United States Patent Office 3,785,979 Patented Jan. 15, 1974

3,785,979

DIBENZIMIDAZOLE GREASE THICKENING AGENTS

August H. Birke, Godfrey, Ill., assignor to Shell Oil Company

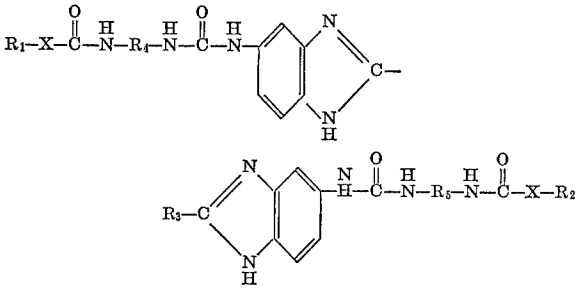
No Drawing. Continuation-in-part of abandoned application Ser. No. 169,459, Aug. 5, 1971. This application Oct. 11, 1972, Ser. No. 296,733

Int. Cl. C10m 5/20

U.S. Cl. 252—51.5 A 10 Claims

ABSTRACT OF THE DISCLOSURE

Dibenzimidazole compounds corresponding to the formula:



wherein R_1 and R_2 are aliphatic hydrocarbyl radicals, R_3 is a hydrocarbylene radical, R_4 and R_5 are aromatic hydrocarbylene radicals and X is —O— or

are highly efficacious grease thickening agents.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending U.S. application Ser. No. 169,459, filed Aug. 5, 1971, and now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention.—This invention relates to a novel class of dibenzimidazole compounds and grease compositions gelled therewith.

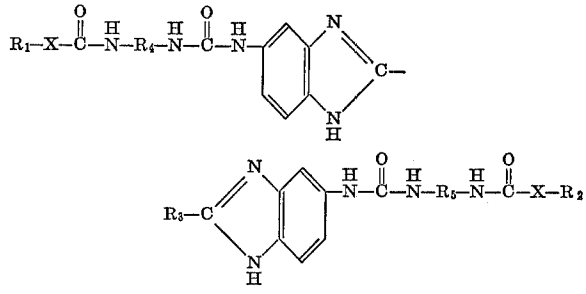
Description of the prior art.—It has become increasingly important that grease compositions be able to provide adequate lubrication at high temperatures, e.g., temperatures of 350° F. to 450° F. or higher. Numerous thickening agents have been proposed for use in such greases, including soap base thickeners, inorganic clay thickeners and organic thickening agents. Examples of this latter class of thickening agents include various polyureas, ureido compounds, aminoaryl diureas, triazines and the like. Such organic thickening agents are typically prepared by reacting one or more mono-, di-, or polyamines with one or more mono-, di-, or polyisocyanates. Other related organic thickeners include arylcarbamyl compounds formed by reacting an aromatic amine with the reaction product of an aromatic diisocyanate and p-aminobenzoic acid.

While organic thickening agents of the aforementioned types produce greases having desirably high dropping points, this is but one measure of a grease's ability to perform satisfactorily at high temperatures. Other important properties include thermal and mechanical stability, high temperatue bearing performance, oxidation and corrosion resistance, etc. While additives are normally incorporated into grease compositions to improve one or more of these properties, the thickening agent itself can significantly affect, either favorably or adversely, the

properties of the finished grease product. Thus, in spite of the numerous organic thickening agents known in the art, there is a continuing need for the development of thickening agents which will not only produce greases having high dropping points, but which will additionally augment other important propetries of the finished product. The present invention provides such a class of thickening agents.

SUMMARY OF THE INVENTION

It has now been found that grease compositions having excellent high temperature lubricating properties can be produced by incorporating into an oleaginous base vehicle, a minor amount of a dibenzimidazole compound corresponding to the formula:



wherein R_1 and R_2 are aliphatic hydrocarbyl radicals, R_3 is a hydrocarbylene radical, R_4 and R_5 are aromatic hydrocarbylene radicals and X is —O— or



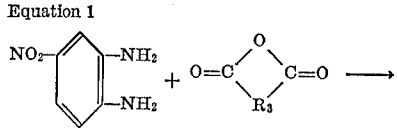
Not only do the grease compositions of the invention have high dropping points, but in addition they have excellent mechanical and thermal stability, and high temperature bearing performance properties as well. These excellent qualities are believed attributable in large part to the unique dibenzimidazole structure of the present thickening agents which produces an extremely stable molecule.

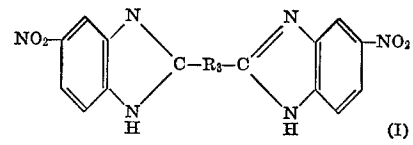
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The aforedescribed dibenzimidazole thickening agents can be conveniently prepared by reacting one mole of a dicarboxylic acid anhydride with two moles of a nitro-substituted phenylenediamine, followed by reduction of the nitro groups to amine groups, and further reaction with two moles of the reaction product of an aromatic diisocyanate with a monohydric alcohol or monoamine. This procedure is illustrated by the following equations:

Preparation of dibenzimidazole-urea-urethane thickeners

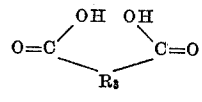
Equation 1



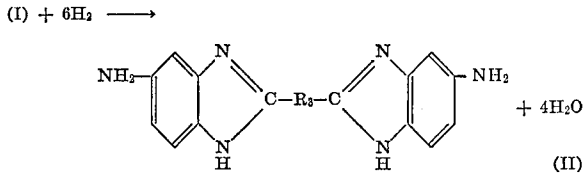


(I)

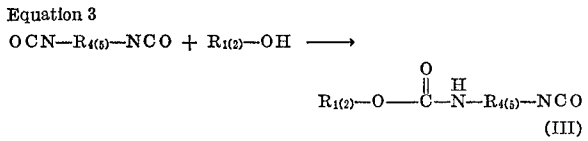
or



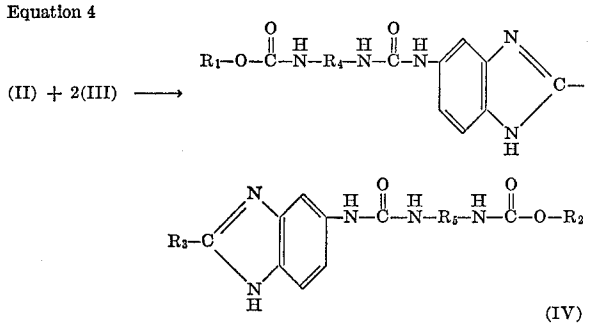
Equation 2



Equation 3

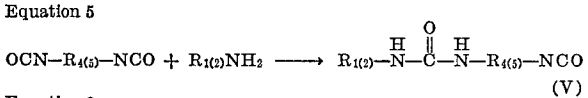


Equation 4

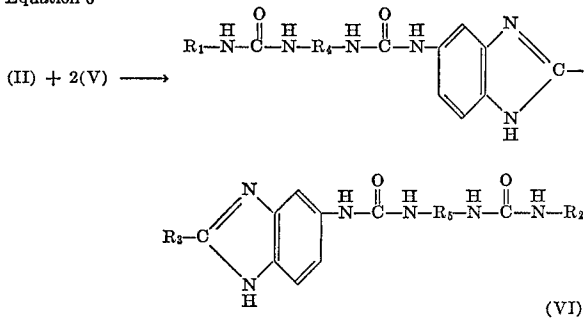


Preparation of dibenzimidazole-urea thickeners

Equation 5



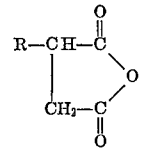
Equation 6



An alternative method of preparing the bis-nitrobenzimidazole (intermediate product I) employed in Equation 2, is to react the diacrboxylic acid or its anhydride with two moles of a phenylene diamine which is not nitro-substituted. The resultan product can be subsequently nitrated to produce bis-nitrobenzimidazole which is then converted to its amino form (intermediate product II) and reacted with two moles of intermediate products III or V as shown in Equations 4 and 6, respectively. A more detailed description of the preparation of the benzimidazole thickeners is given in the examples.

Dicarboxylic acids or anhydrides which can be suitably employed in preparing the thickeners of the invention include the acids or anhydrides of aliphatic dicarboxylic acids such as succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acids or anhydrides, as well as the anhydrides of aromatic dicarboxylic acids such as phthalic, isophthalic or terephthalic acids or anhydrides or their esters. Cyclohexane dicarboxylic acids and anhydrides such as 1,2- or 1,4-cyclohexane dicarboxylic acid or anhydride are likewise suitable as is tetrahydrophthalic acid or anhydride. Hydrocarbyl substituted dicarboxylic acid anhydrides can also be employed, for example, alkyl-

or alkenyl-substituted succinic corresponding to the formula



is an alkyl or alkenyl substituent of from 1 to 16 carbon atoms or more. Aliphatic dicarboxylic acid anhydrides are preferred, and in general are selected so that the R_3 radical of the previously depicted formula has from 2 to 20, preferably from 2 to 12 carbon atoms.

Phenylene diamines suitable for preparing the thickening agents of the invention are ortho-phenylene diamines having a nitro group substituted thereon, e.g., 4-nitro-o-phenylene diamine. In addition to the nitro substituent, o-phenylene diamines having other substituents, e.g., alkyl or halo substituents, can also be employed provided that such substituents do not appreciably interfere with the reaction of the phenylene diamine with the dicarboxylic acid anhydride.

If the alternative procedure discussed above is employed to prepare the bis-nitrobenzimidazole intermediate, the phenylene diamine need not contain a nitro substituent since the addition of the nitro groups is accomplished subsequent to formation of the bis-benzimidazole. Hence, when this procedure is followed, unsubstituted o-phenylene diamine may be utilized or any other o-phenylene diamine having substituents which will not appreciably interfere with the formation of bis-benzimidazole or its subsequent nitration. Specific examples of such phenylene diamines include 4-chloro-o-phenylene diamine and 3,4-toluene diamine.

Aromatic diisocyanates which may be employed in accordance with the invention include mono- or di-nuclear aromatic diisocyanates having a total of from 6 to 20 carbon atoms. Such diisocyanates include biphenylenediisocyanates, naphthylenediisocyanates and monophenylenediisocyanates including tolylenediisocyanate. Illustrative of such diisocyanates are 3,3-dimethylbiphenyl-4,4'-diisocyanate, diphenylmethane-4,4'-diisocyanate, 3,3-dimethyldiphenylmethane-4,4'-diisocyanate, 2,4-tolylenediisocyanate, 1,5-naphthylenediisocyanate and mixtures of 2,4- and 2,6-tolylenediisocyanates. 2,4-Tolylenediisocyanate and mixtures of 2,4- and 2,6-tolylenediisocyanates are particularly preferred diisocyanate reactants.

Monohydric alcohols which can be suitably employed to prepare the dibenzimidazole-diurethane-diurea thickeners include alphatic alcohols having from 8 to 30, preferably from 12 to 24, carbon atoms. Examples of such alcohols include octyl, nonyl, lauryl, tetradecyl, hexadecyl, octadecyl, octadecenyl, eicosyl and docosyl alcohols, etc., and mixtures thereof. Thickeners prepared using stearyl or oleyl alcohols or mixtures thereof have been found to be particularly advantageous.

Monoamines which can be employed to prepare the dibenzimidazole-urea thickeners of the invention are aliphatic monoamines or those having a predominantly aliphatic character having from 8 to 30, preferably from 12 to 24, carbon atoms. Suitable monoamines include octylamine, decylamine, dodecylamine, tetradecylamine hexadecylamine, heptadecylamine, octadecylamine, octadecenylamine, eicosylamine, docosylamine, tetracosylamine, etc. and mixtures thereof.

Mixtures of the above-mentioned monohydric alcohols and monamines can also be employed thereby producing benzimidazole compounds having both alkylurethane and alkylurylene terminal groups.

The thickening agents of the invention are generally employed in grease compositions in an amount sufficient to gel the oleaginous base vehicle to grease consistency. This amount can vary, for example, from about 5–50%

by weight of the total composition. Normally, however, thickener concentrations of 10–35% by weight are sufficient to impart the desired consistency to the inventive compositions.

A wide variety of lubricating oils may be employed as the base vehicle in the present compositions. Suitable base oils include mineral lubricating oils such as naphthenic base, paraffin base or mixed base oils having a viscosity in the range of from 50 SSU at 100° F. to 300 SSU at 210° F.; synthetic hydrocarbon oils such as oligomerized alpha-olefins and oils derived from coal products; synthetic oils such as alkylene polymers, alkylene, oxide-type polymers, polyalkene glycols, polyethers, phosphate esters, dicarboxylic acid esters and pentaerythritol esters. The above oils may be used individually or in mixtures thereof, wherever miscible or made so by the use of solvents. Of the aforementioned base oils, mineral lubricating oils having viscosities of from about 400 to 700 SSU at 100° F. are especially preferred.

In addition to the dibenzimidazole thickeners, the present compositions can also contain anti-corrosion additives such as disodium sebacate, glyceryl monooleate, sodium sulfonates, sodium nitrite, amino- and benzotriazoles, and isostearamides or imidazolines of tetraethylenepentamine; oxidation inhibitors such as phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, diphenylamines, phenothiazine, dithiocarbamates and various analogs and homologs thereof; viscosity index improvers such as methacrylate polymers and copolymers; extreme pressure agents, and any other additive recognized in the art to perform a particular function or functions.

The following examples illustrate the method of preparation of the present thickeners and their excellent properties. It is to be understood, however, that these examples are presented for illustrative purposes only and that the invention in its broader aspects should not be limited thereto.

EXAMPLE I

Preparation of dibenzimidazole-urea-urethane thickening agents

A 4-liter round bottom flask was charged with 302.2 g. (2 moles) of 4-nitro-o-phenylene diamine, 100.0 g. (1 mole) of succinic anhydride and 2 liters of 4 normal hydrochloric acid solution. The flask and its contents were then refluxed, with stirring, for 24 hours. Heating was discontinued and the reactants were cooled to 0° C., filtered, and the filtrate was discarded. The precipitate was collected and neutralized with 1,500 ml. of 5 normal ammonium hydroxide solution, refiltered, and washed twice with water. The neutralized material resulting was dissolved in refluxing ethylene glycol, treated with decolorizing charcoal, filtered and the filtrate cooled. The crystalline precipitate that appeared was collected, washed with ethanol and dried. The yield was 65 grams of 1,2-bis(5-nitrobenzimidazoyl-2)ethane having a melting point of 305° C.

56.04 g. (0.16 mole) of the above product was then suspended in 1,200 ml. of 3 normal hydrochloric acid solution to which was added palladium on charcoal catalyst and reduction of the nitro groups effected in a low pressure hydrogenation apparatus. The catalyst was then filtered off, the filtrate neutralized with sodium bicarbonate and the resulting precipitate collected. After washing with water and drying, 41.5 g. of 1,2-bis(5-aminobenzimidazoyl-2)ethane hydrate was obtained having a melting point of 154–155° C.

A 5-liter 3-necked flask equipped with a mechanical stirrer was charged with 2 liters of chloroform and 522 g. (3 mole) of commercial grade 2,4-tolylenediisocyanate. To this stirred solution was added 270 g. (1 mole) of stearyl alcohol over a period of 2 hours. After the addition, the contents of the flask were poured into 3 liters of hexane and cooled overnight. The resulting precipitate, N-(3 - isocyanato-4-methylphenyl)octadecyl carbamate, was collected and reprecipitated from hexane and vacuum dried. The product had a melting point of 78–79° C.

17.54 g. (0.06 mole) of the previously formed 1,2-bis-(5-amino-benzimidazoyl-2)-ethane was placed into a 500 ml. resin flask equipped with a mechanical stirrer together with 53.4 g. (0.12 mole) of N-(3-isocyanato-4-methylphenyl)octadecyl carbamate in 573 g. of a HVI neutral oil having a viscosity of 70 at 210° F. This suspension was heated with stirring, under nitrogen, to 127° C. When the reaction was complete, the contents were cooled to approximately 110° C. The formulation was then milled three times in a three-roll paint mill. The resulting grease (Grease 1) contained 11.0% by weight thickener and had an ASTM unworked penetration (P_0) of 212 and a worked penetration (P_{60}) of 264.

EXAMPLE II

Preparation of dibenzimidazole-urea thickening agents

The procedure of Example I was essentially repeated except that 269 g. (1 mole) of stearylamine was reacted with 2,4-tolylenediisocyanate in place of stearyl alcohol thereby forming N-(3-isocyanato-4-methylphenyl) octadecyl carbamide.

35.5 g. (0.08 moles) of the carbamaide intermediate was then reacted with 11.7 g. (0.04 mole) of 1,2-bis(5-aminobenzimidazoyl-2)ethane prepared as in Example I in 382 g. of a HVI neutral oil having a viscosity of 70 at 210° F. After completion of the reaction, the contents were cooled and milled three times in a three-roll paint mill. The resulting grease (Grease 2) contained 11.0% by weight thickener and had an ASTM unworked penetration (P_0) of 268 and a worked penetration (P_{60}) of 283.

EXAMPLE III

The procedure of Example I was essentially repeated except that a 60.40 molar ratio of stearyl and oleyl alcohols were employed in place of the stearyl alcohol reactant in Example I. The resulting grease contained 9.5% by weight thickener and had an ASTM unworked penetration (P_0) of 197 and a worked penetration (P_{60}) of 253.

EXAMPLE IV

The procedure of Example I was essentially repeated with the exception that an oligomerized alpha olefin synthetic hydrocarbon oil having a viscosity of 7.7 centistokes at 210° F. was employed in place of the mineral lubricating oil. The resulting grease (Grease 4) contained 14% by weight thickener and had an ASTM unworked penetration (P_0) of 242 and a worked penetration (P_{60}) of 275.

EXAMPLE V

In order to demonstrate the excellent high temperature performance characteristics of the present grease compositions, the greases of Example I and III were subjected to two different high temperature bearing tests. The results of these tests are shown in the following table.

TABLE I

Test procedure	Grease 1 [1]	Grease 3 [1]
Navy high speed bearing test (Fed. test Mtd. No. 331.1) 300° F., 10,000 r.p.m.—bearing life, hours	4,322, 5,118	4,956+
ABEC bearing test (Fed. test Mtd. No. 333) 350° F., 10,000 r.p.m.—hours to failure	[2] 386	[2] 465

[1] Includes 1% wt. phenyl-alpha-naphthylamine, 0.5% Oronite 250 (dilauryl selenide), 1% wt. sodium sebacate and 0.03% wt. 3-amino-1,2,4-triazole.

[2] Average of two runs.

EXAMPLE VI

Other dibenzimidazole thickeners and greases in accordance with the invention include those shown in the following table.

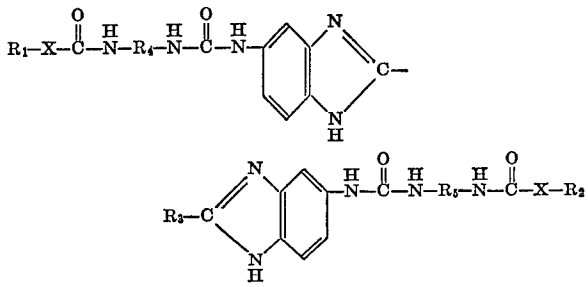
TABLE II

Grease composition	Acid or anhydride	Phenylene diamine	Diisocyanate	Alcohol or amine	Base oil
5	Succinic anhydride	4-nitro-o-phenylene diamine	2,4-tolylene-diisocyanate	80% mole $C_{18}H_{37}OH$; 20% mole $C_{18}H_{37}NH_2$	A
6	Adipic acid	do	3,3-dimethyl-diphenyl-methane-4,4'-diisocyanate.	100% mole $C_{18}H_{37}NH_2$	A
7	1,2-cyclohexane dicarboxylic anhydride.	do	2,4-tolylene-diisocyanate	70% mole $C_{20}H_{41}NH_2$; 30% mole $C_{12}H_{25}NH_2$.	B
8	Dodecyl succinic anhydride	do	3,3-dimethyl-biphenyl-4, 4'-diisocyanate.	100% mole $C_{18}H_{37}OH$	B
9	Phthalic anhydride	do	2,4-tolylene-diisocyanate	75% mole $C_{18}H_{37}OH$; 25% mole $C_{16}H_{33}OH$.	C

NOTE.—Base oil A=Mineral lubricating oil having a viscosity of 500 SSU at 100° F. Base oil B=Mineral lubricating oil having a viscosity at 70 SSU at 210° F. Base oil C=Mixture of hexadecyl isostearate and dimer acid esters.

I claim as my invention:

1. A grease composition consisting essentially of a major amount of a lubricated oil and in an amount sufficient to thicken the lubricating oil to grease consistency, a dibenzimidazole compound corresponding to the formula:



wherein R_1 and R_2 are aliphatic hydrocarbyl radicals having 6 to 30 carbon atoms, R_3 is a hydrocarbylene radical having from 2 to 20 carbon atoms, R_4 and R_5 are aromatic hydrocarbylene radicals having from 6 to 20 carbon atoms and X is —O— or



2. The composition of claim 1 wherein the dibenzimidazole compound is present in the amount of from 5 to 50% by weight.

3. The composition of claim 1 wherein X is —O—.

4. The composition of claim 1 wherein X is

5. The composition of claim 1 wherein R_3 is an alkylene radical having from 2 to 12 carbon atoms.

6. The composition of claim 1 wherein the R_1 and R_2 have from 12 to 24 carbon atoms.

7. The composition of claim 6 wherein R_4 and R_5 are tolylene.

8. The composition of claim 7 wherein R_3 is ethylene.

9. The composition of claim 8 where R_1 and R_2 have 16 to 18 carbon atoms.

10. The composition of claim 9 wherein the lubricating oil is a mineral lubricating oil.

References Cited

UNITED STATES PATENTS

3,015,625	1/1962	Rosscup et al.	252—51.5 A
3,133,883	5/1964	Hayne et al.	252—51.5 A
3,222,285	12/1965	Rai et al.	252—50 X

PATRICK P. GARVIN, Primary Examiner

A. H. METZ, Assistant Examiner

U.S. Cl. X.R.

260—309.2