United States Patent Office 3,108,962 Patented Oct. 29, 1963

3,108,962

GREASE

Fritz A. Buehler, Erlton, and Harry J. Andress, Jr., Pitman, N.J., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

No Drawing. Filed Apr. 20, 1961, Ser. No. 104,258
6 Claims. (Cl. 252—33.6)

This invention has to do with new grease compositions, particularly grease compositions capable of servicing effectively equipment operating at temperature extremes.

In recent years, a number of silicones have been developed for use as lubricants. They have been so used as fluid lubricant compositions and in greases. Since they are stable at temperatures well above temperatures at which mineral oils, and natural and synthetic esters decompose, they have been used extensively as high temperature lubricants. They have also been used at extremely low temperatures, and at normal lubricating temperatures. However, with the demand ever increasing for lubricants capable of resisting still higher operating temperatures, silicones have proven ineffective to meet such conditions. That is, at temperatures of the order of 600° F. and higher, silicones volatilize and gel at undesirable rates. This is exhibited even by certain silicones, namely, phenylmethyl polysiloxanes.

While some progress has already been reported in stabilizing certain polysiloxanes with iron octoate and with a combination of cerium toluate and disalicylalpropylenediamine, it has been found that polysiloxane-base grease compositions have not responded to numerous additives. In fact, some polysiloxane greases lose grease structure—thickener and vehicle separate—when some additives are mixed therewith.

This invention is predicated upon the discovery that certain amine salts stabilize a perylimid-phenylmethyl polysiloxane grease and, in addition, improve the thickening power of the perylimid thickener.

It is an object of this invention, therefore, to stabilize perylimid-phenylmethyl polysiloxane greases.

It is another object to improve the thickening power of the perylimid thickener in said greases.

It is a further object to improve the flow properties of the said greases.

Still another object is to provide anti-rust protection to said greases.

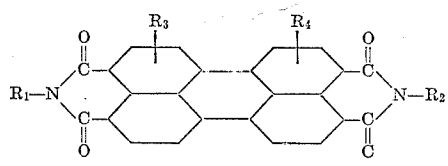
Other objects and advantages of this invention will appear from the following description.

The foregoing objects are realized with compositions comprising:

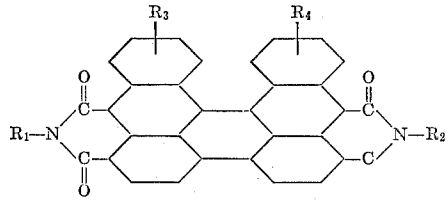
(1) A phenylmethyl polysiloxane,

(2) Iron octoate,

(3) A perylimid thickener represented by the general formulae:



and

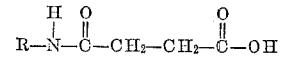


wherein R_1, R_2, R_3 and R_4 can be the same or different

atoms or groups. R_1 through R_4 can be: hydrogen; alkyl such as methyl, ethyl, propyl, etc.; cycloalkyl such as cyclohexyl, etc.; aryl such as phenyl, cresyl, dimethylphenyl, naphthyl, anthraquinyl, etc.; substituted groups such as methoxyphenyl, ethoxyphenyl, monochlorophenyl, dichlorphenyl, aminophenyl, etc.

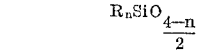
and

(4) An amine salt of a succinamic acid having the formula



wherein R is a monovalent alkyl radical containing between about 12 and about 15 carbon atoms and having a tertiary carbon atom directly attached to the nitrogen atom, with a primary monoalkyl amine wherein the alkyl group contains between about 12 and about 15 carbon atoms and having a tertiary carbon atom directly attached to the $—NH_2$ group.

The phenylmethyl polysiloxanes of this invention have the general formula



wherein n has an average value of from 2.0 to 2.9 and R is both phenyl and methyl, the ratio of phenyl to methyl being from about 1:10 to about 3:2. Typical of such polysiloxanes is one having a phenyl/methyl ratio of 1:7, a molecular weight of approximately 900 (as determined by high temperature mass spectrometry), and the following viscosities (polysiloxane A, hereinafter):

	Centistokes
210° F	20–21
77° F	90
—65° F	About 6800

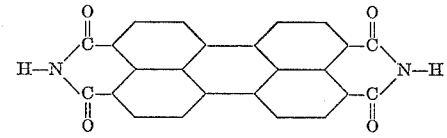
This polysiloxane has a pour point below —75° F.

Such polysiloxanes are described in the text "Chemistry of the Silicones," by Rochow, second edition, 1951, at pages 66–68. They are also described by Eaborn in the text "Organosilicon Compounds."

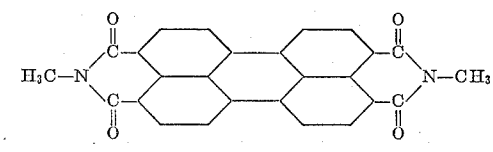
Iron octoate is present in the new compositions to impart protection against gelling of the polysiloxane at high temperatures. The iron salt can be in the ferric or ferrous form, or a mixture thereof. Also, the acid component of the salt or salts can be straight or branched chain. It is present in an amount ranging from about 0.1 to about 0.5 percent by weight of the polysiloxane, and preferably about 0.2 percent by weight.

Typical of the perylimid compounds, used as the thickeners in the new compositions, are:

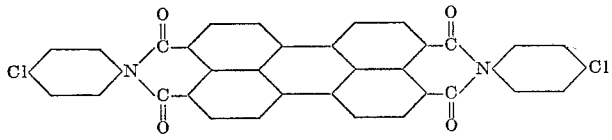
(1) Perylimid



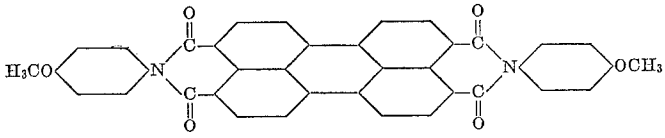
(2) Methyl perylimid



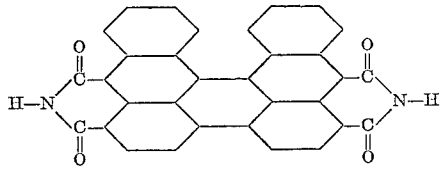
(3) p-Chlorophenyl perylimid



(4) p-Methoxyphenyl perylimid

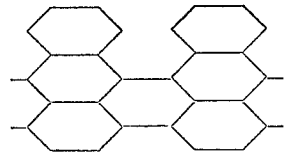


(5) Dibenzoperylimid



Particularly preferred herein is the p-methoxy perylimid shown above as compound (4). This is available as Indo Brilliant Scarlet Toner, a product of Harmon Colors, National Aniline Division of Allied Chemical Corporation. This is a fine powder, having a specific gravity of 1.47, a bulking value of 12.24 pounds per gallon and an oil absorption of 46 (in a slightly bodied oil). Particle size of the powder is 1.3–1.4 microns (length) x 0.2 micron (width).

A method for the preparation of perylimid compounds is given in German Patent No. 386,057. This involves reaction of perylene-3,4,9,10-tetracarboxylic acid with ammonia or with a primary aliphatic or aromatic amine. Modifications of such method are provided in British Patent No. 26,690/13 and in United States Patents Nos. 2,543,747, 2,905,685 and 2,905,686. Methods for the preparation of a compound having a dibenzo perylene group

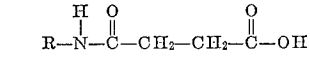


are described in British Patents Nos. 12,584/13 and 1,425/14. Reference is made to such disclosures for details in the preparation of the compounds of this invention.

While it is preferred that the compounds of this invention be used in substantially pure form (toner), it is to be understood that they can be used in the form of reduced toners. In the latter form, they are associated with an inert inorganic material such as an alumina hydrate, barium sulfate, clay, etc. When such inert inorganic materials are present, they are in amounts up to about 70 percent by weight, preferably less than about 50 percent by weight.

It is to be understood also that more than one of the perylimid compounds of this invention can be used together in a grease composition.

Present also in the compositions of this invention is an amine salt of a succinamic acid having the formula



wherein R is a monovalent alkyl radical containing between about 12 and about 15 carbon atoms and having a tertiary carbon atom directly attached to the nitrogen atom, with a primary monoalkyl amine wherein the alkyl group contains between about 12 and about 15 carbon atoms and having a tertiary carbon atom directly attached to the $-NH_2$ group. The amine salt is used in the new compositions in an amount ranging from about 0.02 to about 10 percent by weight of the polysiloxane, and preferably from about 0.5 to about 5 percent.

The amine salts are formed by warming succinic acid anhydride with a mixture of primary amines having a carbon atom of a tertiary butyl group attached to the amine ($-NH_2$) group and containing 12 to 15 carbon atoms per amine molecule and averaging 12 carbon atoms per molecule. This mixture contains, by weight, about 85 percent tertiary-dodecyl primary amine, about 10 percent tertiary-pentadecyl primary amine, and relatively small amounts, i.e., less than about 5 percent of amines having less than 12 or more than 15 carbon atoms. Further details relative to the preparation of the amine salts is provided in copending application Serial No. 707,472, filed January 7, 1958, now U.S. Patent No. 3,031,282.

By way of illustration, an amine salt was prepared in the following manner. A mixture of 50 grams (0.25 mol) of the amine mixture, described above, 25 grams (0.25 mol) of succinic acid anhydride, and 67 grams of xylene diluent was stirred at 85° C. for 1.5 hours. A succinamic acid was formed. To the succinamic acid, at room temperature (about 25° C.), were added 50 grams (0.25 mol) of the same amine mixture to form the amine salt. The product was then stirred at 85–90° C. for an additional 1.5 hours.

In the grease compositions contemplated herein, the perylimid gelling agents are used in quantities from about 5 to about 50 percent by weight, and preferably from about 15 to about 30 percent by weight. The vehicles and additives described above constitute the balance of the compositions, except for relatively small quantities of the following characterizing materials which may be present.

As indicated, the compositions contemplated herein can also contain other characterizing materials. For examples, antioxidants, corrosion inhibitors, viscosity index agents, fillers, etc., can be used. Among such materials are colloidal silica, calcium acetate, calcium carbonate and molybdenum disulfide. These characterizing materials do not detract from the lubricating value of the compositions of this invention, nor do they detract from the beneficial character of the perylimid compounds; rather, these characterizing materials serve to impart their customary properties to the particular compositions in which they are incorporated.

The greases of this invention are prepared by dispersing the perylimid compound in the polysiloxane, which already contains a small amount of the iron compound; and then dispersing the amine salt in the perylimid-polysiloxane dispersion. For example, the perylimid compound can be wetted with a volatile liquid (such as methyl or ethyl alcohol) containing the amine salt, and the polysiloxane can be added thereto. The materials are milled together and warmed in order to remove the alcohol. The resultant product is milled until a homogeneous product is obtained.

Typical illustrative grease compositions are shown in the following examples:

EXAMPLE I

One part by weight of p-methoxy perylimid was wetted

with methyl alcohol and three parts by weight of polysiloxane A (containing 0.2 percent of iron octoate) was added thereto. The materials were milled with a spatula on a glass plate until roughly homogeneous, and were warmed to drive off the alcohol. The disperson was then milled in a colloid mill (0.002 inch clearance). The product is identified as grease I.

Grease I is included herein for comparative purposes, since it does not contain the amine salt characteristic of the new compositions.

EXAMPLE II

Fifty parts by weight of grease I were mixed at 250° F. with one part by weight of the amine salt described above. The mixture was milled on a glass plate with a spatula until a homogeneous grease was formed. The product is grease II.

EXAMPLE III

A grease was prepared from 1 part by weight of p-methoxy perylimid and 4 parts by weight of polysiloxane A (containing 0.2 percent by weight of iron octoate) by the same technique as used in Example I. The product—grease III—is included for comparison with grease IV, following.

EXAMPLE IV

Fifty parts by weight of grease III were blended with one part by weight of the amine salt described above, by the same technique as used in Example II, but the product was homogenized in a colloid mill (0.002 inch clearance). The product is identified as grease IV.

Thickening aid power of the amine salt is shown by the following penetration test values. Penetrations of a quarter scale ASTM cone were measured after working the grease for 60 strokes according to ASTM method D–1403. Full scale penetration values are shown; these are calculated from the equation:

$$P_{\text{full scale}}=P_{1/4\text{ scale}}\times 3.75+24$$

Results are set forth in Table I following:

Table I

Grease	Amine Salt, Wt. Percent	Penetration
I	0	345
II	2	230
III	0	380
IV	2	300

The foregoing results reveal the surprising thickening power of the amine salt in combination with the perylimid thickener. Thus, greases II and IV have a better balance of fluid and thickener than have greases I and III. Fluid or vehicle, such as a polysiloxane, should be released slowly from the grease gel structure, but the grease should not flow from the equipment (e.g., bearing) being lubricated. In a sense, then, the amine salt changes the flow properties of greases I and III, by increasing their "yield values." The latter is defined as the shear stress necessary for a grease to begin to flow. A grease with a higher yield value—as greases II and IV—will stay in place better in a bearing, and there is, therefore, less leakage from the bearing. As a practical matter, it is advantageous that the grease contain a greater amount of polysiloxane fluid, since it can serve for a longer period as a lubricant reservoir. The amine salt permits a greater fluid-to-thickener ratio. For example, a grease containing 80 percent by weight of polysiloxane and a small amount of amine salt has been found to be substantially superior to a grease containing 75 percent of polysiloxane and no amine salt. Here, there is a related saving of about 5 percent in thickener content.

One of the most significant evaluations for silicone greases is the high temperature ball bearing test. This test is conducted according to Coordinating Research Council Incorporated, Test Method L–35, at 600° F. and 10,000 r.p.m. A 204S–17 ball bearing was used without any applied load. The test was run continuously until the bearing no longer turned freely. Results are shown in Table II, below

Table II

Grease	Amine Salt, Wt. Percent	Grease Life, Hrs.
I	0	70
III	0	79
IV	2	450

The grease life in the bearing was significantly prolonged—by a factor of 6—by virtue of the combination of the amine salt and the other components.

Rust inhibition activity of the amine salt is shown by results obtained in the roller bearing rust test, according to ASTM Method D–1473–1960T. At the end of this test, grease is washed off the bearing with Stoddard's solvent. The roller and outer race are inspected. No more than three small rust spots should be evident on a combination of rollers and outer race. The test is run in triplicate, and two of the three bearings must pass the test in order that the grease be given a "Pass" rating. Results are shown below in Table III.

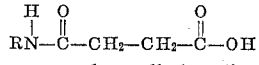
Table III

Grease	Amine Salt, Wt. Percent	Evaluation
I	0	Fail.
II	2	Pass.

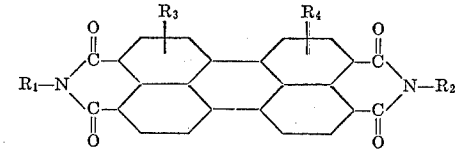
The new greases can be used for a wide range of industrial applications wherein equipment is subjected to temperatures in excess of about 450° F., and particularly in the range of 500 to 700° F. Typical equipment are aircraft, missiles and rockets.

We claim:

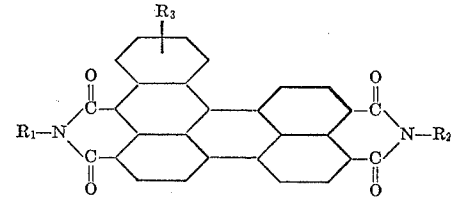
1. A grease comprising: a phenylmethyl polysiloxane having a phenyl/methyl ratio from about 1:10 to about 3:2; a small amount, sufficient to stabilize said polysiloxane, of an iron octoate; from about 0.2 to about 10 percent by weight, of the said polysiloxane, of an amine salt of a succinamic acid having the formula:



wherein R is a monovalent alkyl radical containing between about 12 and about 15 carbon atoms and having a tertiary carbon atom directly attached to the nitrogen atom, with a primary monoalkyl amine wherein the alkyl group contains between about 12 and about 15 carbon atoms and having a tertiary carbon atom directly attached to the $-NH_2$ group; and a grease-forming quantity of a perylimid compound selected from the group consisting of:



and



wherein R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen, alkyl, cycloalkyl, aryl, alkaryl, anthraquinyl, alkoxyaryl, haloaryl and aminoaryl.

2. A grease defined by claim 1 wherein the polysiloxane has a ratio of phenyl to methyl groups of 1:7 and viscosities of 90 centistokes at 77° F., 20–21 centistokes at 210° F. and about 6800 centistokes at −65° F.

3. A grease defined by claim 1 wherein the iron octoate is present in an amount from about 0.1 to about 0.5 percent by weight of the said polysiloxane.

4. A grease defined by claim 1 wherein the amine salt is present in an amount from about 0.5 to about 5 percent by weight of the said polysiloxane.

5. A grease defined by claim 1 wherein the perylimid compound is p-methoxyphenyl perylimid.

6. A grease comprising:

a phenylmethylpolysiloxane having a ratio of phenyl to methyl groups of 1:7 and viscosities of 90 centistokes at 77° F., 20–21 centistokes at 210° F. and about 6800 centistokes at −65° F.;

about 0.2 percent by weight of iron octoate;

about 2 percent by weight of the amine salt defined in claim 1;

and

about 20 percent by weight of p-methoxyphenyl perylimid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,445,567	Elliott	July 20, 1948
2,458,425	Rocchini	Jan. 4, 1949
3,002,927	Awe et al.	Oct. 3, 1961
3,003,960	Andress et al.	Oct. 10, 1961
3,009,877	Nielsen	Nov. 21, 1961
3,025,241	Dreher et al.	Mar. 13, 1962
3,031,282	Andress et al.	Apr. 24, 1962

UNITED STATES PATENT OFFICE

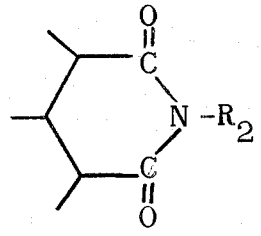
CERTIFICATE OF CORRECTION

Patent No. 3,108,962 October 29, 1963

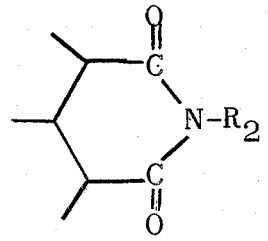
Fritz A. Buehler et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, lines 55 to 61, the right-hand portion of the formula should appear as shown below instead of as in the patent:



same column 1, lines 65 to 71, the right-hand portion of the formula should appear as shown below instead of as in the patent:



Signed and sealed this 30th day of June 1964.

(SEAL)
Attest:

ERNEST W. SWIDER — Attesting Officer

EDWARD J. BRENNER — Commissioner of Patents

UNITED STATES PATENT OFFICE

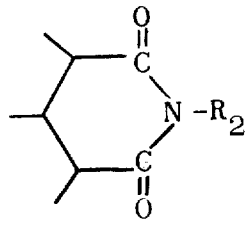
CERTIFICATE OF CORRECTION

Patent No. 3,108,962 October 29, 1963

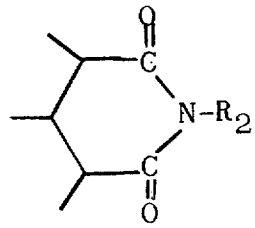
Fritz A. Buehler et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, lines 55 to 61, the right-hand portion of the formula should appear as shown below instead of as in the patent:



same column 1, lines 65 to 71, the right-hand portion of the formula should appear as shown below instead of as in the patent:



Signed and sealed this 30th day of June 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents