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IMIDE COMPOUNDS AND LUBRICANTS CONTAINING THE SAME

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21 Claims. (Cl. 252—33.6)

This invention relates to novel chemical products and novel improved lubricating compositions. More particularly, the invention provides novel chemical compounds comprising imides and metal salts of certain of these imides, novel reaction products of metal alcoholates with imides, including certain of the stated novel imides, and a method of making the same, and novel lubricating compositions comprising an oleaginous base and the novel products provided by this invention.

There is a demand in the lubricant industry for lubricating compositions effective over an increasingly wide operational range of pressures and temperatures. Thus, for example, high speed aircraft with larger power plants and changed structural design are continually designed and placed in operation. These engineering developments present stringent requirements for lubricants for sliding surfaces and for ball bearings. In such applications, anticipated loads may range as high as 100,000–150,000 p.s.i., with ambient temperatures from −65° F. to 600° F. or higher. It is particularly difficult to provide additives for lubricating compositions, such as thickeners, which convert fluid oleaginous bases to greases, extreme pressure agents, which impart lubricity to oleaginous bases, oxidation-stabilizing and degradation-inhibiting compounds and the like, that are effective at the upper end of this temperature range. The known thickeners, such as the ureides prepared by reacting an isocyanate with an amine, begin to decompose at about 500° F. Few of the extreme pressure agents available are effective at such temperatures and pressures. Many of the stabilizers available will also fail under elevated temperature conditions. The present invention is particularly valuable in that it provides compositions capable of effective lubrication under such severe conditions.

The requirements which modern lubricating compositions must meet include not only lubricity under high loads but also good temperature response. Natural oils such as mineral oils are generally of restricted utility; the viscosity-temperature characteristics of even highly refined mineral oils are unfavorable where lubricants must be operative over broad temperature ranges. Synthetic lubricants, such as silicones, polyesters and the like, are available which avoid this defect. However, these synthetic lubricant bases are only poorly responsive to treatment with additives, such as extreme pressure agents, as compared to mineral oils. Accordingly, the production of satisfactory lubricants for wide temperature range operation presents a particularly difficult problem.

It is an object of this invention to provide novel products, including novel compounds, and compositions containing the same.

A particular object of this invention is to provide novel products which are effective high temperature thickeners for use in lubricating compositions.

A further particular object of this invention is to provide novel thickened lubricating compositions.

Another object is to provide novel compounds having utility for the improvement of lubricant properties, such compounds including imides and salts of certain of these imides which are effective to thicken, enhance the extreme pressure properties of, and stabilize oleaginous bases to provide improved lubricating compositions.

Another object is to provide novel improved lubricating compositions comprising an oleaginous base and novel products as set forth hereinafter.

A further object is to provide novel methods of making reaction products of certain imides, and to provide the novel products of such reaction.

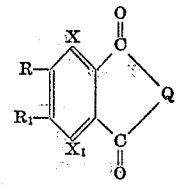
These and other objects will become evident from a consideration of the following specification and claims.

The novel products provided by this invention include novel compounds of structure as stated hereinafter, and novel reaction products.

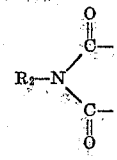
The novel products provided by this invention include,

(A) Compounds of the formula

(I)



in which, (1) when R and R_1 are taken together, R and R_1 together represent the radical



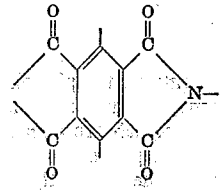
X and X_1 are selected from the group consisting of hydrogen and chlorine, Q is selected from the group consisting of O and N—R_3, and R_2 and R_3 are selected separately from the group consisting of —arylene-COOH and polycyclic conjugated radicals; and (2) when R and R_1 are taken separately, each of X, X_1, R and R_1 is chlorine and Q is —N-arylene-COOH;

(B) Metal salts prepared from the compounds of Formula I which contain a

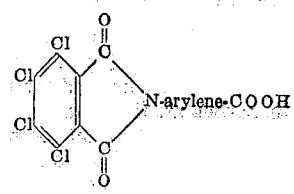


group.

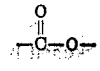
As will be evident from a consideration of the stated formula, the compounds provided hereby comprise pyromellitimides, containing the structure



as defined by the above formula when R and R_1 are taken together (the dangling valences being satisfied as stated above); tetrachlorophthalimides of the structure



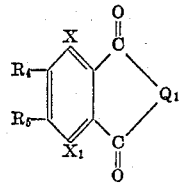
as defined by the stated formula when R and R_1 are taken separately; and metal salts prepared from the pyromellitimides and tetrachlorophthalimides of the stated formula which contain a



group.

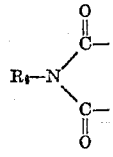
Additionally, it has been found that novel reaction products of particular effectiveness as lubricant thickeners can be produced by reacting an aluminum alcoholate with a compound of the formula:

(II)



in which X and X_1 are selected from the group consisting of hydrogen and chlorine and

(1) When R_4 and R_5 are taken together, R_4 and R_5 together represent the radical



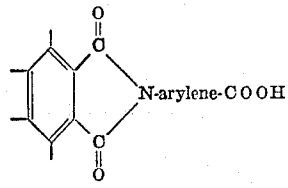
Q_1 is selected from the group consisting of O, N-arylene-COOH, and an N atom substituted by a polycyclic conjugated radical, and R_6 is —arylene-COOH when Q is an N atom substituted by a polycyclic conjugated radical, while R_6 is selected from the group consisting of —arylene-COOH and conjugated polycyclic radicals when Q is O or N-arylene-COOH; and

(2) When R_4 and R_5 are taken separately, R_4 and R_5 are selected from the group consisting of hydrogen and chlorine and Q_1 is —N-arylene-COOH.

As will be evident from a consideration of the formula stated here, the compounds which can be reacted with an aluminum alcoholate to produce these novel reaction products comprise the novel pyromellitimides and tetrachlorophthalimides which contain a



group provided as new compounds as stated above, as well as phthalimides of the formula



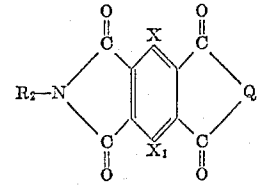
in which the substituents on the phthalimide nucleus may all be hydrogen, or may in part be chlorine. The products of the stated reaction, which are of a presently unknown structure, are different in properties from the above-mentioned metal salts of the presently provided pyromellitimides and tetrachlorophthalimides. This stated method and its products are novel inventions provided hereby.

The novel compositions of this invention are lubricating compositions comprising the stated products and an oleaginous base, as further described hereinafter.

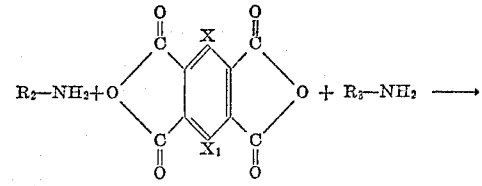
The presently provided novel products are new substances exhibiting unique qualities and useful for a variety of purposes. In particular, they can be used to modify oleaginous bases to produce lubricant compositions operative under service conditions which are substantially more severe than it has been possible to employ advantageously hitherto. The various products differ among themselves as to their degree of effectiveness in imparting one or more desirable properties to lubricating compositions. It is found that these novel products, and particularly the stated reaction products, thicken oleaginous bases, producing greases of outstanding stability. A particularly noteworthy feature of the thickened lubricant compositions of this invention is stability at high temperatures, including temperatures in the range of 500° to 600° F. Additionally, certain of the presently provided novel products, and particularly the presently provided derivatives of tetrachlorophthalimidoarylenecarboxylic acids, are effective to impart extreme pressure properties to lubricating compositions. Others, particularly certain of the pyromellitic type, are especially effective in inhibiting the degradation of such oleaginous bases. Still others may secure several of these benefits simultaneously. A particular advantage of the present invention is that the novel products provided hereby can be used to produce substantial improvement in the high temperature properties of lubricants of the synthetic type. Thus lubricating compositions having a good temperature response in respect to the viscosity-temperature characteristics of the oleaginous base and effective under severe service conditions at high temperature ranges may be produced.

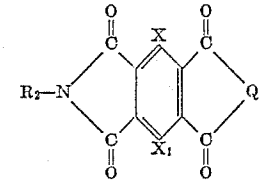
THE PYROMELLITIMIDES

The novel compounds provided by this invention include as a first class pyromellitic imide derivatives of the formula



where Q, R_2, X and X_1 are as defined above. It has been found that such compounds can be prepared by the reaction of a pyromellitic dianhydride with an amine or a mixture of amines as illustrated by the following equation:





where X and X_1 are H or Cl, Q is O or N—R_3, and R_2 and R_3 are the same or different and are each selected from the class consisting of polycyclic conjugated radicals and —arylene-COOH.

The pyromellitic dianhydrides which may be used to prepare the pyromellitimides of this invention include pyromellitic dianhydride, 3-chloropyromellitic dianhydride, and 3,6-dichloropyromellitic dianhydride. The amines which may be used include amines in which an amine radical is attached either to a polycyclic conjugated radical or an —arylene-COOH radical.

The Polycyclic Conjugated Radicals

By a conjugated radical is meant a radical in which double bonds alternate with single bonds and the bond system of which is capable of resonating. The conjugated radicals particularly useful in the practice of this invention are polycyclic conjugated radicals in which double bonds alternate with single bonds throughout the cyclic structure. At least two conjugated cyclic radicals must be present in the polycyclic radical.

The amine selected to prepare the compounds of this invention may be one containing a polycyclic conjugated

radical which is a hydrocarbon radical, either of the fused ring type such as the radicals of α- and β-naphthylamine, the isomeric anthrylamines, the isomeric phenanthrylamines, and so forth, or the linked ring type, such as the radicals of 2-, 3- and 4-biphenylamine, the binaphthylamines, the terphenylamines, and so forth.

The amines useful in preparing these novel compounds also include heterocyclic amines containing a conjugated polycyclic radical. Thus, for example, there may be employed amines including fused azacyclic systems such as a quinolylamine like 2-quinolylamine, an isoquinolylamine like 3-isoquinolylamine, or an acridylamine like 3-aminoacridine, and so forth; linked azacyclic systems such as 4-phenylpyridyl-2-amine and so forth; and polyazacyclic systems such as 4-phenylpyridazyl-5-amine, 4-phenylpyrimidyl-6-amine, 2-quinoxalinylamine, and so forth.

Alternatively, the useful amine may be one wherein rings including monocyclic rings are linked through a structure capable of resonating with the conjugated ring bond system. Thus for example, the amine may comprise a sulfone or sulfoxide such as 4-aminobiphenyl sulfone, 4-amino-1-naphthyl phenyl sulfone, o-(phenylsulfinyl)aniline, and the like; or a ketone such as 4-aminobenzophenone, 4-aminochalcone, phenyl 2-amino-5-quinolyl ketone, and the like.

The polycyclic conjugated radical present in the amines of the class discussed hereinabove may, if desired, be substituted by any of a wide variety of non-interfering substituents. Such substituents may, for example, comprise additional amino radicals. It has been found that apparently only one of the two amino groups of di-amino-substituted polycyclic conjugated radicals reacts with the pyromellitic anhydride during the reaction producing the present novel pyromellitimide derivatives as illustrated by the equation given hereinabove. Thus polyamines can be used to produce the novel compounds of this invention conforming to the formula shown above. Illustrative of such polyamines are, for example, 1,4-naphthylenediamine, 1,4-anthradiamine, 4,4′-biphenyldiamine, 3,4-biphenyldiamine, 2,4-quinolyldiamine, 5,8-quinoxalyldiamine, benzoguanamine (phenylguanamine), 4,4′-diaminodiphenyl sulfone, 4,4′-diaminobenzophenone, and so forth.

There are a number of other substituents which do not interfere in the course of the reaction of the amines of the stated nature with pyromellitic dianhydride to produce the pyromellitimide derivatives of this invention. These include, for example, halogen atoms (Cl, Br, F or I), an hydrocarbon, hydroxy, alkoxy, carboxy, carbalkoxy, and acyl (alkylcarbonyl) radicals. Such substituent radicals will preferably contain up to 6 carbon atoms. Oxo radicals, particularly when located so as to permit resonance thereof with the conjugated ring structure, may also be present in the selected amines. Thus amines useful in the practice of the invention include, for example, 1-aminoanthraquinone, 6-aminobiquinone, 2,2′-dichloro-4,4′-biphenyldiamine, bi-o-tolyl-4,4′-diamine, 2,2′ - dipropyl - 4,4′ - biphenyldiamine, 3,3′ - dihexyl - 5,5′ - biphenyldiamine, 4 - amino - o,o′ - biphenol, 4-methoxy - 1 - naphthylamine, 3 - amino - 5 - acetylquinoline, 4 - amino - 1 - naphthoic acid, 4′ - carbethoxyxenylamine, and so forth.

The —Arylene-COOH Radicals

The second class of presently useful amines comprises aminoarylenecarboxylic acids. The arylene radical of the presently useful acids is a radical containing at least one aromatic nucleus. Arylene radicals containing from 6 to 14 carbon atoms, are preferred, the 1,4-phenylene radical being particularly preferred. While the invention may be practiced to advantage utilizing arylene radicals which are hydrocarbon radicals, the arylene radicals may, if desired, be substituted by a non-interfering substituent such as any of those mentioned above in discussion of the conjugated polycyclic radicals, like oxo, hydroxy and the like. Thus, for example, presently useful amines include 2-, 3- and 4-aminobenzoic acid, 2-amino-3-naphthoic acid, 5-aminoanthroic acid, 4-(4′-aminophenyl)benzoic acid, 4-amino-2-toluic acid, 4-amino-2,5-diisopropyl benzoic acid, 4-(4′-amino-2-tert-butylphenyl)benzoic acid, 4-amino-5-tert-butylnaphthoic acid, 4-aminosalicylic acid, 6-amino-anthraquinone-1-carboxylic acid, 4-(4′-amino-2-chlorophenyl)benzoic acid and the like. The preferred species of this class is 4-aminobenzoic acid.

The Products

The novel pyromellitimide derivatives of this invention which may be produced by the reaction shown above include as a first class N,N′-disubstituted pyromellitic diimides and N-subtituted pyromellitic 1,2-imide 4,5-anhydrides in which the substituents on the N atoms are conjugated polycylic radicals. Illustrative of these compounds are for example symmetrical and asymmetrical N,N′-dihydrocarbyl pyromellitic diimides and N-hydrocarbylpyromellitic 1,2-imide, 4,5-anhydrides such as N,N′-dinaphthylpyromellitic diimide, N,N′-dinaphthyl-3-chloropyromellitic diimide, N,N′-dinaphthyl-3,6-dichloropyromellitic diimide, N,N′-dibiphenylpyromellitic diimide, N-naphthyl - N′ - biphenylpyromellitic diimide, N,N′-bis(4 - amylnaphthyl)pyromellitic diimide, N - naphthylpyromellitic 1,2 - imide 4,5 - anhydride, N - phenanthrylpyromellitic 1,2 - imide, 4,5 - anhydride, N, - biphenyl - 3 - chloropyromellitic 1,2-imide 4,5 - anhydride and so forth. Another type of product within the scope of this class comprises such derivatives in which the conjugated polycylic nucleus is a hydrocarbon radical substituted by a non-interfering substituent. Thus for example, such products include ketone such as N,N′-di-1-anthraquinolylpyromellitic diimide, N,N′-di-8-naphthaquinolyl - 3,6 - dichloropyromellitic diimide, N - (4′-acetyl - 4 - biphenyl) - N′ - biphenylpyromellitic diimide, N,N′ - bis(4 - benzoylphenyl)pyromellitic-diimide and N - naphthaquinonylpyromellitic 1,2 - imide 4,5-anhydride. They include halogen-substituted and amino-substituted products such as N,N′-bis(3′-fluoro-2-biphenyl)pyromellitic diimide, N,N′-bis(4-chloro-1-naphthyl) - 3 - chloropyromellitic diimide, N,N′ - bis(4′-amino - 4 - biphenyl)pyromellitic diimide, N,N′ - bis(4′-amino - 2,3′ - dichloro - 4 - biphenylyl)pyromellitic diimide, N - (aminoanthryl)pyromellitic 1,2 - imide 4,5-anhydride, and so forth. They also include pyromellitic imides containing a variety of other non-interfering substituents on a conjugated polycyclic hydrocarbon nucleus, such as N,N′-bis(4-carbethoxy-1-naphthyl)-3,6-dichloropyromellitic diimide, N,N′-bis(4,2′-dihydroxy-3-biphenylyl)pyromellitic diimide, N,N′-bis(4-methoxy-1-naphthyl)pyromellitic diimide, N,N′ - bis(4 - carboxy-4-biphenylyl)pyromellitic dimide, N,N′ - bis(4′ - amino-2-acetyl - 4 - biphenylyl)pyromellitic diimide, N - 5-chloronaphthyl - N′ - (4 - hydroxy - 1 - naphthyl)-pyromellitic diimide, N-(4′-tert-butoxy-4-biphenylyl)pyromellitic 1,2-imide 4,5-anhydride and so forth.

Another group of pyromellitic imides within the scope of this invention comprises those in which one or both of the imido nitrogens is substituted by a polycyclic conjugated radical in which the resonating conjugated structure includes one or more atoms other than carbon atoms. Thus for example, such products include derivatives of heterocyclic amines such as N,N′ - di - 2 - quinoxalinylpyromellitic diimide, N,N′ - bis(6 - amino - 4-(phenyl) - 2 - triazinyl)pyromellitic diimide, N(4-methylquinolyl) - N′ - (8 - methoxyquinolyl) - 3,6 - dichloropyromellitic diimide, N,N′ - bis(6 - amino-4-(pentachlorophenyl) - 2 - triazinyl)pyromellitic diimide, N - (6 - amino - 4 - (phenyl) - 2 - triazinyl)pyromellitic 1,2 - imide, 4,5 - anhydride, N-(4 - propionyl - 3-acridyl) - 3 - chloropyromellitic 1,2 - imide 4,5 - an-

hydride, and so forth. They also include derivatives of amines such as sulfones and sulfoxides, like N,N' - bis(4-(4' - aminochenylsulfonyl)phenyl)pyromellitic diimide, N,N' - bis(4 - (4' - carboxyphenylsulfinyl)phenyl)-3,6-dichloropyromellitic diimide, N - (4 - (4' - amino - 2-tolylsulfonyl)phenyl) - N' - 4 - biphenylpyromellitic diimide, N - (4 - (4' - aminophenylsulfonyl)phenyl)pyromellitic 1,2-imide 4,5-anhydride, and so forth.

A further class of products provided by this invention consists of N-substituted pyromellitic imides in which at least one of N substituents is an —arylene-COOH radical.

The pyromellitic diimide dicarboxylic acids of this type may conveniently be regarded as "symmetrically substituted" pyromellitic diimides, although it is to be understood that this term is here used as referring to the generic formula of this class only. Specific members of this class of acids may in fact be asymmetric. Illustrative of this class of acids are: N,N'-bis(4-carboxyphenyl)-pyromellitic diimide, N,N'-bis(4-carboxyphenyl)-3-chloropyromellitic diimide, N,N' - bis(4 - carboxyphenyl)-3,6 - dichloropyromellitic diimide, N,N' - bis(3 - carboxyphenyl)pyromellitic diimide, N,N' - bis(5 - carboxy - 1-naphthyl)pyromellitic diimide, N,N' - bis(3 - carboxy-2 - naphthyl) - 3 - chloropyromellitic diimide, N,N'-bis(4' - carboxy - 4 - biphenylyl)pyromellitic diimide, N,N' - bis(4 - carboxy-2,5-dimethylphenyl)pyromellitic diimide, N,N' - bis(4 - carboxy - 3 - isobutylphenyl)-pyromellitic diimide, N,N' - bis(4 - carboxy - 8 - methyl-1 - naphthyl)pyromellitic diimide, N,N' - bis(4 - carboxy - 3 - hydroxyphenyl)pyromellitic diimide, N,N'-bis(6 - carboxy - 1 - anthraquinonyl)pyromellitic diimide, N,N' - bis(6 - carboxy - 1 - anthraquinonyl) - 3,6 - dichloropyromellitic diimide, N,N' - bis(4 - carboxy - 3-chlorophenyl)pyromellitic diimide, N,N' - bis(4' - carboxy - 3 - carbethoxy - 4 - biphenyl)pyromellitic diimide, N.N' - bis(4 - carboxy - 2 - acetyl - 1 - napthyl)pyromellitic diimide, N,N' - bis(4 - carboxy - 3 - (tert-butoxy)phenyl)pyromellitic diimide, N - (4 - carboxyphenyl) - N' - (4-carboxy - 3 - hydroxyphenyl)pyromellitic diimide, N - (4 - carboxyphenyl) - N' - (4 - carboxy-2-naphthyl)pyromellitic diimide, and the like.

In the class here identified as asymmetric pyromellitic diimides, one of the N-substituents is an —arylene-COOH radical and the other N-substituent is a polycyclic conjugated radical. Illustrative of the products of this type provided by the invention are

N-(4-carboxyphenyl)-N'-napthylpyromellitic diimide,
N-(4-carboxyphenyl)-N'-naphthyl-3-chloropyromellitic diimide,
N-(4-carboxyphenyl)-N'-(4-amino-2,3'-dichloro-4-biphenylyl)pyromellitic diimide,
N-(4-carboxynaphthyl)-N'-(2-anthraquinonyl)pyromellitic diimide,
N-(4-carboxyphenyl)-N'-(2-anthraquinonyl)pyromellitic diimide,
N-(4-carboxynaphthyl)-N'-(4-benzoyl-2,3-xylyl)pyromellitic diimide,
N-(3-carboxyphenyl)-N'-(4-(4'-aminophenylsulfonyl)-phenyl)dichloropyromellitic diimide,
N-(4-carboxyphenyl)-N'-(4-benzoylphenyl) pyromellitic diimide,
N-(4-carboxyphenyl)-N-(4-chloro-2-quinolyl) pyromellitic diimide,
N-(4-carboxyphenyl)-N'-(6-amino-4-phenyl-2-triazinyl)-pyromellitic diimide, and the like.

The pyromellitic imides substituted by an

—arylene-COOH

radical provided hereby will also include mono-imides such as

N-(4-carboxyphenyl)pyromellitic 1,2-imide 4,5-anhydride,
N-(3-carboxy-2-napthyl)pyromellitic 1,2-imide, 4,5-anhydride,
N-(6-carboxy-1-anthraquinonyl)pyromellitic 1,2-imide 4,5-anhydride,
N-(4-carboxyphenyl)-3-chloropyromellitic 1,2-imide 4,5-anhydride,
N-(4'-carboxy-2,3'-dichloro-4-biphenylyl)pyromellitic 1,2-imide, 4,5-anhydride, and so forth.

Method of Preparation

To produce the present novel pyromellitic imide derivatives, pyromellitic dianhydride is contacted with the selected amine or mixture of amines in which the radical attached to the amine group is selected from the class consisting of polycyclic conjugated radicals and —arylene-COOH radicals. The synthesis consumes these reactants in a molar ratio of one mole of amine of the stated nature to one mole of the pyromellitic dianhydride to produce the 1,2-imide, 4,5-anhydride, and two moles of such amine per mole of the pyromellitic dianhydride to produce the pyromellitic diimides of this invention. The molar ratios of the stated reactants may if desired vary widely from this theoretical ratio, the molar ratio of dianhydride to total amine varying for example, from about 1:5 to about 5:1. Usually it is preferable to contact the reactants in approximately the ratios required theoretically by the equation of the reaction, to avoid the presence of excessive amounts of unreacted ingredients when reaction is completed. This is particularly the case where the reaction of the pyromellitic dianhydride with the amine is carried out in a reaction medium comprising an oleaginous base. Preparation of the pyromellitic diimide derivatives of this invention within an oleaginous base is a particularly preferred method in the formation of the lubricating compositions of this invention. Alternatively the reaction medium may comprise other solvents or diluents such as hydrocarbons, ethers and the like. Desirably it will be a relatively high-boiling material, which can be used to achieve reaction temperatures above about 200° F. Examples of suitable solvents and diluents are acetic acid or anhydride, pyridine, xylene, dimethylformamide, heptyl glycol ether, and mixtures of the same.

The mixture consisting of the amine and pyromellitic dianhydride reactant will generally be heated to accelerate the reactions thereof. Reaction temperatures as low as about 100° F. may be used, but generally the temperature employed will be at least about 150° F., and usually in the range of about 350° F.–450° F. It may be as high as 600° F. The optimum temperature for conducting the reaction will vary with the type of amine undergoing reaction. When the reaction temperature has been raised sufficiently to initiate the reaction, exotherming is sometimes observed. The occurrence of the desired reaction is characterized by the release of water, which is formed in the condensation of the pyromellitic dianhydride with the amine. Generally the reaction temperature will be such as to boil the water off from the reaction mixture, and the amount of water evolved may be used as a measure of the extent to which the reaction has gone towards completion. Additionally or alternatively the progress of the reaction may be followed by determination of the neutralization number of a sample drawn from the reaction mixture.

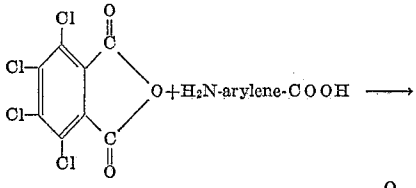
When the reaction is carried out in an organic high-boiling polar or non-polar solvent, the product may precipitate from the reaction medium during the reaction. Where this does not occur, the product may be separated by distillation, extraction or other means. The solvent or diluent or any unreacted reactants may then be recycled for further reaction, and the process may be operated as a batch or continuous method. Where the pyromellitic imide is formed within an oleaginous base, the product may remain suspended in the oleaginous fluid, usually thickening it to a grease consistency.

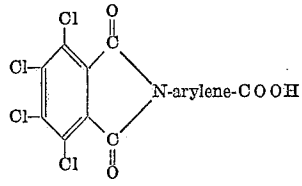
The pyromellitic imides provided by the stated procedure are high-melting compounds of good thermal sta-

bility which are effective thickeners and thermal degradation inhibitors for oleaginous base fluids. As will become evident hereinafter, certain of the pyromellitic derivatives prepared in the above-stated manner may be further reacted if desired, to form other products within the scope of this invention.

THE TETRACHLOROPHTHALIMIDES

Turning now to the tetrachlorophthalimide derivatives provided by this invention, these are prepared by reacting the tetrachlorophthalic anhydride with an amine as illustrated by the following equation





The discussion hereinabove of the aminoarylene carboxylic acids which may be used to prepare pyromellitic imides in accordance with this invention applies also to the amines useful to prepare these tetrachlorophthalimide derivatives.

Illustrative of the tetrachlorophthalimidoarylenecarboxylic acids provided by this invention are, for example, N-(4-carboxyphenyl)tetrachlorophthalimide, N-(3-carboxyphenyl)tetrachlorophthalimide, N-(4-carboxy-3-methylphenyl)tetrachlorophthalimide, N-(4-carboxy-3-chlorophenyl)tetrachlorophthalimide, N-(4-carboxy-1-naphthyl)tetrachlorophthalimide, N-(7-carboxy-1-phenanthryl)tetrachlorophthalimide, N-(4-carboxy-6-ethyl-1-naphthyl)tetrachlorophthalimide, N-(4'-carboxy-4-biphenylyl)tetrachlorophthalimide, N-(4'-carboxy-2,3'-dichloro-4-biphenylyl)tetrachlorophthalimide, N-(4-carboxy-3-hydroxyphenyl)tetrachlorophthalimide, N-(6-carboxy-1-anthraquinonyl)tetrachlorophthalimide, and the like.

The preparation of these tetrachlorophthalimidoarylene-carboxylic acids will be conducted generally as described hereinabove with reference to the pyromellitic imide derivatives. The products are fairly high-melting compounds of good thermal stability. They can be used if desired as thickeners and extreme pressure additives for oleaginous bases. They are particularly useful for the preparation of metal salts and reaction products as described hereinbelow.

THE METAL SALTS

Those members of the group of novel pyromellitimides and tetrachlorophthalimides provided as stated above which contain a



group, and are thus acidic compounds, can be converted to metal salts. Such metal salts are also provided by this invention.

The Useful Imides

There are two types of the stated imides which can be converted to metal salts. One type consists of the pyromellitimides and tetrachlorophthalimides provided by this invention which contain an —arylene-COOH radical. This type includes all of the tetrachlorophthalimides provided by this invention, and it also includes the pyromellitic diimides provided hereby in which at least

one of the imide nitrogen atoms is substituted by an —arylene-COOH radical. These pyromellitic diimides may be "symmetrical" having both N atoms substituted by —arylene-COOH radicals, or "asymmetrical," with one of the imide N atoms attached to an —arylene-COOH radical, and the other to a conjugated polycyclic radical. Imides of the stated type, containing an —arylene-COOH, will form salts in which the metal atom in the salt replaces the H of the —COOH group.

The other type of imide which can be converted to a metal salt in accordance with this invention consists of the pyromellitic mono-imides. These mono-imides include pyromellitic 1,2-imide, 4,5-anhydrides in which the imide nitrogen is substituted by an —arylene-COOH radical. The stated radical will form metal salts in which the metal atom in the salt replaces the H of the —COOH group, like the —arylene-COOH substituted imides discussed above.

Additionally, there is an anhydride group present in all of the mono-imides provided by this invention. The stated anhydride group contains a

group. Metal salts can also be formed from the pyromellitic 1,2-imide 4,5-anhydrides by reaction with this anhydride group. In this case, however, as will be obvious to those skilled in the art, the structure of the initial compound is altered by formation of the salt. The anhydride group is cleaved, forming usually, either two metal carboxylate radicals, or one carboxylic acid and one metal carboxylate radical. Since this alteration of the anhydride structure into a dicarboxylic structure occurs during salt formation, the metal salts formed are not, strictly speaking, salts of the anhydride. For this reason, the metal salts provided by this invention are referred to herein as metal salts "prepared from" the novel pyromellitimides and tetrachlorophthalimides provided hereby which contain a

group. By this is meant metal salts in which the metal replaces the cation attached to a carboxyl group, as occurs with —arylene-COOH groups, and also metal salts formed by cleaving an anhydride group to form at least one metal carboxylate group.

Preparation

While bases such as sodium hydroxide or the like are generally effective for the neutralization of organic acids such as benzoic acid in aqueous solution to form the salt of the acid, it is not possible to obtain the salts of this invention by treating the stated imides with such strongly basic metal derivatives. The imide ring is cleaved by the base. However, it has been found that such salts can be prepared by procedures which avoid the exposure of the stated acidic compounds to high alkalinity. This can be effected in various ways.

Where the imide is an —arylene-COOH substituted compound, the salt may be formed from the aminoarylene carboxylic acid before it is converted to the imide by reaction with pyromellitic dianhydride or tetrachlorophthalic anhydride.

Alternatively, the acidic imide compounds can be converted to corresponding metal salts by various techniques avoiding high alkalinity. For example, an aqueous ammoniacal solution of a heavy metal halide like zinc or cadmium chloride can be admixed with a solution of one of the presently provided compounds containing a

group in an organic solvent to provide the desired metal salt. It is not necessary that the solutions be mutually

miscible but that intimate contacting through vigorous agitation be effective in permitting reaction between the materials in each solution. This same type of technique can be applied with solid metal hydroxides of difficultly soluble metal compounds such as lead wherein the actual pH of the solution containing the imides does not rise above a value of 10. In addition to the ammoniacal salts of heavy metal compounds in the emulsion operation described above, other soluble salts can be used if desired. For example, many metals including light metals like Al and heavy metals like Cr have soluble acetate salts which can be dissolved in water and admixed with a coupling agent such as dioxane or ethylene glycol with an organic system such as dimethyl formamide solution of the above described acidic compounds. Isolation of the metal salts produced by the stated procedures can be effected by means usual in the art; generally, the metal salts will precipitate and can be removed from the mother liquor or mixture of two mother liquors by filtration.

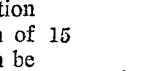
Another technique whereby hydrolysis of the imide can be avoided consists in utilizing an organic soluble metal compound such as a metal alcoholate wherein the metal is not sufficiently basic to destroy the imide system. For example, aluminum isopropylate can be used in an organic solvent in conjunction with the above stated acidic compounds to prepare a reaction product which may be considered to be an aluminum complex of the materials in question. It has been observed that aluminum complexes produced in this fashion have extraordinarily effective thickening properties. The reaction product apparently comprising an aluminum complex formed in the reaction with aluminum isopropylate is substantially different from the aluminum salt which is produced from aluminum acetate or other ionic forms of the metal. It is a much more potent thickener. This difference may possibly reside primarily in the physical structure of the aluminum alcoholate reaction product which makes it particularly desirable for the thickening action mentioned above. However, since it is not presently known with any certainty wherein these reaction products differ from aluminum salts produced by other techniques, except for the fact that they have such different and advantageous properties, these reaction products are not grouped with the salts considered in the present discussion, which are the simple metal salts prepared from the stated acidic compounds, but are considered as separate products, as further set forth hereinafter.

The Salts

The metal salts of the novel acids of this invention provided hereby include salts of these carboxylic acids with alkali metals, with alkaline earth metals, with heavy metals, with the transition metals, and so forth. The metal salts prepared from pyromellitimides in accordance with this invention have been found particularly useful as thickeners and, in some cases, stabilizers. Salts useful for this purpose include salts of both light metals, such as alkali (group I) metals, like sodium or lithium, and metals in higher groups of the periodic table, like aluminum, the rare earths, and so forth, as well as heavy metals such as cadmium, zinc, chromium and so forth. The salts of tetrachlorophthalimide derivatives provided by this invention can also be used as thickeners for lubricating compositions. Useful thickening can be achieved with a variety of such salts, including salts with both light and heavy metals. Additionally, it has been found that the tetrachlorophthalimide derivatives provided by this invention can be used advantageously to impart extreme pressure properties to oleaginous bases employed in lubricating compositions.

The heavy metal salts of the tetrachlorophthalimidoarylenecarboxylic acids are particularly useful members of the stated class of salts in this connection. Lubricating compositions comprising such salts have good load-carrying properties and minimal corrosivity even at high temperatures. Particularly preferred in this connection are heavy metals of group II of the periodic table, including mercury, cadmium, zinc, and of group IV, especially tin and lead. Alternatively, the selection depending on such considerations as the reactivity and availability of the metals, there may be employed salts of other heavy metals, such as those of group I, like copper, silver and so forth; of group III, like indium and thallium; of group IV, like thorium, antimony and bismuth; group V, like tungsten and tellurium; and of the transition elements, like iron, cobalt, nickel and so forth.

As will be appreciated by those skilled in the art, when a salt of a polyvalent metal is formed, the



radical of the acidic componnd may satisfy all or less than all of the valences of the metal. Both partial metal salts and metal salts fully substituted by carboxylic radicals are useful in the practice of the present invention. When the metal salt is formed in aqueous solution, for example, a basic salt may be produced in which one or more of the metal valences is satisfied by a hydroxide ion; other anions may alternatively be introduced if desired, although this will usually require additional manipulative steps without corresponding benefit. For practical purposes, in any case, anion radicals when present in the salts will usually be inorganic radicals and generally of relatively low molecular weight, as for example a halide ion such as chloride, bromide or fluoride ion, or an oxygen-containing radical such as hydroxide or carbonate, bicarbonate or sulfate.

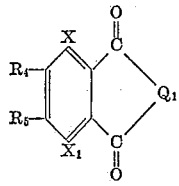
The presently provided metal salts accordingly include salts of N-carboxyaryl-substituted pyromellitic diimides such as, for example, the Li salt of N,N-bis(4-carboxyphenyl)pyromellitic diimide, the Ca salt of N,N'-bis(4-carboxy-2-naphthyl)pyromellitic diimide, the Al salt of N,N'-bis(4-carboxyphenyl)pyromellitic diimide, the Ti salt of N,N'-bis(4-carboxyphenyl)pyromellitic diimide, the Cr salt of N,N'-bis(4-carboxyphenyl)pyromellitic diimide, the Na salt of N,N'-bis(6-carboxy-1-anthraquinonyl)pyromellitic diimide, the Cd salt of N,N'-bis(4-carboxyphenyl)-3,6-dichloropyromellitic diimide, the Zn salt of N,N'-bis(4-carboxy-3-hydroxyphenyl)pyromellitic diimide, the basic Zn salt of N,N'-bis(4-carboxyphenyl) pyromellitic diimide, the Li salt of N-(4'-amino-2,3'-dichloro-4-biphenylyl) - N' - (4-carboxyphenyl)pyromellitic diimide, the Mg salt of N-naphthyl-N'-(4-carboxyphenyl) pyromellitic diimide, the La salt of N-(6-amino-4-(phenyl)-2-triazinyl)-N'-(3-carboxy-5-butyl-2-naphthyl)-3-chloropyromellitic diimide, and so forth. They will also include metal salts prepared from pyromellitic monoimides such as, for example, the Na salt prepared from N-1-naphthylpyromellitic 1,2-imide 4,5-anhydride, the Co salt prepared from N-(4-(phenylsulfonyl)phenyl)pyromellitic 1,2-imide 4,5-anhydride, the Pb salt prepared from N-(6-amino-4-(phenyl) - 2 - triazinyl)-3-chloropyromellitic 1,2-imide 4,5-anhydride, the Mg salt prepared from N-(4-carboxylphenyl)pyromellitic 1,2-imide 4,5-anhydride, the Al salt prepared from N-(4-carboxylphenyl) pyromellitic 1,2-imide, 4,5-anhydride, the Cd salt prepared from N-(5-carboxy-1-naphthaquinonyl)-3,6-dichloropyromellitic 1,2-imide 4,5-anhydride, and so forth. Additionally, they will include the metal salts of tetrachlorophthalimide derivatives which may be light metal derivatives such as the Na salt of N-(4-carboxyphenyl) tetrachlorophthalimide, the Li salt of N-(3-carboxy-1-naphthyl)tetrachlorophthalimide, the Mg salt of N-(4-carboxy-1-anthraquinonyl)tetrachlorophthalimide, the Sb salt of N-(4-carboxy(tetrachlorophenyl)tetrachlorophthalimide, the Ce salt of N-(3-carboxy-4-isopropylphenyl)tetrachlorophthalimide, and so forth; and particularly advantageously may be heavy metal derivatives of the tetrachlorophthalimide derivatives of the invention such as the Cd salt of N-(4-carboxyphenyl)tetrachloro-

phthalimide, the Zn salt of N-(4-carboxyphenyl)tetrachlorophthalimide, the Zn salt of N-(4-carboxy-3-hydroxy)tetrachlorophthalimide, the Sn salt of N-(4'-carboxy-4-biphenylyl)tetrachlorophthalimide, the Pb salt of N-(3-carboxy-2-naphthyl)tetrachlorophthalimide, the basic Zn salt of N-(4-carboxyphenyl)tetrachlorophthalimide, the Th salt of N-(4-carboxy-2-acetoxy-1-anthryl) tetrachlorophthalimide, the Cr salt of N-(6-carboxy-1-anthraquinonyl)tetrachlorophthalimide, the Co salt of N(4-carboxyphenyl)tetrachlorophthalimide, the Cd chloride salt of N-(3-carboxyphenyl)tetrachlorophthalimide, and so forth.

REACTION PRODUCTS

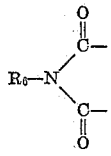
An additional class of novel compounds provided by this invention consists of the reaction products of an aluminum alcoholate with a compound of the formula

(II)



in which X and X_1 are selected from the group consisting of hydrogen and chlorine and

(1) When R_4 and R_5 are taken together, R_4 and R_5 together represent the radical



Q_1 is selected from the group consisting of O, N-arylene-COOH, and an N atom substituted by a polycyclic conjugated radical, and R_6 is —arylene-COOH when Q is an N atom substituted by a polycyclic conjugated radical, while R_6 is selected from the group consisting of —arylene-COOH and conjugated polycyclic radicals when Q is O or N-arylene-COOH; and

(2) When R_4 and R_5 are taken separately, R_4 and R_5 are selected from the group consisting of hydrogen and chlorine, and Q_1 is —N-arylene-COOH.

The compounds represented by the stated formula are acidic compounds containing a



group. They include the novel pyromellitimides and tetrachlorophthalimides of this invention, containing a



group, which form metal salts as discussed hereinabove; and also phthalimido- and chlorinated phthalimidoarylene-carboxylic acids, as discussed hereinafter.

The stated reaction products form a particularly preferred embodiment of this invention. They are uniquely effective thickeners for lubricating compositions. Lubricating compositions comprising an oleaginous base and such reaction products are greases of outstanding resistance to extreme conditions, especially high temperatures over the range of from about —65° F. to above 500° F., where thickeners used to form greases hitherto become unsatisfactory. Moreover, some of these reaction products, especially those containing the tetrachlorophthalimide structure, are particularly good extreme pressure agents.

As mentioned above, it has been found that the stated reaction of an aluminum alcoholate with compounds conforming to the formula stated above produces a reaction product which differs in properties from metal salts produced in other ways. Thus for example, reaction of N,N'-bis(4-carboxyphenyl)pyromellitic diimide with aluminum isopropylate produces a reaction product which effectively thickens an oleaginous base to a grease in concentrations as low as 5–20% by weight. The novel nature of this reaction product is demonstrated by contrast thereof to aluminum salts of the same acid produced in other ways, such as by the reaction of the aluminum salt of 4-aminobenzoic acid with pyromellitic dianhydride, or by the reaction of N,N'-bis(4-carboxyphenyl) pyromellitic diimide with aluminum acetate. The salts produced by the latter procedures, used in the same amounts as the stated reaction product, do not have a comparable thickening effect.

Preparation

To prepare the stated reaction products, an acidic imide compound of the formula stated above is reacted with an aluminum alcoholate. For the present purposes, alcoholates of lower alkanols, containing from 1 to 6 carbon atoms, are preferred. Illustrative of such alcoholates are aluminum methylate, aluminum ethylate, aluminum propylate, aluminum isopropylate, aluminum butylate, aluminum amylate, aluminum hexylate, and so forth. Aluminum isopropylate forms the preferred reactant for this preparation. This alcoholate of aluminum is commercially available.

Some of the acidic compounds of the formula given above, which may be used to prepare the novel reaction products of this invention, and specifically the pyromellitic imides and tetrachlorophthalimidoarylenecarboxylic acids conforming to this formula, are novel compounds provided by this invention as described hereinabove. The useful compounds among the pyromellitimides provided by this invention are those containing a



group, as discussed above in connection with the metal salts of such compounds provided hereby. Reference is made to the preceding description for a discussion of these acidic pyromellitimides and tetrachlorophthalimides and lists of illustrative acidic compounds of these types.

Additionally useful for the preparation of the present reaction products and included among compounds of the stated formula are phthalimidoarylenecarboxylic acids and chlorinated phthalimidoarylenecarboxylic acids. The arylenecarboxylic radicals in such phthalimide derivatives will conform to the same description as that of such radicals in the pyromellitimide and tetrachlorophthalimide derivatives provided by this invention for which reference may be made to the discussion hereinabove. Illustrative of this class of reactants are

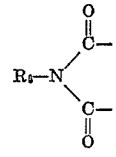
N-(4-carboxyphenyl)phthalimide,
N-(3-carboxyphenyl)phthalimide,
N-(4-carboxy-2-tert-butylphenyl)phthalimide,
N-(4-carboxy-1-naphthyl)phthalimide,
N-(3-carboxy-5-acetyl-1-phenanthryl)phthalimide,
N-(4-carboxy-1-anthraquinonyl)phthalimide,
N-(4'-carboxy-3-methoxy-4-biphenylyl)phthalimide,
N-(4-carboxy-3-hydroxyphenyl)phthalimide,
N-(4-carboxy-5-chloro-1-naphthyl)phthalimide,
N-(4-carboxyphenyl)-3-chlorophthalimide,
N-(4-carboxy-4-biphenyl)-3-chlorophthalimide,
N-(4-carboxy-1-naphthyl)-3,4-dichlorophthalimide,
N-(4-carboxy-3-isopropylphenyl)-3,4,5-trichlorophthalimide,
N-(4-carboxy-3-hydroxyphenyl)-3-chlorophthalimide,
N-(4-carboxy-3-(pentachlorophenyl)phenyl)-3,6-dichlorophthalimide,
N-(4-carboxyphenyl)-3,6-dichlorophthalimide,

and the like.

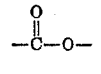
Some of these carboxylic acids such as N-(4-carboxyphenyl)phthalimide are known compounds. The others can be prepared by procedures analogous to the known

preparative methods for such phthalimidoarylenecarboxylic acids. For the preparation of the lubricating compositions provided by the present invention, their preparation, for example by condensation of an aminobenzoic acid with phthalic anhydride, will preferably be effected in a reaction medium comprising the oleaginous base which is to form a component of the lubricating composition. Thus for example, phthalic anhydride may be intimately mixed with p-aminobenzoic acid and the intimate mixture added to an oleaginous base which is at an elevated temperature such as about 350° F. to produce rapid formation of N-(4-carboxyphenyl)phthalimide. The resulting imido carboxylic acid may then be converted to the reaction product thereof with an aluminum alcoholate in accordance with this invention, still employing the oleaginous base as the reaction medium. The oleaginous base is thus thickened to a grease as the novel reaction product producing the thickening effect is formed within it, and losses inherent in separation and handling of the product are avoided.

A mixture of any two or more of the acidic compounds of the formula given above may be used to prepare the present reaction products. Particularly contemplated in this connection is a mixture of (1) at least one pyromellitimide compound of the stated formula, in which R_4 and R_5 are then taken together to represent the radical

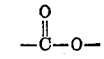


(where R_6 has the meaning stated above); and (2) at least one phthalimide compound of the said formula, in which R_4 and R_5 are then taken separately to represent hydrogen. It has been found that use of such a mixture has advantages in connection with use of the present reaction products in the lubricating compositions of this invention. The resulting compositions exhibit the outstandingly good mechanical and heat stability characteristic of these reaction products derived from the pyromellitimide derivatives, while the inclusion of the reaction product derived from a phthalimidoarylenecarboxylic acid improves the storage stability of the composition. By inclusion of a tetrachlorophthalimidoarylenecarboxylic acid in the mixture of imides containing



groups reacted with the aluminum alcoholate, extreme pressure properties can also be conferred on the reaction product. Thus for example, a mixed reaction product which is a potent thickener and produces particularly useful greases can be produced by reacting aluminum isopropylate with a mixture of N,N'-bis(4-carboxyphenyl)pyromellitic diimide, N-(4-carboxyphenyl)phthalimide and N-(4-carboxyphenyl)tetrachlorophthalimide. The tetrachlorophthalimide derivative can if desired be omitted, or it may be converted to a reaction product in accordance with the invention separately, and the reaction product admixed with the mixed reaction product of the pyromellitimide and phthalimide derivatives with substantially equally good results.

The preparation of the reaction products of the invention is effected by contacting the aluminum alcoholate such as aluminum triisopropylate, with the selected acidic compound of the formula given above, or a mixture of such acidic compounds. The proportions in which these reactants will be combined will vary with the number of carboxyl groups present per mole of the acidic compound. In general, the aluminum alcoholate appears to be consumed in a ratio of one mole of the alcoholate per three mols of

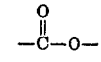


groups. Thus, the molar ratio of the aluminum alcoholate to a monocarboxylic acid compound such as N-(4-carboxyphenyl)phthalimide will be 1:3. Correspondingly greater quantities of the alcoholate are consumed in reaction with a pyromellitic diimide derivative containing two carboxylic acid radicals: thus for example, 1.5 moles of aluminum isopropylate are consumed per mole of N,N'-bis(4-carboxyphenyl)pyromellitic diimide in forming the present reaction products. As will be well understood by those skilled in the art, the anhydride group in the pyromellitic mono-imides which may be used in the practice of this invention in effect contains two



groups, and may accordingly consume ⅔ of a mol of the alcoholate.

Moreover, the molar ratios of the reactants may if desired vary from the stated ratios. Generally this will not affect the course of the reaction, but merely lead to the presence of unreacted ingredients at the end of the reaction. This may be desirable. Thus for example, presently useful pyromellitimide and tetrachlorophthalimide derivatives themselves may contribute useful properties to lubricating compositions, as disclosed above. Use of an excess of such compounds as compared to aluminum alcoholate may accordingly be advantageous. It may also be advantageous in ensuring complete reaction of the aluminum alcoholate, since it has been observed that unreacted aluminum alcoholate may react with certain oleaginous bases, particularly silicone fluids, at high temperatures, leading to an undesirable change in the properties of lubricating compositions comprising such an oleaginous base. On the other hand, with certain compounds, it may be beneficial to use the aluminum alcoholate in excess. When an —arylene-COOH radical contains a hydroxy group ortho to the carboxyl group, for example, sufficient aluminum alcoholate may be used to react with this hydroxy group in addition to the carboxy group. Usually, however, with most of the present reactants, it will be preferable to employ a ratio supplying one aluminum molecule to each three



groups.

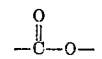
Preparation of the reaction products provided by this invention in a reaction medium comprising an oleaginous base provides the lubricating compositions of this invention in a particularly direct and simple manner. Sometimes better thickening action is obtained by such preparation in the base. Alternatively the reaction medium may comprise other solvents or diluents such as a hydrocarbon like xylene, an ether like heptyl glycol ether or dioxane, an amide like dimethylformamide and so forth.

The reaction mixture consisting of the aluminum alcoholate, the selected acidic imide derivative and the reaction medium will generally be heated to accelerate the formation of the reaction product. Reaction temperatures as low as about 100° F. may be used but generally the temperature employed will be at least about 350° F. It may be as high as 600° F. Occurrence of formation of the reaction product is characterized by release of the alcohol moiety of the aluminum alcoholate. Generally, the preferred temperature range for producing the reaction product will be from about 400° F. to about 500° F., but it is to be realized that the optimum temperature

for conducting the reaction will vary with variation in the type of the reactants.

When the reaction is carried out in a solvent or diluent and it is desired to separate the product and isolate it as such, this may be effected by means usual in the art such as distillation, extraction, precipitation of similar means. The solvent or diluent and any unreacted reactants may then be recycled for further reaction and the process may be operated as a batch or continuous method. Where the reaction product is formed in an oleaginous base, the product may remain suspended in the oleaginous fluid, usually thickening it to a grease consistency. When a grease is prepared in this fashion, the reaction mixture comprising a lubricating composition as provided by this invention will generally then be milled before use, to further the homogeneous distribution of the salt in the oleaginous fluid.

The reaction products produced by the above-described procedure, as noted above, are complex substances the nature of which is not fully understood. They are accordingly characterized herein by reference to their method of preparation. It is to be appreciated that the reaction products as provided by this invention include the products of reaction of an aluminum alcoholate, and particularly aluminum isopropylate, with any of the various pyromellitimide, tetrachlorophthalimide and phthalimide derivatives containing



groups within the scope of the formula stated above, and with mixtures thereof, as well as mixtures of such reaction products.

LUBRICATING COMPOSITIONS

Coming now to the lubricating compositions of this invention, these are compositions comprising an oleaginous base and one or more of the novel products provided by this invention. The preferred method of preparing such compositions is by preparation of the stated products in the oleaginous base, as noted hereinabove.

After the product has been introduced into the oleaginous base, the composition is preferably heated for 1–20 hours at an elevated temperature of about 400–500° F. This treatment is believed to effect completion of reaction and removal of volatiles. The lubricating composition will then desirably be milled or homogenized.

Many of the products provided by this invention can be used advantageously to thicken oleaginous bases, providing greases. Compositions wherein the presently provided products are used for this purpose will contain an amount of the product effective to provide the required degree of thickening.

The thickening powers of the individual products differ, and the effectiveness of a given product varies with a change in the nature of the oleaginous base. Generally, thickened lubricating compositions as provided by this invention will comprise from about 5% to about 70% by weight of one or more of the products of this invention. Concentrates are sometimes made, and these may contain even higher concentration. Usually from about 10% to about 50% of the weight of finished greases will consist of the thickener.

Where the products of this invention are used for other purposes, such as to impart extreme pressure properties to an oleaginous base, somewhat different proportions may be preferred. For example, an extreme pressure lubricating composition may comprise from about 0.05% to about 30%, and preferably 0.1% to 20% by weight of the product. Where one of the present products is employed in the oleaginous base to inhibit its oxidative and thermal degradation, again the amount to be used will vary over a fairly wide range depending on the individual product selected, the nature of the oleaginous base, and the severity of the operating conditions under which the lubricant composition is to be used in service.

The oleaginous base used in the compositions may be selected from a wide variety of natural or synthetic lubricants. Thus for example, natural oils can advantageously be employed. Illustrative of such natural oleaginous bases are mineral oils such as naphthene and paraffin base oils, vegetable oils such as cotton seed oil and castor oil; animal and marine oils such as sperm whale oil, lard oil, blown fish oil and degras; and mixtures thereof. Of the natural oil bases, mineral oils are preferred. A typical mineral oil base for extreme pressure lubrication will be characterized by a viscosity of 35–350 Saybolt Universal seconds at 210° F., a viscosity index in the range of from −25 to 150, and a flash point of between about 275 and 600° F.

Polyorganosiloxanes, also known as silicones, or silicone polymers, comprise one class of synthetic lubricant bases of commercial importance which may be improved in properties to a substantial degree by modification in accordance with this invention. Polysiloxanes are compounds comprising essentially silicon atoms connected to one another by oxygen atoms. In liquid polyorganosiloxanes, or silicones, of the lubricating oil viscosity range, a preponderant number of the remaining valences of the silicon atoms are satisfied by the substitution thereon of organic radicals, attached by a carbon-to-silicon bond. Examples of such organic radicals are aliphatic radicals including alkyl radicals such as methyl, ethyl, propyl, butyl, and so forth; alicyclic radicals such as phenyl, cyclohexyl, diphenyl, anthracyl, naphthyl, and so forth; aralkyl radicals such as benzyl and alkaryl radicals such as tolyl, xylyl, and so forth; and the like. Relatively common oils of this type are dimethylsilicone polymer, phenylmethylsilicone polymer, chlorophenylmethylsilicone polymer, and so forth. Of particular utility for lubricating purposes are silicones in which the silicon atoms are substituted by two different organic radicals, e.g., methyl and phenyl radicals. Especially effective properties have been obtained when the organic radicals substituted on the silicon atoms in the silicone polymers are in turn substituted by halogen atoms, especially chlorine atoms. Thus for example, the silicone may be substituted by chlorophenyl radicals such as dichlorophenyl, trichlorophenyl and tetrachlorophenyl radicals, other valences of the silicon atoms being satisfied by the hydrocarbon radicals such as methyl radicals or the like. As is well known in the art, the silicones intended for use as oleaginous bases will desirably contain an average of from 1.9 to 2.67 organic groups per silicon atom. Remaining valences, if any, of the silicon atoms may be satisfied by radicals attached to the silicon atoms in the compounds from which the silicone polymers are prepared, such as hydrolyzable organo-substituted silanes; or by the product of hydrolysis of such radicals, such as hydroxide radicals.

Another class of synthetic oleaginous bases of particular interest in the practice of the present invention comprises organic polyesters. On the one hand, these may comprise esters of polycarboxylic acids, such as dicarboxylic acid diesters. Thus for example, such synthetic ester lubricants may have the general formula

$$R(COOR_1)(COOR_2)$$

where R is an aliphatic or cycloaliphatic hydrocarbon radical of from 2 to 8 carbon atoms and R_1 and R_2 are the same or different and are branched chain alkyl or alkyl-substituted cycloalkyl radicals of at least 4 carbon atoms. Such esters may be derived from succinic, maleic, pyrotartaric, glutaric, adipic, pimelic, suberic, azelaic, sebacic, pinic, thiopropionic or oxypropionic acids or the like, specific esters of this nature including for example di(1-methyl-4-ethyloctyl)glutarate, di(2-ethylhexyl)oxydibutyric acid, di(2 - ethylhexyl)adipate, di(3- methylbutyl)azelate, di(2-ethylhexyl)azelate, di(2-ethylhexyl)-

sebacate, di(3,5,5-trimethylhexyl)sebacate, di(2-ethylhexyl)maleate, di(methylcyclohexyl)adipate, 2-ethylhexyl 1-methylhexyl sebacate and the like. Alternatively, instead of derivation from a polycarboxylic acid, the polyester synthetic oleaginous bases may be produced by reacting a polyhydric alcohol with a monocarboxylic acid. Thus for example, a polyhydric alcohol such as ethylene glycol or pentaerythritol is esterified with an acid of relatively long chain length such as caproic, pelargonic, capric, lauric, myristic, palmitic or stearic acid, to produce a polyester of lubricating oil viscosity. Specific examples of such polyesters derived from polyols are pentaerythritol tetrapelargonate, pentaerythritol tetracaprate, pentaerythritol tetrapalmitate, pentaerythritol tetrastearate, ethylene glycol divalerate, diethylene glycol dicaprate, propylene glycol dicaprylate, and so forth. Another type of synthetic polyester lubricants which may be used as oleaginous bases in accordance with this invention will be complex esters obtained by esterifying a polycarboxylic acid with a diol, together with a monohydric alcohol and/or a monocarboxylic acid. Thus, complex esters which may be employed as oleaginous bases may be obtained by esterifying one mole of a dicarboxylic acid with 2 moles of a glycol and 2 moles of a monocarboxylic acid; or by esterifying one mole of a dicarboxylic acid with one mole each of a glycol, a monocarboxylic acid and a monohydric alcohol. Specific examples of a suitable complex ester are the ester prepared from one mole of ethylene glycol, two moles of sebacic acid and two moles of 2-ethylhexanol; and the ester prepared from one mole of triethylene glycol, one mole of adipic acid, one mole of n-caproic acid and one mole of 2-ethylhexanol.

In addition to the above-mentioned classes of synthetic lubricating base stocks comprising types of present major commercial importance, there are a number of other oleaginous bases which can be used if desired in the practice of this invention. Thus for example, such lubricant bases may comprise hydrocarbon oils prepared by polymerization of unsaturated hydrocarbons. Polyethers of the nature of high molecular weight polyoxyalkylene compounds, derived for example from ethylene oxide, propylene oxide and the like substances, form another useful class of lubricant bases, and similarly, there may be employed oleaginous bases of related structure, such as propylene oxide-tetrahydrofuran copolymers, and polyaryl ethers. Besides the silicones discussed above, additional silicon derivatives of interest in this connection comprise silanes, silphenylenes, organosilicates and disiloxanes such as hexaalkoxydisiloxanes of lubricating oil viscosity. Other synthetic oleaginous bases which may be mentioned include fluorocarbon oils such as perfluorinated petroleum oils; tetra-substituted ureas; and esters such as dimethylcyclohexyl phthalate, trioctyl phosphate; and similar fluids adapted for lubricant applications.

Mixtures of oleaginous bases may sometimes be preferred to any single lubricant fluid, and are included in the scope of this invention.

The compositions of this invention may also comprise other property-modifying components which supplement or complement the effect of the present salts, such as antioxidants, structure stabilizers or viscosity improvers, extreme pressure additives, thickeners or the like.

Extreme pressure additives particularly preferred for use in lubricating compositions prepared in accordance with this invention comprise pentachlorophenylmercapto compounds selected from the class consisting of pentachlorobenzenethiol, heavy metal salts of pentachlorobenzenethiol such as the zinc salt, pentachlorophenylmercaptoacetic acid, heavy metal salts of the stated acid such as the cadmium or zinc salt, and esters of pentachlorophenylmercaptoacetic acid. The stated extreme pressure agents are particularly effective in imparting very high load-carrying properties over wide temperature ranges to synthetic oleaginous bases, as further described in the copending application of the present inventors, assigned to the same assignee as the present invention, Ser. No. 763,832, filed September 29, 1958. As noted hereinabove, certain of the presently provided products and especially the presently provided heavy metal salts and reaction products of tetrachlorophthalimidoarylenecarboxylic acids, are also useful as extreme pressure agents. Other extreme pressure agents known to the art may alternatively be employed in the compositions of this invention if desired.

Lubricating compositions including compositions as provided by this invention may also advantageously comprise stabilizers, antioxidants and the like. As antioxidants, there may be used for example an alkylphenol such as 2,4,6-trimethylphenol, pentamethylphenol, 2,4,6-tri-tert-butylphenol and the like, and aminophenol such as benzylaminophenol, an amine such as dibutylphenylenediamine, diphenylamine, phenyl-β-naphthylamine, phenathiazine, dinaphthylamine and so forth, or a metal salt such as iron octoate and so forth. Stabilizers which tend to preserve the desired properties of the greases may also be included in the compositions. Such stabilizers may comprise, for example, α-aminoanthraquinone, benzanthracene, fluoroanthene, α-naphthylamine, N,N'-dinaphthylphenylenediamine, benzoguanamine, di-tert-butylhydroquinone, quinazarine and Indanthrene blue, as well as inorganic materials such as mica, graphite, glass fibers and silica. Certain of the compounds provided by this invention such as certain pyromellitic imides like N-(6-amino-4-phenyl-2-triazinyl) and N-anthraquinone derivatives are stabilizers, limiting the effects of thermal degradation, for example, and may be included in lubricating compositions for this purpose in accordance with this invention.

While other thickeners for lubricating compositions cannot match the high temperature stability of the presently provided products, it may sometimes be advantageous to introduce thickeners of types known in the art hitherto into lubricating compositions comprising the products of this invention, as for example, where such products are employed as extreme pressure additives. Thickeners which may be used in such case may comprise, for example, a soap such as the lithium salt of hydroxystearic acid; a silica material such as an aerogel; a ureide, urethane or the like such as a ureide prepared by reacting a diisocyanate such as tolylene diisocyanate with an amine such as aniline, p-chloraniline, or a mixture of the two; and so forth.

Other components which may similarly be employed in lubricating compositions comprising the novel products of this invention will be readily obvious to those skilled in the art.

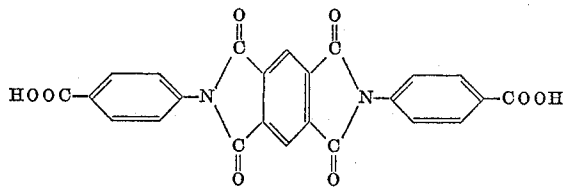
The invention is illustrated but not limited by the following examples, in which all parts are by weight:

EXAMPLE I

This example illustrates the preparation of a pyromellitic bis(imidoarylenecarboxylic acid) comprising N,N'-bis(4-carboxyphenyl)pyromellitic diimide.

Reaction temperatures ranging from 266° to 392° F. are achieved by using as reaction media xylene, dimethylformamide singly and in combination with various ratios of xylene, and heptyl glycol ether. Pyromellitic dianhydride and p-aminobenzoic acid, in a molar ratio of 1:2, are dissolved or dispersed in these reaction media. The starting materials are soluble in the solvents except for xylene. The reaction mixtures are then raised to reflux temperature, whereupon the escape of water vapor and exotherming are observed. The reaction products precipitate out and are filtered from the reaction mixture. The analysis of representative samples prepared (*a*) in dimethylformamide and (*b*) in heptyl glycol ether is given below; the analysis corresponds to that calculated

for N,N'-bis(4 - carboxyphenyl)pyromellitic diimide ($C_{24}H_{12}O_8N$) of the formula:



	Calculated for $C_{24}H_{12}O_8N$	Found (a)	Found (b)
C, percent	63.16	62.86	62.56
H, percent	2.64	2.96	2.85
O, percent	28.05	27.95	27.90
N, percent	6.13	5.99	6.11

N,N'-bis(4-carboxyphenyl) pyromellitic diimide melts above 1100° F. and is insoluble in high-boiling solvents of polar and non-polar nature.

EXAMPLES II–V

These examples illustrate the preparation of N,N-bis-(4-carboxyphenyl)pyromellitic diimide in oleaginous bases, providing lubricating compositions comprising this compound.

The oleaginous bases serving as reaction media for the condensation of the pyromellitic acid dianhydride with the p-aminobenzoic acid are as follows:

II. A polymethylphenyl silicone supplied by Dow Chemical Co., Midland, Michigan; viscosity 50 cs. at 210° F., 300 cs. at 100° F., ASTM slope 0.41; 1.9% evaporation loss in 22 hours at 400° F., ASTM cell; freezes —8° F.; flash point 575° F.; identified as DC–710.

III. A polyester in the lubricant viscosity range supplied by Emery Industries, Inc., Cincinnati, Ohio, and reputed to be an aliphatic acid derivative of a neopentyl alcohol; viscosity 8.54 cs. at 210° F., 15.15 cs. at 100° F.; evaporation loss 9.0% in 22 hours at 400° F., ASTM cell; pour point —42° F.; flash point 565° F.; fire point 615° F.; identified as polyester 3168R.

IV. A polyester in the lubricant viscosity range supplied by Emery Industries, Inc., Cincinnati, Ohio, and reputed to be an aliphatic acid derivative of a neopentyl alcohol; viscosity 20.9 cs. at 210° F., 199.0 cs. at 100° F.; volatility at 300° F., 0.12% after 6 hours, 0.24% after 24 hours and 0.40% after 48 hours; pour point —13° F.; cloud point —10° F.; flash point 605° F.; fire point 690° F.; acid number 0.08; identified as polyester 3170R.

V. A heavy mineral oil characterized by a viscosity of 1750 Saybolt Universal seconds (SSU) at 100° F.; 38 cs. at 210° F., 400 cs. at 100° F.; ASTM slope 0.54; pour point +30° F.; flash point 545° F.; fire point 610° F.

Pyromellitic acid dianhydride in each case is dispersed in the base fluid and p-amino benzoic acid added in small portions at 360° F., in an amount to provide 2 moles of the amino compound per mole of the pyromellitic dianhydride. The exothermic reaction proceeds very rapidly as indicated by the escape of water vapor and the rapid rise of temperature. On completion of the reaction, the neutralization number of the mixtures indicates the formation of the diimide. The products are rather thin greases which do not change in consistency upon milling.

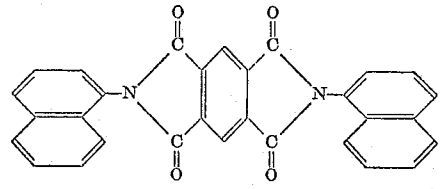
By using procedures substantially as described in the foregoing Examples I–V, N,N'-bis(carboxyarylene)pyromellitic diimides in which the arylene radical is polycyclic and in which the arylene radical bears non-interfering substituents, and lubricating compositions comprising the same in thickening amounts, are prepared by reacting pyromellitic dianhydride with p-aminosalicylic acid to provide N,N'-bis(4-carboxy-3-hydroxyphenyl(pyromellitic diimide; with 2-aminonaphthalene-3-carboxylic acid to provide N,N'-bis(3-carboxy-2-naphthyl)pyromellitic diimide; and with 1-aminoanthraquinone-6-carboxylic acid to provide N,N'-bis(6-carboxy-1-anthraquinonyl)pyromellitic diimide. Illustrative condensations of these reactants to provide imidoarylenecarboxylic acids are described in subsequent examples.

An N-(carboxyarylene)pyromellitic 1,2-imide 4,5-anhydride is provided by reacting pyromellitic dianhydride in a 1:1 molar ratio with an aminoarylenecarboxylic acid such as, for example, p-aminobenzoic acid, to produce N-(4-carboxyphenyl)pyromellitic 1,2-imide 4,5-anhydride.

EXAMPLE VI

This example illustrates the preparation of a N,N'-dihydrocarbyl pyromellitic diimide, and a grease-like lubricating composition comprising the same.

Pyromellitic dianhydride and α-naphthylamine, in a 1:2 molar ratio, in an amount calculated to give 50% thickener, are reacted in the silicone oleaginous base employed in Example II at 230° C. The initial reaction product comprising N,N'-di-α-naphthylpyromellitic diimide of the formula:



is a thick grease, which is cooled, milled, and tested.

A substantially similar procedure may be followed to produce N,N-di-α-naphthyl-3,6-dichloropyromellitic diimide in thickening amounts in an oleaginous base.

EXAMPLE VII

This example illustrates test procedures used in measuring properties of the lubricating compositions of this invention.

Penetration determinations are made according to ASTM method D–217–48 using the Shell micro cone and cup. The Shell micro cone and shaft weight 58.3 g. as compared to the weight of 150 g. for the ASTM cone and shaft. The following table presents a relationship between the values obtained for worked penetration using the ASTM versus the Shell cone.

ASTM Cone	Shell Cone
355–385	220
310–340	155–195
265–295	115–145
220–250	80–105

Heat stability of the lubricant compositions is measured by heating the grease sample for 16 hours at 500° F., or, in some cases, for 20 hours at 600° F., in a covered beaker.

The ASTM micropenetration of the N,N'-di-α-naphthylpyromellitic diimide thickened grease of Example VI is approximately 320. The grease is stable after 20 hours heating at 600° F.

EXAMPLES VIII–X

These examples illustrate the preparation of a N,N'-disubstituted pyromellitic diimide wherein the N substituents are oxo-substituted conjugated polycyclic radicals, providing thickened lubricating compositions.

The oleaginous base fluids used in these samples as reaction media are as follows:

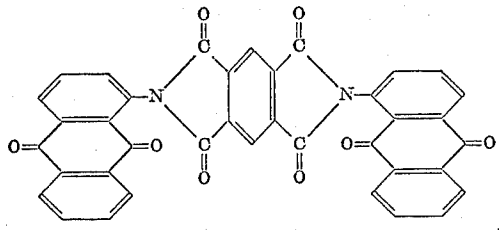
VIII. The polymethylphenylsilicone fluid of Example II.

IX. The polyester fluid of Example III.

X. A light mineral oil with a viscosity of 100 SSU at 100° F., 38 SSU at 210° F.

In each case, 44.6 parts of α-aminoanthraquinone dispersed in 90 parts of the oleaginous base fluid are reacted with 21.8 parts by weight of pyromellitic dianhydride (2:1

molar ratio) at 200° C. A heating period of 45 minutes produces a thickened product of grease-like consistency, consisting of a lubricating composition comprising 41% by weight of N,N'-bis(α-anthraquinonyl)pyromellitic diimide of the formula:



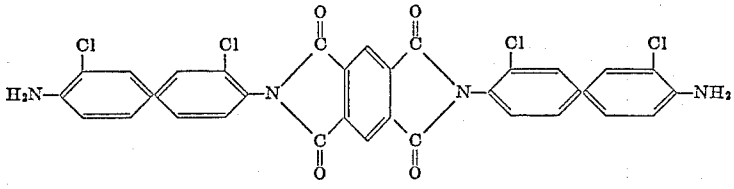
The greases have the following ASTM penetrations values:

VIII. Unworked	335
IX. Unworked	324
Worked, 60 strokes	>360
X. Unworked	282
Worked, 60 strokes	>360

EXAMPLE XI

This example illustrates another preparation of another N,N'-disubstituted pyromellitic diimide in which the N substituents are polycyclic conjugated radicals carrying non-interfering substituents, providing a lubricating composition comprising the same.

A lubricating composition comprising 42% by weight of N,N' - bis(4'-amino-2,3'-dichloro-4-biphenylyl)pyromellitic diimide of the formula:



is prepared, by slowly adding 68.7 parts of 3,3'-dichloro-4,4'-diphenyldiamine to a suspension of 65.4 parts of pyromellitic dianhydride in 178 parts of the oleaginous fluid of Example II, containing 0.4 part of fluoranthene, heated to 200° C. The resulting slightly grainy slurry is heated at 260° C. for 16 hours, cooled, milled and tested. It has an (unworked) ASTM penetration of 350; after 4 hours in the Shell roller at room temperature, this value remains unchanged.

The Shell roller is used to test the mechanical stability of greases as described in a National Lubricating Grease Institute publication.

As will be noted upon a consideration of the foregoing formula, the second amino group of a diamine condensed with the pyromellitic dianhydride apparently remains unreacted. When pyromellitic dianhydride is reacted in a 1:1 molar ratio with a diamine comprising 4,4'-diaminodiphenyl sulfone, as described in a subsequent example, the product is found to be N-(4-(4'-aminophenylsulfonyl)phenyl)pyromellitic 1,2-imide 4,5-anhydride, the second amino group of the amine reactant similarly remaining unreacted, to provide a pyromellitic mono-imide as comprised in the scope of this invention.

EXAMPLE XII

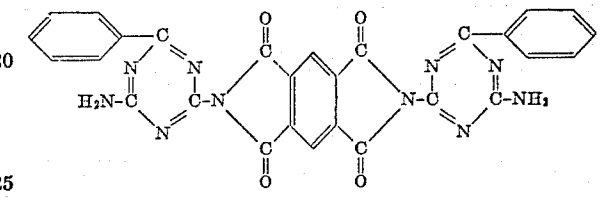
This example illustrates the preparation of still another pyromellitic diimide in which each imide nitrogen is substituted by a polycyclic conjugated radical bearing non-interfering substituents; and of a lubricating composition comprising the same.

The oleaginous base in which this preparation is conducted is a mixture of two base fluids:

(1) A polymethylphenylsilicone base fluid characterized by a kinematic viscosity of 11.8 cs. at 210° F. and 33.2 cs. at 100° F.; pour point —85° F.; flash point 535° F.; supplied by Dow Chemical Co., and identified by the supplier as DC 4039.

(2) A chlorinated polymethylphenylsilicone supplied by General Electric Co., Schenectady, N.Y.; kinematic viscosity 22.8 cs. at 200° F., 61.6 cs. at 100° F.; 0.85% evaporation loss in 6.5 hours at 400° F., ASTM cell; flash point 525° F., fire point 650° F.; identified as GE 81406 and also known as Versilube F–50.

To prepare the pyromellitic diimide of this example, 74 parts of pyromellitic dianhydride are added to a mixture of 175 parts each of the two stated base fluids at 160° C. Then 127 parts of benzoguanamine are introduced over a 50 minute period at 200° C. The reaction mixture is then held at 200–250° C. for 1½ hours, and finally cooled to produce a grease-like lubricant comprising N,N - bis(6 - amino - 4 - (phenyl) - 2 - triazinyl)-pyromellitic diimide of the structure:

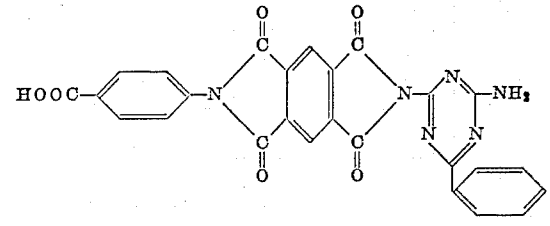


When the lubricant composition prepared as described above is heated for 16 hours at 500° F., the weight loss is only 4%. The concurrent lack of degradation products, as evidenced by the absence of color-bodies indicates this material to be suitable for high temperature applications.

EXAMPLE XIII

This example illustrates the preparation of a N,N'-disubstituted pyromellitic diimide in which the substituents on the two nitrogen atoms are different, and a lubricating composition comprising the same.

To 43.6 parts by weight of pyromellitic dianhydride dispersed in 186 parts of the silicone base fluid of Example II at 200° C. is added 37.4 parts of benzoguanamine and 27.4 parts of p-aminobenzoic acid. An exothermic reaction occurs, and the mixture thickens considerably, forming a grease containing a 35% concentration of N - (4 - carboxyphenyl) - N' - (6 - amino - 4 - phenyl - 2-triazinyl)pyromellitimide of the structure:



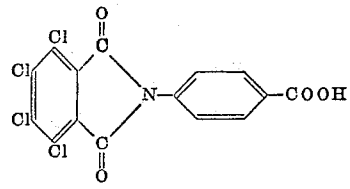
The ASTM penetration of the resultant grease is 335, which becomes 295 upon subsequent heating for 16 hours at 400° F. After 4 hours in the Shell roller, the ASTM penetration is 360. No change in color or consistency is noticeable after 16 hours at 500° F., showing the utility of this compound as a degradation inhibitor. The dropping point of the grease is 628° F.

EXAMPLE XIV

This example describes the preparation of an N-(carboxyaryl)tetrachlorophthalimide.

A solution of 286 parts of tetrachlorophthalic anhy-

dride and 137 parts of p-aminobenzoic acid in a mixture of 1620 parts of xylene and 1380 parts of a high flash petroleum naphtha is refluxed for 6 hours at 147° C. A yield is obtained of 380 parts of N-(4-carboxyphenyl)-tetrachlorophthalimide, of the structure:



This novel compound has a melting point of 363–367° C. Heating this material for 2 hours at 370° C. produces no measurable decomposition, demonstrating its utility for compositions to be used at such temperatures. This arylenecarboxylic acid can be used as a thickener and extreme pressure additive for lubricating compositions. It is particularly useful for the preparation of salts and reaction products as described hereinafter.

This N-(carboxyphenyl)tetrachlorophthalimide and other N-(carboxyaryl)tetrachlorophthalimides provided by this invention can also be prepared in a reaction medium comprising an oleaginous base, to form a lubricating composition, as appears in a subsequent example.

EXAMPLE XV

This example illustrates preparation of a salt of one of the novel imides of this invention, and a lubricating composition comprising the same.

Twenty parts of N-(4-carboxyphenyl)tetrachlorophthalimide are dissolved in a mixture of 450 parts of dioxane and 100 parts of dimethyl formamide. A solution of 4.6 parts of cadmium chloride in 15 parts of water and 25 parts concentrated ammonium hydroxide is added to the dioxane solution over a forty minute period. The resulting precipitate is filtered and worked with water to produce about 15 parts of the cadmium salt of N-(4-carboxyphenyl)tetrachlorophthalimide.

The heat stability of this Cd salt is excellent, and it has valuable extreme pressure properties. Thus, for example, a grease prepared as described in Example XVII has a mean hertz load of 19. Addition of 6% of the Cd salt identified above increases the mean hertz load of the grease to 55.

The mean hertz load is a measure of the extreme pressure properties of a lubricant. It is measured as described in Federal Standard VVL–791, Method 6503. A mean hertz load of 55 is a high rating.

EXAMPLE XVI

This example describes preparation of other salts as provided by this invention.

The Al salt of p-aminobenzoic acid is obtained in 84% yield by reacting the acid with aluminum triisopropylate in refluxing dioxane. On gradual addition of the stated salt to pyromellitic dianhydride in boiling heptyl glycol ether, condensation occurs rapidly at 392° F. as indicated by evolution of water. Results of analysis indicate that each amino group has reacted with ½ mol of pyromellitic anhydride to produce an aluminum salt of N,N'-bis(4-carboxyphenyl)pyromellitic diimide.

The stated salt is alternatively prepared by dissolving aluminum triacetate in water, mixing this aqueous solution with dioxane as a coupling agent, and adding the resulting mixture to a solution of N,N'-bis(4-carboxyphenyl)pyromellitic diimide in dimethyl formamide, at a temperature such as to evolve acetic acid.

By a similar procedure, substituting chromium triacetate for the aluminum salt, the chromium salt of N,N'-bis(4-carboxyphenyl)pyromellitic diimide is prepared.

A salt such as the aluminum salt is prepared from a pyromellitic 1,2-imide 4,5-anhydride in accordance with this invention by reacting, for example, aluminum triacetate with N-anthraquinonylpyromellitic 1,2-imide 4,5-anhydride or N-(4-(4'-aminosulfonylphenyl)phenyl)pyromellitic 1,2-imide 4,5-anhydride.

EXAMPLE XVII

This example illustrates preparation of a reaction product of an aluminum alcoholate with an N-(carboxyaryl)-phthalimide, and a lubricating composition comprising the same.

The oleaginous fluid used as reaction medium in this preparation is a polymethylphenyl silicone supplied by Dow Chemical Company, Midland, Michigan, viscosity 20.3 cs. at 210° F., 60.7 cs. at 100° F., ASTM slope, 0.34; freezes at <—75° F.; flash point >550° F.; identified as DC XF–6–7012.

To a suspension of 59.2 parts of phthalic anhydride in 320 parts by weight of the stated fluid at 180° C. are added 54.8 parts of p-aminobenzoic acid to form N-(4-carboxyphenyl)phthalimide. Then 30 parts of aluminum isopropylate are added while the temperature is maintained at 215–220° C. Isopropyl alcohol is evolved. The resulting thickened lubricating composition is heated at 260° C. for 16 hours. Cooling and milling gives a thick grease with a dropping point of over 675° F., ASTM penetration, unworked 325, worked (60 strokes) 330.

EXAMPLE XVIII

This example illustrates the conversion of a tetrachlorophthalimidoarylenecarboxylic acid to a reaction product with an aluminum alcoholate, and lubricating compositions comprising such a product.

N-(4-carboxyphenyl)tetrachlorophthalimide is prepared by adding 114.5 parts of tetrachlorophthalic anhydride at 180° C. to 248.7 parts of the oleaginous base fluid of Example II, followed by the slow addition of 54.8 parts of p-aminobenzoic acid. The exothermic reaction proceeds very rapidly as indicated by the escape of water vapor and a rapid rise in temperature. The mixture is heated at 200° C. for 1 hour to complete the imide formation. Following this, 30 parts of Al-isopropylate are added. The temperature is then raised to 260° C. The essentially dry paste is hard and grainy but mills to a smooth consistency of a grease exhibiting an ASTM penetration of 340 (unworked). After a storage time of 1 month, the grease has hardened very slightly (unworked 325). The corrosion properties of this grease are measured by covering a cleaned and polished 4340 steel panel with a ⅛ inch layer of the grease and keeping the panel in a sealed jar at 400° F. for 24 hours. The panel is stained, but not corroded or pitted.

EXAMPLE XIX

This example illustrates the preparation of a reaction product of a pyromellitic imidoarylenecarboxylic acid with an aluminum alcoholate, and a lubricating composition comprising the same.

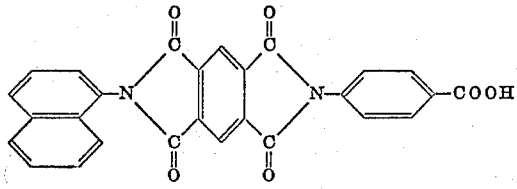
A suspension of 27.1 parts of pyromellitic dianhydride in 500 parts of the base fluid of Example II is heated to 180° C. and 34.2 parts p-aminobenzoic acid are added slowly, while a rapid escape of water vapor occurs. The reaction mixture is heated for one hour to complete the imide formation. During the following addition of 18.5 parts Al-isopropylate, the temperature is gradually raised to approximately 215° C. to ease the removal of isopropanol. The temperature is then raised to 260° C. and the mixture heated with agitation until the silicone oil thickens to a semi-solid, grease-like consistency. Following this, the grease is subjected to a 16 hour heating cycle to stabilize the grease structure. After cooling and milling, the grease has an ASTM penetration of 300 unworked, 320 worked, 30 strokes.

EXAMPLE XX

This example illustrates the preparation of the reaction product of an "asymmetrical" pyromellitic diimide, and a lubricating composition containing the same.

Pyromellitic dianhydride, 43.6 parts, is suspended in 200 parts of the base fluid of Example II. At 180° C.,

a mixture of 28.6 parts α-naphthylamine and 27.4 parts of p-aminobenzoic acid is added gradually. While the temperature is kept between 180 and 190° C., the mixture is heated for 1 hour to complete the formation of N-(4-carboxyphenyl)-N'-1-naphthylpyromellitic diimide of the formula.



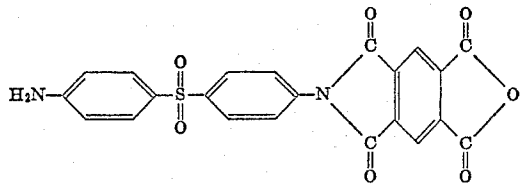
During the subsequent addition of 14 parts of Al isopropylate, the temperature is raised to 240–250° C. At this point, the mixture thickens to a grease. Upon milling through a Morehouse mill, the grease is tested according to ASTM specifications.

Penetration (unworked)	319
Penetration (worked, as tested in 4 hour shell roller test)	310
Evaporation loss (ASTM method D972–42, 22 hours, 400° F.	8.8
Dropping Point (ASTM method D566–42) ° F.	>675

EXAMPLE XXI

This example illustrates preparation of a reaction product of an aluminum alcoholate with a pyromellitic 1,2-imide 4,5-anhydride, and a lubricating composition comprising the same.

A suspension of 44 parts (0.2 mole) of pyromellitic dianhydride in the oleaginous base of Example II is heated to 180° C., and to this are gradually added 50 parts (0.2 mole) of 4,4'-diaminodiphenyl sulfone. The mixture is heated for 2½ hours at 180°–200° C. to provide N-(4-(4'-aminophenylsulfonyl) phenyl)pyromellitic 1,2-imide 4,5-anhydride, of the structure



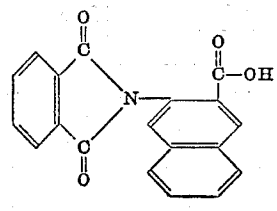
To the suspension of this mono-imide in the oleaginous base at 150° C. are added 21 parts of aluminum triisopropylate, and the temperature is maintained for one hour. On cooling and milling the resulting reaction mixture at 0.002" through a Morehouse mill, a lubricating composition of grease consistency is obtained which has an ASTM penetration of 360.

After 4 hours in the Shell roller, the observed penetration is 352, showing excellent mechanical stability. A sample heated at 500° F. for 16 hours exhibits a weight loss of only about 10%, showing that this grease also has desirable thermal stability.

EXAMPLE XXII

This example illustrates preparation of a reaction product of an aluminum alcoholate with an imidoarylenecarboxylic acid in which the N substituent is a condensed ring radical, and lubricating compositions comprising the same.

N-(3-carboxy-2-naphthyl)phthalimide of the formula:



is produced through reaction of 14.8 parts of phthalic anhydride with 16.6 parts of 2-amino-3-naphthoic acid in 180 parts of acetic acid at reflux for six hours. Subsequently an additional 14.8 parts of phthalic anhydride are incorporated in the reaction mixture and refluxing is continued for three more hours. The precipitated phthalimidonaphthoic acid is removed by filtration and the mother liquor diluted with water to obtain a total of 26.6 parts of crude phthalimidonaphthoic acid. Purification through recrystallization from ethanol produces pale green crystals with a melting point of 259° C. The compound has the following analysis:

Percent	Calculated	Found
C	71.93	71.63
H	3.49	4.06
O	19.72	20.07
N	4.41	4.53

This N-(3-carboxy-2-naphthyl)phthalimide is incorporated in the oleaginous base fluid described in Example XVII, and the resulting mixture treated with aluminum triisopropylate as described in Example XXVII. The lubricating composition produced thereby is particularly adapted for use at high temperatures.

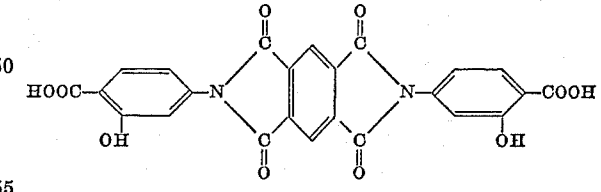
The preparation of the corresponding (N-carboxynaphthyl)tetrachlorophthalimide and N,N'-bis(carboxynaphthyl)pyromellitic diimides and their conversion to aluminum alcoholate reaction products is effetced substantially similarly.

EXAMPLE XXIII

This example illustrates preparation of the reaction product of an aluminum alcoholate with an imidoarylenecarboxylic acid wherein the arylene radical carries a substituent comprising a hydroxy group; and a lubricating composition comprising the same.

The base fluid in which this preparation is conducted is the mixture of oleaginous fluids comprising a polymethylphenylsilicone base fluid and a chlorinated polymethylphenylsilicone base fluid described in Example XII.

The arylenecarboxylic acid is produced by reacting 30.8 parts of p-aminosalicylic acid with 21 parts of pyromellitic dianhydride in a mixture of 175 parts each of the stated oleaginous base fluids at 190° C. over a total of 70 minutes, to form N,N'-bis(4-carboxy-3-hydroxyphenyl)pyromellitic diimide of the formula



Then 15 parts of aluminum triisopropylate are added and isopropyl alcohol is removed at gradually increasing temperatures until a temperature of 250° C. is attained after an additional 35 minutes.

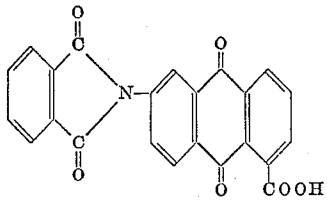
On cooling, 360.2 parts of a lubricating composition comprising 13.7% of the reaction product of the aluminum alcoholate and the stated acid are obtained. After milling, this lubricating composition of grease consistency is found to have a worked penetration of 295 ASTM units.

EXAMPLE XXIV

This example illustrates the preparation of an aluminum alcoholate reaction product with an imidoarylenecarboxylic acid in which the arylene radical is polycyclic and substituted by radicals in addition to the carboxylic acid group; and a lubricating composition comprising the same.

Phthalic anhydride, 14.8 parts, in a mixture of 180 parts acetic acid and 12 parts acetic anhydride, is reacted at reflux with 13.4 parts of 6-aminoanthraquinone-1-carboxylic acid. The precipitate is filtered off and worked

with acetone to provide 15 parts of crude N-(1-carboxy-6-anthraquinonyl)phthalimide, of the formula



Recrystallization from a mixture of dimethylformamide and acetone produces olive green crystals of this compound, M. 287° C. (slight decomp.).

On treatment with aluminum triisopropylate in an oleaginous base by the procedure of Example XXVII, isopropanol is evolved to produce a thickened, grease-like lubricating composition suited for use at high temperatures, comprising the reaction product of the acid.

The corresponding N-(carboxyaryl)pyromellitic diimides and tetrachlorophthalimides are prepared and converted to their respective reaction products with aluminum triisopropylate by proceeding in substantially the same manner.

EXAMPLE XXV

This example illustrates preparation of a lubricating composition comprising a mixture of the reaction products of this invention.

To a heated mixture consisting of 307.9 parts of the base fluid of Example XVII, 57.2 parts tetrachlorophthalic anhydride and 44.4 parts phthalic anhydride, 68.5 parts of p-aminobenzoic acid are added slowly at 190° C. The mixture is then heated for an additional 2 hours to complete the imide formation. Then 37.5 parts Al isopropylate are added with agitation and heating to 250° C. The resulting grease is subjected to a 16 hour heating cycle, allowed to cool to room temperature and then passed through a Morehouse mill. The grease has the following properties:

ASTM penetration, inches	½
Dropping point, ASTM method D566–42, ° F.	678
Evaporation loss, 22 hours, at 400° F., ASTM method D972–42, percent	9.08
High temperature Shell roller test, 4 hours at 400° F.	208
Mean hertz load estimate	52
Shell 4 ball wear test, 2 hours, 60 r.p.m., 600° F. load, kg. 20.	
Average scar diameter, mm	2.18

The Shell 4 ball wear test is described in our copending application Ser. No. 763,832, filed September 29, 1959, assigned to the same assignee as the present invention. High temperature tests are run in the Brown-GE modification of the tester, available from Roxana Machine Works, St. Louis, Missouri, using M–10 ½" steel balls.

EXAMPLE XXVI

This example describes a different preparation of a grease comprising the mixture of thickening reaction products present in the composition of the preceding example.

The base grease is prepared as described in Example XVII, by reacting N-(4-carboxylphenyl)phthalimide with aluminum isopropylate in the oleaginous fluid described in that example. After completion of addition of the aluminum isopropylate, the grease is heated for 16 hours at 500° F.

The reaction product of aluminum isopropylate with N-(4-carboxyphenyl)tetrachlorophthalimide is prepared separately in solvent. A slurry of 22 parts aluminum isopropylate in 550 parts dioxane is brought to reflux. Then 122 parts of N-(4-carboxyphenyl)tetrachlorophthalimide prepared as described in Example XIV are added gradually, and the mixture is refluxed for 4 hours. On filtration and drying, 129 parts of the reaction product are obtained.

The stated base grease comprising the phthalimide derivative reaction product is combined with 76 parts of the tetrachlorophthalimide derivative reaction product and passed through a Morehouse mill to yield a grease having an ASTM penetration of 325 (330 worked, 60 strokes). The final thickener concentration amounts to 39.8%, consisting of 23.8% of the phthalimide derivative reaction product and 16% of the tetrachlorophthalimide derivative reaction product. The grease has the following properties:

ASTM penetration	325
ASTM penetration after high temp. Shell roller test, 4 hours, 400° F.	312
Shell 4-ball wear test, 600 r.p.m., 600° F., 2 hours, load, kg. 10.	
Average scar diameter, mm	2.1
Mean hertz load, estm	50

The grease comprising only the phthalimide derivative reaction product as described in Example XVII has a mean hertz load of only 18. Thus inclusion of the tetrachlorophthalimide reaction product substantially improves the extreme pressure properties of the composition.

EXAMPLE XXVII

This example illustrates the preparation of a lubricating composition containing a mixture of three of the reaction products of this invention.

In the first step, the reaction product of N,N'-di(4-carboxyphenyl)pyromellitic diimide is prepared as described in Example XIX, but using the fluid of Example XVII, by reacting 7.6 parts of pyromellitic dianhydride with 9.6 parts of p-aminobenzoic acid, followed by treatment with 5.2 parts of Al isopropylate. As soon as the oil thickens to gel like consistency, the mixture is thinned out by the addition of 224.1 parts of the fluid of Example XVII.

In the second step, a mixture of 81.1 parts N-(4-carboxyphenyl)tetrachlorophthalimide and 26.7 parts of N-(4-carboxyphenyl)phthalimide are added at 200° C. During the following addition of 22.5 parts of Al isopropylate, the very thick mixture is stirred with high speed agitation at 230° C. until the majority of isopropanol has been removed. After an additional heating period of one hour at 260° C. the material is then allowed to cool and passed through a Morehouse mill. The weight ratio of the above mentioned thickener mixture amounts to 3.7% of the pyromellitic diimide, 18.4% of the tetrachlorophthalimide, and 6.1% of the phthalimide derivative reaction products.

ASTM penetration (unworked)	270
ASTM penetration (worked 60 strokes)	272
After 3 days (worked 60 strokes)	229
After 3 weeks (worked 60 strokes)	229
After high temp. Shell roller test (4 hours, 400° F.)	213
Dropping point, ASTM method D566–42, ° F.	675
Mean hertz load	56

EXAMPLE XXVIII

This example illustrates an alternative procedure for the preparation of a lubricating composition containing a mixture of two of the reaction products described in this invention.

The oleaginous base used in this preparation is a mixture of the chlorinated polymethylphenylsilicone fluid described in Example XII, to which has been added 0.03% of a soluble tin compound (supplied by General Electric Co., Schenectady, N.Y.; identified as GE 81717); and the base fluid described in Example XVII.

A mixture of 111 parts each of the two stated base fluids

is heated to 200° C., and 36 parts of tetrachlorophthalic anhydride and 22 parts of pyromellitic dianhydride are dissolved in the base fluid. Then 69 parts of p-aminobenzoic acid are added over a 70 minute reaction period. Thirty-eight parts of aluminum isopropylate are added over a 30 minute period and the reaction temperature raised to 250° C. for a total reaction time of 340 minutes. After a heat treatment at 260° C. for 16 hours, the grease is milled at 0.002 inch. The final thickener content is 45.9%. The worked penetration of the resulting grease is 225 ASTM units.

EXAMPLE XXIX

This example illustrates the extraordinary extreme pressure properties of the lubricant prepared in Example XXVIII upon the addition of pentachlorophenylmercaptoacetic acid.

Ninety-four parts of the grease from Example XXVIII are milled with 6 parts of pentachlorophenylmercaptoacetic acid. The resulting grease has essentially the same penetration and dropping point as the original grease. The extreme pressure characteristics as defined by the mean hertz load are:

Untreated grease from Example XXVIII	55
Treated grease as described above	84

A mean hertz load of 55 is exceptionally good for a grease based upon silicone fluids which generally have limited lubricity characteristics. The value of 84 observed for the additive-treated grease is most unusual and indicates the treated grease is particularly suited for gear lubrication or other extreme pressure applications where metal-to-metal forces as great as 150,000 p.s.i. may be encountered.

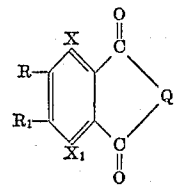
While the invention has been illustrated with reference to various particular embodiments thereof, it is to be appreciated that modification and variations can be made within the scope of the invention.

What is claimed is:

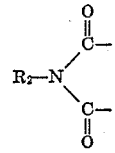
1. A lubricating composition consisting essentially of an oleaginous base and a product selected from the group consisting of

(A) compounds of the formula

(I)



in which (1) when R and R_1 are taken together, R and R_1 together represent the radical



X and X_1 are selected from the group consisting of hydrogen and chlorine, Q is selected from the group consisting of O and N—R_3, and R_2 and R_3 are selected separately from the group consisting of —arylene-COOH and polycyclic conjugated radicals; and (2) when R and R_1 are taken separately, each of X, X_1, R and R_1 is chlorine and Q is —N-arylene-COOH;

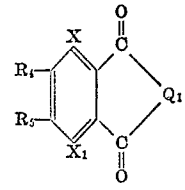
(B) metal salts prepared from the compounds of Formula I which contain a



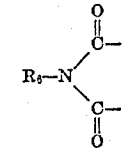
group; and

(C) the products of the reaction of an aluminum alcoholate with a compound of the formula

(II)

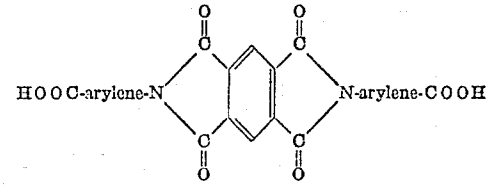


in which X and X_1 are selected from the group consisting of hydrogen and chlorine and (1) when R_4 and R_5 are taken together, R_4 and R_5 together represent the radical



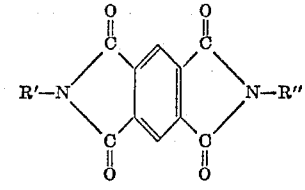
Q_1 is selected from the group consisting of O, N-arylene-COOH, and an N atom substituted by a polycyclic conjugated radical, and R_6 is —arylene-COOH when Q is an N atom substituted by a polycyclic conjugated radical, while R_6 is selected from the group consisting of —arylene-COOH and conjugated polycyclic radicals when Q is selected from the group consisting of O and N-arylene-COOH; and (2) when R_4 and R_5 are taken separately, R_4 and R_5 are selected from the group consisting of hydrogen and chlorine, and Q_1 is N-arylene-COOH.

2. A lubricating composition consisting essentially of an oleaginous base and a pyromellitic diimide of the formula



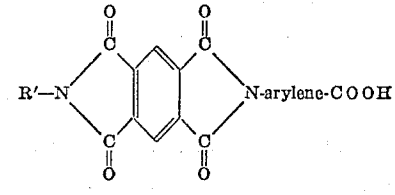
3. A lubricating composition consisting essentially of an oleaginous base and a metal salt of the pyromellitic diimide defined in claim 2.

4. A lubricating composition consisting essentially of an oleaginous base and a pyromellitic diimide of the formula



where R' and R'' are conjugated polycyclic radicals.

5. A lubricating composition consisting essentially of an oleaginous base and a pyromellitic diimide of the formula

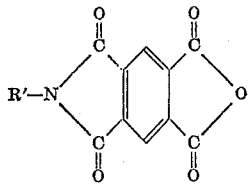


where R' is a conjugated polycyclic radical.

6. A lubricating composition consisting essentially of an oleaginous base and a metal salt of the pyromellitic diimide defined in claim 5.

7. A lubricating composition consisting essentially of an oleaginous base and a pyromellitic mono-imide of the

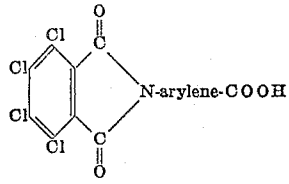
formula



where R′ is a conjugated polycyclic radical

8. A lubricating composition consisting essentially of an oleaginous base and a metal salt prepared from the imide defined in claim 7.

9. A lubricating composition consisting essentially of an oleaginous base and a tetrachlorophthalimide of the formula



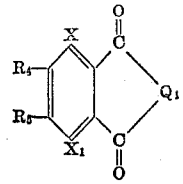
10. A lubricating composition consisting essentially of an oleaginous base and a metal salt of the imide defined in claim 9.

11. A lubricating composition consisting essentially of an oleaginous base and a product consisting of a heavy metal salt of an N-(carboxyaryl) tetrachlorophthalimide as defined in claim 9.

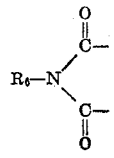
12. A lubricating composition consisting essentially of an oleaginous base and the cadmium salt of N-(4-carboxyphenyl)-tetrachlorophthalimide.

13. The method of preparing a novel lubricating composition which comprises reacting an aluminum alcoholate, in an oleaginous base, with a compound of the formula

(II)



in which X and X_1 are selected from the group consisting of hydrogen and chlorine, and (1) when R_4 and R_5 are taken together, R_4 and R_5 together represent the radical

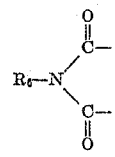


Q_1 is selected from the group consisting of O, N-arylene-COOH, and an N atom substituted by a polycyclic conjugated radical, and R_6 is —arylene-COOH when Q is an N atom substituted by a polycyclic conjugated radical, while R_6 is selected from the group consisting of —arylene-COOH and conjugated polycyclic radicals when Q is selected from the group consisting essentially of O and N-arylene-COOH; and (2) when R_4 and R_5 are taken separately, R_4 and R_5 are seleceted from the group consisting of hydrogen and chlorine, and Q_1 is N-arylene-COOH.

14. The method of preparing a lubricating composition which comprises preparing an aluminum alcoholate reaction product in an oleaginous base by the method of claim 13 and thereafter heating the resulting reaction mixture at an elevated temperature.

15. A lubricating composition consisting essentially of the product of the method of claim 13.

16. A lubricating composition consisting essentially of an oleaginous base and a mixed reaction product prepared by reacting an aluminum alcoholate with a mixture of at least one pyromellitimide compound of the Formula II in claim 13 in which R_4 and R_5 are taken together to represent the radical



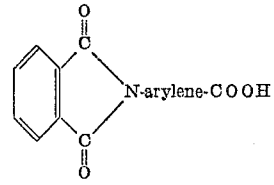
and at least one phthalimide compound of the said formula in which R_4 and R_5 are taken separately to represent hydrogen.

17. A lubricating composition as defined in claim 16, consisting essentially of an oleaginous base and a mixed reaction product, in which the reaction of the aluminum alcoholate with the pyromellitimide and phthalimide compounds producing said reaction product is conducted in an oleaginous base, and said mixed reaction product is formed in an amount sufficient to thicken said base.

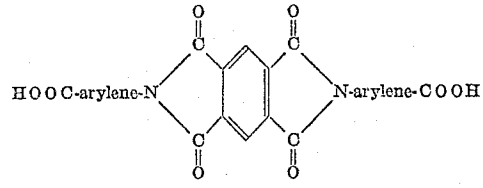
18. A lubricating composition consisting essentially of an oleaginous base and the reaction product prepared by the reaction of aluminum triisopropylate with a mixture of N,N′-bis(4-carboxyphenyl)pyromellitic diimide and N-(4-carboxyphenyl)phthalimide, said reaction being conducted in an oleaginous base, said reaction product being present in an amount sufficient to thicken said base.

19. The lubricating composition of claim 18, said composition additionally containing a cadmium salt of N-(4-carboxyphenyl)tetrachlorophthalimide.

20. A lubricating composition consisting essentially of an oleaginous base and a reaction product prepared by the reaction of an aluminum alcoholate and a phthalimide of the formula



21. A lubricating composition consisting essentially of an oleaginous base and a reaction product prepared by the reaction of an aluminum alcoholate and a pyromellitic diimide of the formula



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