4</sup> Tan solid.

<sup>5</sup> Tan plastic solid.

Table II hereinbelow illustrates still further the preparation of amides of benzene polycarboxylic acids useful herein as non-emulsible rust inhibitors in lubricating oil compositions using pyromellitic dianhydride.

Table II

Sample No.	4	5	6	7	8	9	10	11	12	13
Anhydride, grams	109	218	218	109	109	55	27	41	35	55
Armeen SD, grams	269									
Substituted aniline <sup>1</sup> grams		520								
Armeen 2C, grams			764							
Armeen 2S, grams				530						
Armeen 2HT, grams					524					
Sec.-eicosyl, docosyl amine, grams						222				
Gilsonite amine <sup>2</sup> , grams							296	300		
Hercules Rosin amine <sup>3</sup> , grams									95	
Duomeen T <sup>4</sup> , grams										200
Temperature, ° C	130	140	55-120	164	105	120-145	100	95	75-100	130
Time, hours	1	0.5	0.5	0.5	0.5	1	1	1	1	0.5
Appearance	Tan Brittle Solid	Brown Brit. Solid	Plastic Tan Solid	Brown Gum	Brit. Tan Solid	Brit. Tan Solid	Black Tar	Black Tar	Tan Brit. Solid	Waxy Tan Solid
Melting point range, ° C	125-140	150-170	71-76	55	60-70	62-67	50-60	50-70	135-150	105-115
Acid No.										
Found	160	140	140	100	100	113	82	97	150	100
Theoretical	150	150	160	90	90	100			140	110

<sup>1</sup> The substituted aniline was an aniline containing an alkyl group having 12 carbon atoms.

<sup>2</sup> The Gilsonite Amines are mixed heterocyclic and other amines derived from the carbonaceous mineral, Gilsonite.

<sup>3</sup> The Hercules Rosin Amine D is a primary amine consisting primarily of dehydroabietylamine sold by the Hercules Powder Co., Wilmington, Delaware.

<sup>4</sup> Duomeen T is an N-tallow propylenediamine.

thereof is added with agitation. It is not critical as to the order of addition of the reactants. Because the reaction with the anhydrides is exothermic, a considerable increase in temperature is obtained, and the temperature can be thus maintained above the melting point of the reactants until the reaction is complete. The amines are reacted with the benzene polycarboxylic acids, or their anhydrides, at temperatures in the range of 40 to 350° F., preferably from 60 to 200° F.

The amides of benzene polycarboxylic acids are used herein in lubricating oil compositions in amounts sufficient to inhibit rusting, such as amounts from 0.1% to 5%, by weight, more preferably amounts from 0.5% to 3%, by weight.

Example I hereinbelow illustrates the preparation of the non-emulsible rust inhibitors of this invention.

#### EXAMPLE I

A mixture of 222 grams of the secondary amine, eicosyl-docosylamine, and 96 grams of trimellitic anhydride was heated at 115° C. for one hour to yield a creamy hard solid having a melting point range of 98-110° C. The acid number of the product was found to be 180 (calculated —180).

Table I hereinbelow illustrates further the preparation of the non-emulsible rust inhibitors described herein.

Lubricating oil compositions of the amides of benzene polycarboxylic acids were evaluated as rust inhibitors in lubricating oil compositions as set forth by the data hereinbelow.

Tables III and IV present data obtained in the Humidity Cabinet Test and the HBr Neutralization Test described as follows:

#### HUMIDITY CABINET TEST

A sand-blasted steel panel 1/8" x 2" x 4" was dipped in the oil to be tested, drained of free oil at room temperature, and placed in a humidity cabinet at 120° F. and 100% humidity for the number of hours noted in the tables.

#### HBR NEUTRALIZATION TEST

Three sand-blasted steel panels 1/8" x 2" x 4" were totally immersed for no more than one second in 0.1% aqueous HBr, and within one second after removing the test panels from the HBr solution, these test panels were dipped in the oil to be evaluated at room temperature. These three panels were dipped and removed from the test oil twelve times during a period of 60 seconds, after which they were suspended in air for four hours at room temperature, then examined for rusting to determine the percent rust occurring thereon.

5

In the tables hereinbelow, the sample numbers correspond to the sample numbers of Tables I and II hereinabove. In Tables III and IV hereinbelow, the oils being evaluated contained 2% by weight of the product of the noted sample number. The base oil was a California solvent refined oil.

Table III

	Sample No.					
	Base oil	2	3	4	5	6
Humidity cabinet test, percent rust, hours:						
24	100					
100					1	
200		30	0	5	30	0

Table IV

	Sample No.					
	Base oil	7	10	11	12	13
Humidity cabinet test, percent rust, hours:						
24	100					
100			10		1	
200		0	15	1	1	0

Table V hereinbelow presents data obtained by evaluating these rust inhibitors in the Turbine Oil Rust Test.

The turbine oil rust test was run by thoroughly mixing 300 ml. of the oil being tested with 30 ml. of distilled water or synthetic sea water at 140° F. A cylindrical steel spinet was immersed therein for 24 hours. Any rust appearing on the spinet and observed by the naked eye was evaluated as a failure for that oil.

Table V

	Sample No.				
	Base oil	6	8	10	12
Concentration in oil (wt. percent)		0.1	0.05	0.15	0.1
Emulsibility	2% pass	None (pass)	4% (pass)		
Turbine rust test:					
Distilled water	Heavy rust	No rust	No rust	2% rust	No rust.
Synthetic sea water	do	Light rust	Mod. rust	30% rust	2 spots.

Table VI hereinbelow presents data on the use of amides of benzene polycarboxylic acids as rust inhibitors in grease compositions. The test was the "Bearing Protection Test" described in Military Specification

MIL-G-3278A

The base grease consisted of 15% lithium stearate in di(2-ethylhexyl)sebacate.

Table VI

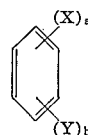
	Sample No.					
	Base grease	3	6	7	10	12
Concentration of amide (wt. percent)						
Bearing rollers rusted (12 total)		2	2	2	2	2
	4	0	1	0	0	0

In addition to the rust inhibitors described herein, the lubricating oil compositions may contain other lubricating oil additives such as oxidation inhibitors, corrosion inhibitors, viscosity index improving agents, detergents, etc.

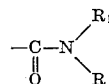
6

I claim:

1. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 0.1% to 5%, by weight, of a benzene polycarboxylic acid amide of the formula

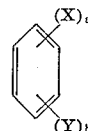


wherein X is a carboxyl radical, Y is an amide radical of the formula

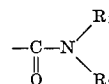


20  $a$  is a number having a value of at least 2,  $b$  is a number having a value of at least 1, the sum of  $a$  and  $b$  being in the range of 3 to 6,  $R_1$  is an aliphatic hydrocarbon radical containing from 1 to 30 carbon atoms,  $R_2$  is selected from the group consisting of hydrogen and aliphatic hydrocarbon radicals containing from 1 to 30 carbon atoms, and wherein said amide radical is on a benzene carbon atom adjacent to a carbon atom containing a carboxyl group.

25 2. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 0.5% to 3%, by weight, of a benzene polycarboxylic acid amide of the formula

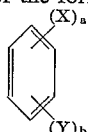


wherein X is a carboxyl radical, Y is an amide radical of the formula



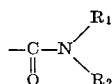
55  $a$  is a number having a value of at least 2,  $b$  is a number having a value of at least 1, the sum of  $a$  and  $b$  being in the range of 3 to 6,  $R_1$  is an aliphatic hydrocarbon radical containing from 1 to 22 carbon atoms,  $R_2$  is selected from the group consisting of hydrogen and aliphatic hydrocarbon radicals containing from 1 to 22 carbon atoms, and wherein said amide radical is on a benzene carbon atom adjacent to a carbon atom containing a carboxyl group.

60 3. A grease composition having as grease thickeners a member of the group consisting of metal salts of fatty acids and of terephthalamic acids having incorporated therein from 0.1% to 5% by weight of a benzene polycarboxylic acid amide of the formula



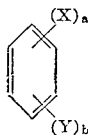
7

wherein X is a carboxyl radical, Y is an amide radical of the formula



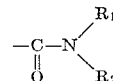
$a$  is a number having a value of at least 2,  $b$  is a number having a value of at least 1, the sum of  $a$  and  $b$  being in the range of 3 to 6,  $\text{R}_1$  is an aliphatic hydrocarbon radical containing from 1 to 30 carbon atoms,  $\text{R}_2$  is selected from the group consisting of hydrogen and aliphatic hydrocarbon radicals containing from 1 to 30 carbon atoms, and wherein said amide radical is on a benzene carbon atom adjacent to a carbon atom containing a carboxyl group.

4. A grease composition having as grease thickeners a member of the group consisting of metal salts of fatty acids and of terephthalamic acids having incorporated therein from 0.5% to 3% by weight of a benzene polycarboxylic acid amide of the formula



8

wherein X is a carboxyl radical, Y is an amide radical of the formula



5

10

15

20

25

$a$  is a number having a value of at least 2,  $b$  is a number having a value of at least 1, the sum of  $a$  and  $b$  being in the range of 3 to 6,  $\text{R}_1$  is an aliphatic hydrocarbon radical containing from 1 to 22 carbon atoms,  $\text{R}_2$  is selected from the group consisting of hydrogen and aliphatic hydrocarbon radicals containing from 1 to 22 carbon atoms, and wherein said amide radical is on a benzene carbon atom adjacent to a carbon atom containing a carboxyl group.

5. The grease composition of claim 4, wherein said grease composition contains lithium stearate as a grease thickening agent.

6. The grease composition of claim 4, wherein said grease composition contains a metal salt of terephthalamic acid as a grease thickening agent.

7. The grease composition of claim 6, wherein said metal salt of terephthalamic acid is N-octadecyl, sodium terephthalamate.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

2,450,222	9/1948	Ashburn et al. ....	252—42.1
2,945,813	7/1960	Dreher et al. ....	252—33.6
3,056,832	10/1962	Stromberg .....	260—518

##### FOREIGN PATENTS

511,882	4/1955	Canada.
809,198	2/1959	Great Britain.

DANIEL E. WYMAN, *Primary Examiner.*