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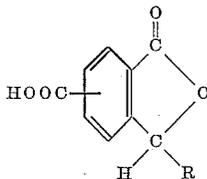
**LUBRICANT ADDITIVE AND LUBRICATING COMPOSITIONS**

Omar O. Juveland, South Holland, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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This invention relates to improved lubricant additives and lubricating compositions containing the same. More particularly, it relates to oil-soluble telomerization products, which are alkyl-substituted derivatives of carboxy-phthalides, and to lubricant compositions containing such telomerization products.

The telomerization products of my invention are produced by the reaction of 1-alkenes with carboxy-phthalides. The general formula for the resulting novel compounds is as follows:



where R is an alkyl group containing at least four carbon atoms. Compounds of this general type are useful as anti-rust agents in lubricant compositions; when reacted with alkyleneamine compounds, they are useful as detergent additives in motor oils, capable of dispersing various impurities and neutralizing acid products formed in motor oils during their use in internal combustion engines. I have found that particularly useful compositions for these purposes are those which are the telomerization reaction products of lower alkenes, e.g. ethylene, propylene, 1-butene and 1-pentene, with 5-carboxy-phthalide and the ethyleneamine derivatives thereof, such as those made by reaction with tetraethylene pentamine.

Internal combustion engines employing leaded fuels, commonly gasoline containing tetramethyl and/or tetraethyl lead, undergo blowby of combustion products past the pistons. As a result, various compounds of lead work their way past the pistons rings to accumulate on many engine parts, such as the oil ring slots, oil lines, and the like. These lead-containing accumulations frequently obstruct the normal flow of lubricating oils used in the engines. Moreover, during the combustion of fuel in an internal combustion engine various oil oxidation products, fuel soots and resins, and other type of insoluble matter are produced as a result of piston blowby of combustion products, high temperatures, sulfur compounds in fuels, etc. It is important that these materials be kept in suspension or dispersion in the oil so that they will not settle out or adhere to metal surfaces, whereby they build up as sludge or varnish deposits. The manner in which dispersant additives function is roughly analogous to the use of soap to bring some non-compatible material, such as soot, into a suspension with water, so that the soot does not settle out in lumpy masses. In like fashion, oxidation products, resins, soots, etc. will not mix readily with petroleum oils and will tend to settle out and adhere to engine surfaces. If a dispersant is added to the oil, these insoluble materials are dispersed or suspended so that settling and agglomeration into sludgy deposits is minimized. The dispersants act by adsorbing onto the foreign particles in such a way as to increase the distance of closest approach of the particles and thus to decrease the effective inter-particle cohesive field of force.

Heretofore, aromatic hydrocarbons to which are attached long hydrocarbon substituent chains have been used as dispersants, and a variety of metallic additives have also been used in internal combustion engines to prevent tarnish formation and to disperse oil-soluble materials. These latter additives very often consist of such compounds as the alkali and alkaline earth salts of organic acids, such as sulfonates, phenates and phosphosulfurized hydrocarbons or mixtures thereof. Unfortunately, many of the metal-containing additives promote the oxidation of oil in an engine, so that their use is disadvantageous.

The increased use of passenger automobiles for high speed driving between major towns has led over the past decade to the development of larger and more powerful internal combustion engines for such vehicles. In practice, however, many of these vehicles are employed, for the major proportion of their lives, in city driving. The conditions an engine encounters in city driving are recognized to be much more severe than the conditions encountered in long distance, high speed driving. During the city driving the automobile engines develop only a small proportion of their maximum power output and as a consequence of the lower power output, these large engines work for long periods at temperatures lower than their full power working temperature. As a result, the alkali and alkaline earth salts of organic acids which hitherto functioned successfully as detergents and dispersants in crankcase lubricating compositions have been found to be less successful in dispersing the sludge formed under the low temperature operating conditions of city driving. Apparently, different types of dirt require different dispersants and the sludge formed under low temperature operating conditions, termed "cold sludge," has presented particular problems not encountered in the dispersing of high temperature sludge compositions. Further, acidic by-products of fuel combustion tend to accumulate in engine oil at a faster rate during city driving conditions wherein the oil does not become thoroughly warmed. A wide range of polypolar polymers have been disclosed as dispersants for the "cold sludge." These polypolar polymers have usually been manufactured by copolymerizing monomers of relatively low polarity, particularly unsaturated esters such as esters of vinyl alcohol, with monomers of higher polarity.

I have found that surprisingly effective compounds for use as cold sludge dispersant and acid neutralizing agents can be made from alkyl-carboxy-phthalides. The alkyl-carboxy-phthalides contain functional groups which can be reacted with other materials known to be of value as extreme pressure lubricating agents, detergents, acid-neutralizers, etc. for the preparation of additive molecules capable of replacing several of the individual additives otherwise required in motor oils designed for severe service conditions. Further, the alkyl-carboxy-phthalides themselves possess a carboxylic acid function which is capable of adsorption onto the engine wall so as to provide rust inhibition, as will be shown by example hereinbelow.

The additive compositions of my invention can be added to lubricating oils in amounts as great as 30 percent by weight and more. Generally, the total amount of additives in a lubricating oil for severe service does not exceed about 20 percent by weight, even in a high detergent oil. Smaller amounts of my additives can be used, depending upon the severity of the service encountered by the particular lubricating oil and desirably can be amounts of from about 0.01 percent by weight to about 15 percent by weight and, preferably, from about 0.25 percent by weight to about 10 percent by weight of the lubricant base stock.

The average carbon chain length of the alkyl substituent in the alkyl-carboxy-phthalides is selected according to the degree of solubility desirable for incorporating the alkyl-carboxy-phthalides and the ethyleneamine derivatives of the alkyl-carboxy-phthalides in a lubricant base stock. A very short alkyl substituent provides an additive with relatively low oil solubility, because of the desolubilizing influence of polar substituents in the total molecule; a very long alkyl substituent also provides an additive with relatively low solubility because of the decrease in solubility which accompanies an increase in molecular size; when the alkyl substituent is highly branched, it can in general contain more carbon atoms than a non-branched alkyl substituent at a given solubility level, since branched alkyl chains are more oil-soluble than unbranched alkyl chains. Alkyl substituents containing from 10 to 1500 carbon atoms are generally most useful in rust-inhibiting and dispersant additives; those substituents containing up to 3,000 carbon atoms are useful in some applications and a preferred range is from 20 to 300 carbon atoms. My preferred dispersant compounds are in general the lower ethyleneamine derivatives of such carboxy-phthalide telomers of polyolefins.

Suitable lubricant base stocks for use with the additives of my invention are such as the mineral lubricating oils, synthetic hydrocarbon lubricating oils, synthetic lubricating oils of the polyalkylene oxide type, for example the "Ucon" oils marketed by Carbide and Carbon Corporation, as well as polycarboxylic acid ester type synthetic lubricating oils, such as the esters of adipic acid, sebacic acid, azelaic acid, etc. While the additives of the present invention can be used alone in the base oil, they can also be used in combination with minor amounts, for example 0.02 weight percent to 10 weight percent, based upon the lubricant oil, of other lubricant addition agents, such as zinc dialkyl dithiophosphates, sulfurized terpenes, e.g. sulfurized dipentene, viscosity index improvers, pour point depressors, rust inhibitors, extreme pressure additives, etc.

One mode of preparation of the compounds of my invention is a telomerization reaction carried out with peroxide-type polymerization initiators under such conditions of temperature and pressure as to maintain a liquid phase in the reaction vessel. The product of such reaction will, of course, not have one precise alkyl chain length substituted in the carboxy-phthalide molecule; it will be a mixture of compounds having alkyl substituents near the average alkyl chain length in size.

Effective polymerization initiators are materials such as ditertiary-butyl peroxide, benzoyl peroxide, acetyl peroxide, various hydroperoxides, azo-bis-isobutyronitrile, etc.

The temperature for the telomerization reaction must be high enough to generate sufficient free-radicals from the polymerization initiator to start the reaction; the pressure should be sufficient to maintain a liquid phase in the reaction vessel. The selection of the proper combination of initiators, temperature and pressure for most effective reaction can be readily determined through simple experimentation by the ordinary worker in this art in light of my disclosure. A specific preparation of a compound within the scope of my invention was performed as follows:

Carboxy-phthalide starting material, comprising chiefly 5-carboxy-phthalide was prepared by hydrogenating trimellitic anhydride in tetrahydrofuran solvent at 180° C. under hydrogen pressure of 1500 to 1800 p.s.i.g. The hydrogenation catalyst was 5% palladium on charcoal, and the total catalyst amounted to 5% of the weight of trimellitic anhydride. When no more hydrogen was absorbed, the hydrogenation vessel was depressured and the reaction solution was filtered to remove catalyst. The tetrahydrofuran solvent was removed by evaporation, and the residual material was recrystallized twice from water.

A portion of the purified product was converted to the methyl ester and subjected to gas chromatographic

analysis. The analysis indicated that the total purified product consisted of a mixture of 5- and 6-carboxy-phthalides containing about 82% of the 5-carboxy-phthalide and 18% of the 6-carboxy-phthalide. This mixture was used without separation for the preparations which follow. Other carboxy-phthalides can be made through similar preparative procedures performed upon the appropriate starting materials; e.g., 4- and 7-carboxy-phthalides can be made starting with hemimellitic anhydride.

To a 250 ml. Magne-Dash reactor there was charged 100 ml. of benzene as solvent, 10 g. of carboxy-phthalide and 3 ml. of di-tertiary butyl peroxide, as initiator. The reactor was closed and ethylene was added to a pressure of 500 p.s.i.g. The reactor and contents were brought to a temperature of 150° C., at which time the pressure reached 900 p.s.i.g. Polymerization was carried out for about 4 hours at 900 to 1200 p.s.i.g. of ethylene, after which time the reactor was cooled and depressured. The reaction product mixture was filtered and material insoluble in benzene at 25° C. was separated. The filtrate was frozen at -80° C., and the benzene removed at <1 mm. Hg to yield a white solid amounting to 10.5 g., identified as Fraction 1. Fraction 1 was analyzed for acid number, saponification number, and molecular weight. This fraction was also analyzed by gas chromatography to determine whether any starting material remained. The results of the analyses were as set forth below:

Acid number -----	43 ml. KOH/gram.
Saponification number -----	71 mg. KOH/gram.
Molecular weight -----	1082.
Gas chromatography analysis for starting materials -----	None present.

Fraction 1 was examined by infrared and the results indicated compound formation between the carboxy-phthalide and the ethylene.

The material insoluble in benzene at room temperature was extracted with boiling benzene and the extract solution was freeze-dried; 12.4 g. of product was obtained, identified as Fraction 2. Fraction 2 was extracted with acetone to remove any residual starting material and was analyzed for properties set forth below in the tabulation of analyses and results:

Acid number -----	11 ml. KOH/gram.
Saponification number -----	20.1 mg. KOH/gram.

The alkyl group attached to the compound identified as Fraction 1 contained an average of about 64 carbon atoms per molecule based on the molecular weight results. The alkyl group of the compound identified as Fraction 2 contained an average of about 284 carbon atoms per molecule, on a similar basis. The saponification numbers indicate slightly longer substituent groups.

In similar fashion, propylene, 1-butene, isobutylene, 1-pentene, mixtures thereof, and the like, can be used in the preparation of telomerization products with carboxy-phthalides. The length of the alkyl group substituted into the carboxy-phthalide molecules can be readily varied by adjusting the proportions of the reactants, as will be evident to those skilled in this art.

The telomerization product identified as Fraction 1 was tested as an anti-rust agent for industrial oils using ASTM Test D665-60. At a concentration of 0.15 weight percent in Grade 10 oil using distilled water, the telomer gave a zero rating. In sea water, a telomer concentration of 0.3 weight percent gave a zero rating.

Another preparation of a compound within the scope of my invention was performed as follows:

To a 250 ml. Magne-Dash reactor there was charged 100 ml. of benzene as solvent, 6 g. of the 5-, 6-carboxy-phthalides mixed product and 3 ml. of di-tertiary butyl peroxide, as initiator. The reactor was closed and the reactor and contents were brought to a temperature of 150° C. Ethylene was added to a pressure of about 1165

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p.s.i.g. and polymerization was carried out for about four hours after which the reactor was cooled and de-pressured. The reactor contents were filtered at 25° C. There was obtained 4.7 g. of material, insoluble in benzene at 25° C., soluble in boiling benzene, identified as Fraction A.

The benzene filtrate was freeze-dried to yield a benzene-soluble product, identified as Fraction B, amounting to 21.0 g.

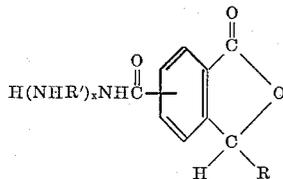
Fraction A had a saponification number of 88 mg. KOH/gram.

Fraction B had the following properties:

Saponification number ----- 100 mg. KOH/gram.  
Molecular weight ----- 1034.

A 5.0 g. sample of Fraction B was dissolved in 50 cc. of benzene and to this solution was added 1.7 g. of tetraethylene pentamine in 50 cc. of benzene. The resulting mixture was heated to boiling and the benzene solvent was removed by vaporization. The solid residue was dried in a vacuum oven at 70° C. overnight and about 6.6 g. of the tetraethylene pentamine derivative of polyethylene carboxylic-phthalide was obtained.

The alkyleneamine derivatives of carboxy-phthalides made according to the above procedure are most likely amide compounds of the general formula



wherein R is an alkyl group, R' is an alkylene group and x is an integer depending upon the particular alkyleneamine chosen, suitably from 1 to 20. It may be, however, that the phthalide ring opens for reaction with the amine, and therefore, a definite structure cannot be assigned my alkyleneamine derivatives of carboxy-phthalides.

The ethyleneamine derivative made as described above was subjected to a qualitative test for dispersancy as follows:

Into a 4-ounce tall form vial there was placed about 0.375 g. of the derivative. This was dissolved in hexane to give 75 g. of solution. To the solution there was added 4 g. of a carbon black-white oil suspension. The mixture was stirred thoroughly and allowed to stand undisturbed for 48 hours. A blank was prepared as above, except for omission of the ethyleneamine derivative, and allowed similarly to stand for 48 hours. At the end of the test period, the carbon suspended in the blank sample had settled out of suspension; that in the test sample remained in suspension. Even after a period of three weeks a substantial amount of carbon remained in suspension in the test sample.

The ethyleneamine compounds suitable for preparation of the ethyleneamine-alkylcarboxy-phthalide derivatives of my invention are those of the general formula  $H_2N(R_2NH)_xH$  wherein x is at least 1 and R is an alkylene group, preferably ethylene. The upper limit for the value of x is dependent upon the degree of solubility desirable for a particular derivative. A practical upper limit is about 20 when R is ethylene; that is, about 40 carbon atoms. Suitable alkyleneamines are such compounds as ethylene diamine, diethylene triamine, triethylene tetra-amine, pentaethylene hexamine, etc. Suitable compounds are also such as the homologues of the ethyleneamines, e.g. propylene amines, etc. Further, monoamines can be employed for preparation of the carboxy-phthalide derivatives, suitable monoamines being such as ethylamine, propylamine, butylamine, and, in general, alkylamines containing from about 1 to about 40 carbon atoms.

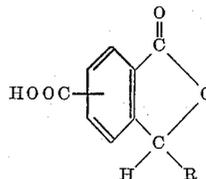
It is apparent from the above results that the com-

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pounds of this invention possess utility as anti-rust and dispersant additives in lubricant base oils. Although the present invention has been described with reference to specific embodiments thereof, variations within its scope will be apparent to those of ordinary skill in this art.

Having thus described my invention, what I claim is:

1. As new compositions of matter, organic compounds of the structure:



wherein R is an alkyl group containing at least 4 to about 3,000 carbon atoms.

2. As new compositions of matter, the carboxy-phthalide telomers of an aliphatic polyolefin hydrocarbon which contains from about 4 to about 3,000 carbon atoms in the polyolefin chain.

3. The compositions of claim 2 wherein the polyolefin is polyethylene.

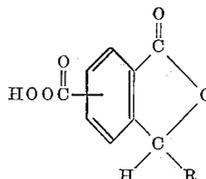
4. The compositions of claim 2 wherein the polyolefin is polypropylene.

5. The compositions of claim 2 wherein the polyolefin is polyisobutylene.

6. A lubricant composition comprising major proportion of a normally liquid lubricant oil base stock and a minor amount of an anti-rust additive sufficient to inhibit rust, wherein said additive is 3-(alkyl)-carboxy-phthalide which contains from about 4 to about 3,000 carbon atoms in the alkyl group.

7. The method of preparing carboxy-phthalide telomers of an aliphatic polyolefin hydrocarbon which contains from about 4 to about 3,000 carbon atoms in the polyolefin chain which comprises reacting a lower 1-alkene with carboxy-phthalide, said reaction being initiated by a free-radical polymerization initiator.

8. As a new composition of matter, the reaction product made by reacting an organic compound of the structure:

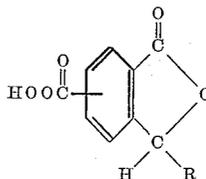


wherein R is an alkyl group containing at least 4 to about 3,000 carbon atoms with an amine of the structure:  $H(NHR')_xNH_2$  wherein R' is a lower alkylene group and x is an integer of from 1 to 20, said reacting being accomplished by heating said organic compound and said amine to boiling.

9. The composition of claim 8 wherein R contains from about 4 to about 3,000 carbon atoms, R' is ethylene and x is from 1 to 10.

10. The composition of claim 8 wherein R is polyethylene, R' is an ethylene group and x is 4.

11. A lubricant composition comprising a major proportion of a normally liquid lubricant oil base stock and a minor amount sufficient to impart dispersancy of a dispersant, wherein said dispersant is the reaction product made by reacting an organic compound of the structure:



wherein R is an alkyl group containing at least 4 to about 3,000 carbon atoms with an amine of the structure:  $H(NHR')_xNH_2$  wherein R' is a lower alkylene group and x is an integer of from 1 to 20, said reacting being accomplished by heating said organic compound and said amine to boiling.

12. The method of preparing a dispersant additive for lubricant compositions which comprises reacting 3-(alkyl)-carboxy-phthalide wherein the alkyl group contains at least 4 to about 3,000 carbon atoms with an alkylene amine of the general structure  $H-(NHR)_xNH_2$  wherein R is a lower alkylene group and x is an integer of from 1 to 20, said reacting being accomplished by

heating said 3-(alkyl)-carboxy-phthalide and said alkylene amine to boiling.

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DANIEL E. WYMAN, *Primary Examiner.*

P. P. GARVIN, *Assistant Examiner.*