

[54] GREASE COMPOSITION

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[22] Filed: **May 29, 1973**

[21] Appl. No.: **364,853**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 348,399, April 5,
1973.

[52] U.S. Cl. **252/17**, 252/51.5 R, 252/51.5 A,
252/392

[51] Int. Cl. **C10m 5/20**, C10m 7/32, C10m 7/30

[58] Field of Search 252/51.5 R, 51.5 A, 392,
252/17

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[57]

ABSTRACT

A grease composition is disclosed comprising (a) a lubricating oil base, (b) a mono or polyurea thickener, (c) a Mannich Base prepared by reacting formaldehyde, phenol and an amine selected from diethanolamine, N,N-diethanol alkylenediamine, and diethylamine, and (d) an alkaline earth metal aliphatic monocarboxylate having from 1 to 3 carbons.

12 Claims, No Drawings

GREASE COMPOSITION

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. application Ser. No. 348,399 filed Apr. 5, 1973.

BACKGROUND OF THE INVENTION

Modern technology is currently supplying the general public and the process industries with machinery capable of operating under severe conditions. Many of these machines require lubricants having properties which are not available with the conventional greases and oils. Thus modernization of the mechanical devices has strained the petroleum industry for the development of a second generation of lubricants capable of satisfying the lubricating requirements of the new machines.

Recently, a new grease composition has been developed containing a novel polyurea thickening agent. This grease has been found to exhibit superior endurance and high temperature lubricating properties. A particularly advantageous property is that of anti-thixotropy, i.e., the ability to increase in viscosity with increasing shear. The polyurea thickening agent is disclosed in U.S. Pat. Nos. 3,243,210; 3,243,372; 3,346,971; and 3,401,027.

While this grease solves many of the problems associated with the older lubricants, it is handicapped by a poor rust inhibition. This is a typical problem associated with most multipurpose grease thickeners. Rusting is a major problem in many machines exposed to a corrosive environment. To combat the rust problems, conventional rust inhibitors have been incorporated into the greases. The conventional inhibitors, however, are quite selective for the particular grease involved and often interfere with the essential properties of the grease. For example, some inhibitors may impart satisfactory rust inhibition but only at the expense of adversely softening the grease. Conversely, some inhibitors may be quite compatible with the grease but are relatively ineffective in rust protection.

It is, therefore, an object of this invention to provide an improved grease composition.

It is an additional object to provide a polyurea grease composition containing a compatible rust inhibitor.

It is another object of this invention to provide a polymer grease having improved rust inhibition.

Other objects and their attendant advantages will become apparent from the following description of the invention and appended claims.

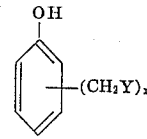
SUMMARY OF THE INVENTION

The aforementioned objects can be realized by incorporating into a mono or polyurea containing grease a minor amount of a Mannich Base prepared by reacting phenol with formaldehyde and an amine selected from the class consisting of diethanolamine, N,N-diethanol alkylenediamine, and diethylamine. The molar ratio of formaldehyde to amine to phenol in the Mannich Base product should preferably be between about 0.5-5:0.5-5:1.

By incorporating this particular Mannich Base into the mono or polyurea grease, the rust inhibition of the grease is significantly increased. Concomitantly, the other physical properties of the novel grease are not seriously affected.

DETAILED DESCRIPTION OF THE INVENTION

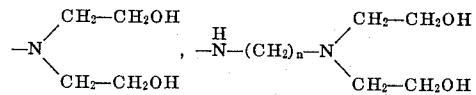
The improved grease composition of the instant invention can be realized by admixing in a major portion of a lubricating oil, from 0.5 to 20 weight percent of a mono or polyurea thickener and from 0.1 to 10 weight percent of a Mannich Base. The Mannich Base is a mixture of compounds prepared by reacting phenol, formaldehyde and an amine. It is believed that a major portion of the compounds have the following generalized structure:



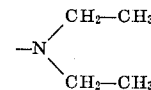
wherein:

x is an integer from 1 to 4 and preferably from 1 to 3;

Y is a univalent amino radical selected from the group consisting of



and



and

wherein:

n is an integer from 1 to 4 and preferably from 2 to 3.

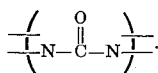
The above structural formula represents a broad and simplified version of the Mannich Base useful in the practice of this invention. The product is a mixture of compounds wherein x varies from 1 to 4. In addition, compounds not described by the above formula may be present, e.g., compounds wherein the hydroxyl unit on the phenolic group enters into a reaction with the formaldehyde or amino co-reactant, etc. Other reactions between the three reactants or any two of them may also take place and the reaction products present in the mixture. Thus, it is apparent that while the above chemical formula is descriptive of the majority of the compounds within the mixture, it should not be interpreted as limiting the invention to the compounds having exact structure as shown. The preferred Mannich Base is prepared by reacting phenol, formaldehyde and diethanol amine.

The compounds are prepared by contacting phenol, formaldehyde and amine in a suitable reactor at a temperature of 150° to 400°F and preferably from 200° to 300°F under sufficient pressure to maintain the three reactants in liquid phase, generally from 0 to 150 psig. The contacting is conducted for a period of 0.5 to 25 hours and preferably from 3 to 20 hours. An inert reaction solvent may be employed or the reaction can be conducted with an excess of one or more of the reactants. The solvents, if employed, should preferably be a mutual solvent or possess good solvency for the reactants. Exemplary reaction solvents include aliphatic alcohols having from 1 to 8 carbons such as isobutyl alcohol, pentanol, isopropyl alcohol, etc.

The amount of reactants charged to the reaction vessel usually varies from 0.5 to 5 molar parts of formaldehyde and from 0.5 to 5 molar parts of amine for each molar part of phenol. The preferred molar ratio varies from 2 to 4.4 parts of formaldehyde and from 2 to 4 parts of amine per part of phenol.

Mono or Polyurea Thickening Agent

The mono or polyurea thickening agent as employed in this invention is a water and oil-insoluble organic compound having a molecular weight between about 350 and 2,500 AMUs and having at least one ureido group and preferably between about 2 and 6 ureido groups. A ureido group as referred to herein defined as

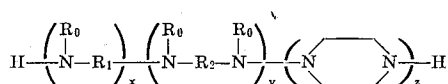


The mono or polyurea compound should preferably have as few terminal primary amine groups, i.e., a compound having a terminal (NH₂) group, as possible and should preferably not have any free carboxylic acid groups. A particularly preferred polyurea compound has an average between 3 and 4 ureido groups and has a molecular weight between about 600 and 1200 AMUs.

The mono or polyurea compounds are prepared by reacting the following components:

I A diisocyanate having the formula: OCN-R-NCO wherein R is a hydrocarbylene having from 2 to 30 carbons and preferably an arylene having from 6 to 15 carbons and more preferably an arylene having 7 carbons;

II A polyamine having a total of 2 to 40 carbons and having the formula:



wherein R₁ and R₂ are the same or different type of hydrocarbylenes having from 1 to 20 carbons and preferably from 2 to 10 carbons and more preferably from 2 to 4 carbons;

R₃ is selected from hydrogen or a C₁-C₄ alkyl and preferably hydrogen;

x is an integer from 0 to 2;

z is an integer from 0 to 1; and

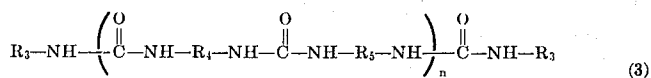
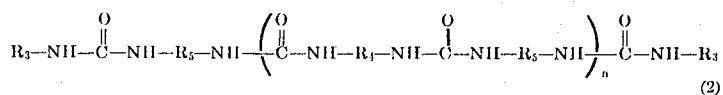
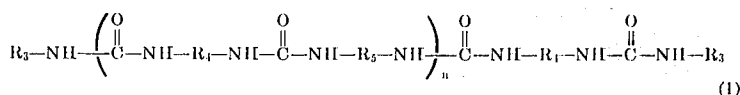
y is an integer equal to 1 when z is 0 and 0 when z is 1.

III A monofunctional compound selected from the group consisting of monoisocyanate having from 1 to 30 carbons, preferably from 10 to 24 carbons, a monoamine having from 1 to 30 carbons preferably from 10 to 24 carbons, or mixtures thereof.

The reaction can be conducted by contacting the three reactants in a suitable reaction vessel at a temperature between about 60° to 320°F, preferably from 100° to 300°F, for a period from 0.5 to 5 hours and

preferably from 1 to 3 hours. The molar ratio of the reactants present usually varies from 0.1-2 mols of monoamine or monoisocyanate and 0-2 mols of polyamine for each mol of diisocyanate. When the monoamine is employed, the molar quantities are preferably (n+1) mols of diisocyanate, (n) mols of polyamine and 2 mols of monoamine. When the monoisocyanate is employed, the molar quantities are preferably (n) mols of diisocyanate, (n+1) mols of polyamine and 2 mols of monoisocyanate.

A particularly preferred class of mono or polyurea compounds has structures defined by the following general formulae:



wherein:

n is an integer from 0 to 3;

R₃ is the same or different hydrocarbyl having from 1 to 30 carbon atoms, preferably from 10 to 24 carbons;

R₁ is the same or different hydrocarbylene having from 2 to 30 carbon atoms, preferably from 6 to 15 carbons; and

R₅ is the same or different hydrocarbylene having from 1 to 30 carbon atoms, preferably from 2 to 10 carbons.

As referred to herein, hydrocarbyl is a monovalent organic radical composed of hydrogen and carbon and may be aliphatic, aromatic or alicyclic or combinations thereof, e.g., aralkyl, alkyl, aryl, cycloalkyl, alkylcycloalkyl, etc., and may be saturated or olefinically unsaturated (one or more double bonded carbons, conjugated or nonconjugated). The hydrocarbylene, as defined in R₁ and R₅ above, is a divalent hydrocarbon radical which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., alkylaryl, aralkyl, alkylcycloalkyl, cycloalkylaryl, etc., having its two free valences on different carbon atoms.

The mono or polyureas having the structure presented in Formula 1 above are prepared by reacting (n+1) mols of diisocyanate with two mols of a monoamine and (n) mols of a diamine. (When n equals zero in the above Formula 1, the diamine is deleted.) Mono or polyureas having the structure presented in Formula 2 above are prepared by reacting (n) mols of a diisocyanate with (n+1) mols of a diamine and two mols of a monoisocyanate. (When n equals zero in the above Formula 2, the diisocyanate is deleted.) Mono or polyureas having the structure presented in Formula 3 above are prepared by reacting (n) mols of a diisocyanate with (n) mols of a diamine and one mol of a monoisocyanate and one mol of a monoamine. (When n equals zero in Formula 3, both the diisocyanate and diamine are deleted.)

In preparing the above mono or polyureas, the desired reactants (diisocyanate, monoisocyanate, diamine and monoamine) are admixed within a suitable reaction vessel in the proper proportions. The reaction may proceed without the presence of a catalyst and is

initiated by merely contacting the component reactants under conditions conducive for the reaction. Typical reaction temperatures range from 20°C to 100°C under atmospheric pressure. The reaction itself is exothermic and, accordingly, by initiating the reaction at room temperature, elevated temperatures are obtained. However, external heating or cooling may be desirable.

The mono or polyurea thickener will usually be present in the grease composition at a concentration of 0.5 to 20 weight percent and preferably from 3 to 10 weight percent and sufficient to thicken the final composition to the consistency of grease.

Mono or Polyurea Reactants

The monoamine or monoisocyanate used in the formulation of the mono or polyurea will form the terminal end groups. These terminal end groups will have from 1 to 30 carbon atoms, but are preferably from 5 to 28 carbon, and more desirably from 6 to 25 carbon atoms.

Illustrative of various monoamines are pentylamine, hexylamine, heptylamine, octylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, eicosylamine, dodecenylamine, hexadecenylamine, octadecenylamine, octadecadienylamine, abietylamine, aniline, toluidine, naphthylamine, cumylamine, bornylamine, fenchylamine, tertiary butyl aniline, benzylamine, beta-phenethylamine, etc. Particularly preferred amines are prepared from natural oils or fats or from straight chain acids derived therefrom. These starting materials may be converted to amides by reactions with ammonia and the amides dehydrated to give nitriles. The nitriles are then reduced to give the desired amines. Exemplary amines prepared by the method include stearylamine, laurylamine, palmitylamine, oleylamine, petroselinylamine, linoleylamine, linolenylamine, eleostearylamine, etc. The unsaturated amines are particularly preferred.

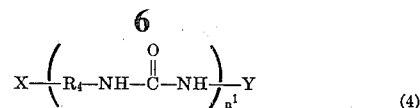
Illustrative of monoisocyanates are hexylisocyanates, decylisocyanate, dodecylisocyanate, tetradecylisocyanate, hexadecylisocyanate, phenylisocyanate, cyclohexylisocyanate, xyleneisocyanate, cumeneisocyanate, abietylisocyanate, cyclooctylisocyanate, etc.

Polyamines, which form internal hydrocarbon bridges between the ureido groups usually contain from 2 to 40 carbon atoms, preferably from 2 to 30 carbon atoms, and more desirably from 2 to 20 carbon atoms. Exemplary polyamines include diamines such as ethylenediamine, propylenediamine, butylenediamine, hexylenediamine, dodecylenediamine, octylenediamine, hexadecylenediamine, cyclohexylenediamine, cyclooctylenediamine, phenylenediamine, tolylenediamine, xylenediamine, dianiline methane, ditoluidinemethane, bis(aniline), bis(toluidine), piperazine, etc.

Triamines such as N-amino-ethyl piperazine, diethylenetriamine, dipropylene triamine, tert-N-methyldiethylene triamine, etc., and higher polyamines such as triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, etc.

Representative examples of diisocyanates include hexylenediisocyanate, decylenediisocyanate, octadecylenediisocyanate, phenylenediisocyanate, tolylenediisocyanate, bis-(diphenylisocyanate), methylene bis(phenylisocyanate), etc.

Another class of mono or polyurea compounds which may be successfully employed in the practice of this invention include the following:



wherein: n^1 is an integer of 1 to 3, R_4 is defined supra; X and Y are monovalent radicals selected from Table I below.

TABLE I

X	Y
$\text{R}_8 - \overset{\text{O}}{\parallel} \text{C} - \text{NH} -$ $\text{R}_7 - \overset{\text{O}}{\parallel} \text{C} - \text{N} -$ $\text{R}_5 -$	$\text{R}_8 - \overset{\text{O}}{\parallel} \text{C} - \text{NH} - \text{R}_5 -$ $\text{R}_7 - \overset{\text{O}}{\parallel} \text{C} - \text{N} - \text{R}_5 -$ $\text{R}_5 -$

In the Table, R_5 is defined supra, R_6 is the same as R_3 and defined supra, R_7 is selected from the group consisting of arylene radicals of 6 to 16 carbon atoms and alkenyl groups of 2 to 30 carbon atoms, and R_8 is selected from the group consisting of alkyl radicals having from 10 to 30 carbon atoms and aryl radicals having from 6 to 16 carbon atoms.

Mono or polyurea compounds described by the above formula (4) can be described as amides and imides of mono, di, and tri ureas. These materials are formed by reacting in the selected proportions suitable carboxylic acids or internal carboxylic anhydrides, with a diisocyanate and an amine or diamine. The mono or polyurea compounds are prepared by blending the several reactants together in a suitable reaction vessel and heating them to a temperature ranging from 70°F. to 400°F. for a period sufficient to cause formation of the compound, generally from 5 minutes to 1 hour.

Suitable carboxylic acids include aliphatic carboxylic acids of about 11 to 31 carbon atoms and aromatic carboxylic acid of 7 to 17 carbon atoms. Examples of suitable acids include aliphatic acids such as lauric, myristic, palmitic, margaric, stearic, arachidic, behenic, lignoceric acid, etc.; and aromatic acid such as benzoic acid, 1-naphthoic acid, 2-naphthoic acid, phenylacetic acid, hydrocinnamic acid, cinnamic acid, mandelic acid, etc. Suitable anhydrides which may be employed are those derived from dibasic acid which form a cyclic anhydride structure, for example, succinic anhydride, maleic anhydride, phthalic anhydride, etc. Substituted anhydrides, such as alkenyl succinic anhydride of up to 30 carbon atoms are further examples of suitable materials.

Examples of suitable diisocyanates, monoisocyanates, monoamines and diamines are described supra.

The mono or polyurea compounds are generally mixtures of compounds having structures wherein n^1 varies from 0 to 4, or n^1 varies from 1 to 3, existent within the grease composition at the same time. For example, when a monoamine, a diisocyanate and a diamine are concurrently present within the reaction zone, as in the preparation of ureas having the structure shown in Formula 2, some of the monoamine may react with both sides of the diisocyanate to form a diurea. In addition to the formulation of diurea, simultaneous reactions

can be occurring to form the tri, tetra, penta, hexa, octa, etc., ureas. Particularly good results have been realized when the polyurea compound has an average of four ureido groups.

The lubricating oil generally has a viscosity of 35 to 55,000 SUS at 100°F and preferably from 20 to 500 SUS at a temperature of 210°F.

In a particularly preferred embodiment, an alkaline earth metal aliphatic monocarboxylate is also included within the formulation. By incorporating the metal carboxylate into the grease composition, the total amount of mono or polyurea required to thicken the grease to the desired consistency can be substantially reduced. Moreover, the presence of the metal carboxylate imparts good extreme pressure properties to the grease.

The alkaline earth metal aliphatic monocarboxylate has from 1 to 3 carbons. Any of the alkaline earth metals can be employed herein, e.g., magnesium, calcium, strontium, barium, etc. However, calcium is the most preferred. The carboxylate group preferably has from 1 to 2 carbon atoms and more preferably 2 carbon atoms. Exemplary compounds which may be successfully employed herein include calcium formate, barium formate, magnesium formate, magnesium acetate, calcium acetate, strontium acetate, barium acetate, calcium propionate, barium propionate, magnesium propionate, etc.

The amount of alkaline earth metal aliphatic monocarboxylate present within the grease composition may vary depending upon the lubricating property desired, the particular mono or polyurea constituent selected, the type of alkaline earth metal aliphatic monocarboxylate selected, etc. However, generally the metal carboxylate will range from 3 to 30 weight percent of the final grease composition and preferably between about 4 and 15 weight percent. The ratio of alkaline earth metal aliphatic monocarboxylate to the mono or polyurea constituent will also vary depending upon the aforementioned conditions, but will generally range on a weight basis from 1 to 15 parts of metal carboxylate per part of mono or polyurea and preferably from 3 to 7 parts per part of mono or polyurea.

Preparation of Grease Composition

The greases exhibiting superior properties of this invention are preferably prepared by the in situ production of the mono or polyurea within the lubricating oil. In instances where an alkaline earth metal carboxylate is also employed, it may also be prepared in situ. In this embodiment, the lubricating oil is charged to the grease kettle along with the mono or polyurea precursors, i.e., the reactants which combine to form the mono or polyurea.

After the formation of the mono or polyurea compounds, the grease kettle is charged with an alkaline earth metal hydroxide or oxide and a carboxylic acid. The ratio of alkaline earth metal hydroxide to carboxylic acid on an equivalent basis can vary from 1 to 4:1 and is preferably between 1 and 2:1. The kettle is maintained at a temperature between 70°F and 150°F during the process to effect the neutralization reaction of the alkaline earth metal hydroxide or oxide and the carboxylic acid. During the reaction, water is released and is preferably removed from the system by applying a slight vacuum on the kettle of 20 to 29 inches of mercury and heating to about 212°F and higher.

The Mannich Base made can then be added to the grease composition to the proper concentration. Gen-

erally, from 0.1 to 10 weight percent of the Mannich Base will be present in the grease composition for best results and more preferably from 0.5 to 2 weight percent.

The grease composition can be further processed by subjecting it to shear hardening. Shear hardening is performed by milling the grease in an extrusion type mill under elevated pressures. This milling improves the dispersion of the mono or polyurea and metal carboxylate throughout the base oil resulting in a grease of greatly improved consistency. U.S. application Ser. No. 111,517 filed Feb. 1, 1971, now abandoned discloses a preferred method of shear hardening a grease which can be successfully employed for the composition of this invention.

Other Additives

In addition to the thickening agents, alkaline earth metal carboxylate and Mannich Base rust inhibitor, other additives may be successfully employed within the grease composition of this invention without affecting its high stability ad performance over a wide temperature scale. One type of additive is an antioxidant or oxidation inhibitor. This type of additive is employed to prevent varnish and sludge formation on metal parts and to inhibit corrosion of alloyed formation on metal parts and to inhibit corrosion of alloyed bearings. Particularly useful grease antioxidants include phenyl-alpha-naphthyl amine, bis-(alkylphenyl)amine, N,N-diphenyl-p-phenylenediamine, 2,2,4-trimethyldihydroquinoline oligomer, bis(4-isopropylaminophenyl)ether, N-acyl-p-aminophenol, N-acylphenothiazines, N-hydrocarbylamides of ethylenediamine tetraacetic acid, alkylphenol-formaldehyde-amine poly condensates, etc.

Another additive which may be incorporated into the grease composition of this invention is an anticorrosive. The anticorrosive is employed to inhibit oxidation so that the formation of acidic bodies is suppressed and to form films over the metal surfaces which decrease the effect of corrosive materials on exposed metallic parts. A particularly effective corrosion inhibitor is sodium nitrite.

Another type of additive which may be employed herein is a metal deactivator. This type of additive is employed to prevent or counteract catalytic effects of metal on oxidation generally by forming catalytically inactive complexes with soluble or insoluble metal ions. Typical metal deactivators include complex organic nitrogen and sulfur-containing compounds such as certain complex amines and sulfides. An exemplary metal deactivator is mercaptobenzothiazole.

In addition to the above, several other grease additives may be employed in the practice of this invention and include stabilizers, tackiness agents, dropping point improvers, lubricating agents, color correctors, odor control agents, etc.

The following examples are presented to illustrate the practice of specific embodiments of this invention and should not be interpreted as imitations upon the scope of the invention.

EXAMPLE 1

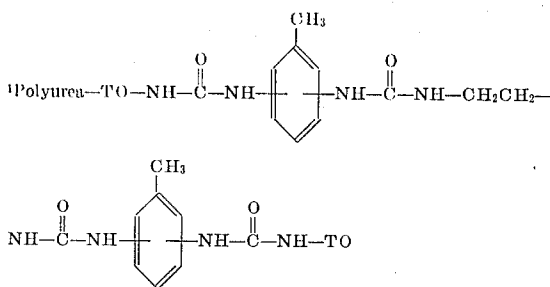
This example is presented to illustrate the preparation of a preferred polyurea/alkaline earth metal carboxylate grease. A 48-liter stainless steel reaction vessel equipped with a stirrer is charged with 7,500 grams of a blend of a paraffinic and naphthenic oil having a

viscosity of 78 SSU at 210°F hereinafter referred to as "base oil", 880 grams of tall oil fatty amine and 92 grams of ethylene diamine. The contents of the vessel are stirred for 20 minutes at 130°F and thereafter admixed with 6,000 grams of base oil and 548 grams of tolylene diisocyanate. The vessel is agitated and held at a temperature of 150° for a 30-minute period.

The vessel contents are thereafter milled in an extrusion type mill at a pressure of 7,500 psi and then heated to 200°F. A small sample of the grease is analyzed and trace amounts of diisocyanate are detected. An additional 40 grams of ethylene diamine are charged to the vessel and mixed with the milled grease for a period of 10 minutes at a temperature of 210°F. At the end of the 10-minute period, the vessel is cooled to 150°F. At the end of the 10-minute period, the vessel is cooled to 150°F and 5,000 grams of additional base oil with 2,480 grams of hydrated lime ($\text{Ca}(\text{OH})_2$) are charged to the vessel. The lime and base oil are admixed with the previously milled grease for 5 minutes at which time an additional 5,460 grams of base oil and 2,800 grams of acetic acid are slowly charged to the vessel over a 25-minute period. The admixture is agitated for 30 minutes at 150°F to assure that the neutralization reaction between the calcium hydroxide and acetic acid is complete. Thereafter, an aqueous solution of 320 grams of a commercial sodium nitrite rust inhibitor is charged to the vessel and the contents milled at 7,500 psi. The grease is heated to 250°F to remove water and then cooled to 160°F. The grease is then admixed with 8,920 grams of base oil and recycled through a mill at a pressure of 7,500 psi. The product grease has an undisturbed penetration (P_0) of 232 and after 60 strokes a worked penetration (P_{60}) of 286 (ASTM 217). The ASTM dropping point is about 460°F (ASTM-D-2265).

A sample of the grease is calculated to have the following:

Calcium Acetate	11.7 wt %
Polyurea ¹	3.8 wt %
Base Oil	82 wt %



wherein TO is a tall oil radical.

EXAMPLE 2

The preparation of an exemplary Mannich Base of the type useful in this invention is illustrated in this example. A 2-liter glass flask is charged with 141 grams of phenol, 198 grams of formaldehyde, 630 grams of diethanol amine and 270 grams of isobutyl alcohol. The reactor contents are heated to reflux at 220°F under atmospheric pressure and maintained at these conditions for 20 hours. The solvent is then stripped from the product. The product Mannich Base is recovered or analyzed. The nitrogen content is measured at 9.63 wt percent. The product alkalinity value is 364 mgKOH/gm.

EXAMPLE 3

A 2-liter flask is charged with 23.5 grams of phenol, 33 grams of formaldehyde, 162 grams of aminopropyl diethanol amine and 125 ml of isobutyl alcohol. The contents are heated to reflux under atmospheric pressure and maintained at those conditions for 20 hours. The solvent is then stripped from the product. The product is analyzed and found to contain 13.9 weight percent nitrogen.

EXAMPLE 4

A 2-liter flask is charged with 23.5 grams of phenol, 33 grams of formaldehyde, 73.1 grams of diethylamine and 125 ml of isobutyl alcohol. The contents are heated to reflux under atmospheric pressure and maintained at these conditions for 20 hours. The solvent is then stripped from the product. The product had an alkalinity value of 454 mgKOH/gram.

EXAMPLE 5

This example is presented to illustrate the effectiveness of the Mannich Bases of this invention as compared to other comparable Mannich Bases. The preparation of the instant Mannich Base is substantially the same as described in Example 2, the reactant having been present in a ratio of 4.4. mols of formaldehyde and 4 mols of diethanol amine for each mol of phenol employed. The Mannich Base is referred to as $\text{C}_6\text{H}_5\text{OH}/\text{CH}_2\text{O}/\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$. The comparison Mannich Base is prepared substantially as above except that tetrapropenyl phenol is substituted for the phenol above. It was made by reacting 4.4 mols of formaldehyde and 4 mols of diethanol amine for each mol of tetrapropenyl phenol. This base is referred to as $\text{Alk-C}_6\text{H}_5\text{OH}/\text{CH}_2\text{O}/\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$.

The Mannich Base prepared by Example 3 is referred to as $\text{C}_6\text{H}_5\text{OH}/\text{CH}_2\text{O}/\text{NH}-\text{C}_3\text{H}_6-\text{N}(\text{C}_2\text{H}_4\text{OH})_2$. The Mannich Base prepared by Example 4 is referred to as $\text{C}_6\text{H}_5\text{OH}/\text{CH}_2\text{O}/\text{NH}(\text{C}_2\text{H}_5)_2$.

Thereafter, varying amounts of the Mannich Bases are incorporated into a grease prepared substantially by the method of Example 1 except containing 3.9 wt percent of the polyurea thickener, 12.9 wt percent of the calcium acetate, about 2 wt percent NaNO_2 , and a blend of paraffinic base oils having a viscosity of 55 SSU at 210°F.

The following Table I illustrates the effect of the Mannich Bases on the hardness of the grease as measured by ASTM D-217 (worked penetration). On those greases which were not substantially affected, a modified AASTM D-1743 rust test is performed with 3 percent synthetic sea water (ASTM 665) and 97 percent distilled water. The rust test rating is 0 = no rust and 5 = very rusty with intermediate values between 0 and 5 representing increasing degrees of rust. This rating system is more fully described in IR 220 (British Institute of Petroleum) and is sometimes called the Emcor rating system. Ratings are determined after the bearing is stored for 1 day at 77°F.

TABLE I

Properties of Mono or Polyurea Grease				
Ex.	Type of Additive	Content (wt %)	Worked Pen. (P_{60})	ASTM Rust Rating
1	none	—	319	4
2	$\text{C}_6\text{H}_5\text{OH}/\text{CH}_2\text{O}/\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$	5	311	0

TABLE I-Continued

Properties of Mono or Polyurea Grease				
Ex.	Type of Additive	Content (wt %)	Worked Pen. (P ₆₀)	ASTM Rust Rating
3	same	2.5	313	0
4	Alk-C ₆ H ₅ OH/CH ₂ O/NH-(C ₂ H ₅ OH) ₂	5	439	—
5	same	2.5	439	—
6	C ₆ H ₅ OH/CH ₂ O/NH ₂ -C ₃ H ₆ N-(C ₂ H ₅ OH) ₂	1	294	0
7	C ₆ H ₅ OH/CH ₂ O/NH(C ₂ H ₅) ₂	1	290	0
8	C ₆ H ₅ OH/CH ₂ O/NH ₂ C ₂ H ₄ OH*	1	296	3

*Prepared by the steps recited in Ex. 2 except substituting ethanol amine for the diethanol amine.

The above table clearly illustrates the superiority of the Mannich Base of the present invention over the comparable Mannich Bases. As shown, in Experiments 2 and 3 (employing a Mannich Base of the instant invention), the additive slightly hardened the grease from 319 to 311 or 313 whereas in Experiments 4 and 5, the additive significantly defeated the thickening action of the polyurea by softening the grease to a penetration of 439.

The above table also illustrates the excellent rust inhibition from using the claimed Mannich Bases over a close homolog (comparison of Experiments 2, 3, 6 and 7 with Experiment 8).

EXAMPLE 6

This example is presented to illustrate the breadth of the instant Mannich Bases and the effectiveness of these various bases in reducing rust while not substantially interfering with the physical properties of the grease. The Mannich Bases are prepared in substantially the same manner as described in Example 2. The molar ratio of the various reactants are varied.

The Mannich Bases are incorporated into a polyurea grease prepared by the method of Example 1 except containing 3.9 wt percent of the polyurea thickener and 13.9 wt percent of the calcium acetate and a blend of paraffinic base oils having a viscosity of 55 SSU at 210°F.

The ASTM worked penetration and the ASTM rust rating of the greases are measured and reported in the following Table II.

TABLE II

Effect of Mannich Base on Mono or Polyurea Grease			
Mannich Base Additive		Worked Pen. (P ₆₀)	Rust Test (3% Sea Water)
Mol Ratio of Reactants *	Conc. (wt %)		
—	—	319	3
1 : 4.4 : 4	5	311	0
do.	2.5	313	0
do.	1.0	290	0
do.	0.5	282	0
do.	0.25	280	2
1 : 3.3 : 3	1.0	271	0
do.	0.5	290	0
1 : 2.2 : 2	1.0	278	0
do.	0.5	273	0
1 : 1.1 : 1	1.0	267	0
do.	0.5	280	0

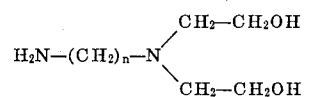
* Molar ratio of phenol to formaldehyde to diethanol amine in reaction product.

We claim:

1. A grease composition comprising a major portion of an oil of lubricating viscosity, (1) from 0.5 to 20

weight percent of a water and oil-insoluble mono or polyurea thickening agent having at least one ureido group and having a molecular weight between about 350 and 2,500, (2) from 3 to 30 weight percent of an alkaline earth metal aliphatic monocarboxylate having from 1 to 3 carbons, and (3) from 0.1 to 10 weight percent of a Mannich Base prepared by reacting phenol with formaldehyde and an amine selected from the class consisting of diethanolamine, N,N-diethanol alkylenediamine and diethylamine, the molar ratio of formaldehyde to amine to phenol being between about 0.5 and 5:0.5 and 5:1.

2. The grease composition defined in claim 1 wherein said N,N-diethanol alkylenediamine has the formula:



wherein n is an integer from 1 to 4.

3. The grease composition defined in claim 1 wherein said Mannich Base is prepared by reacting between 2 and 4.4 molar parts of formaldehyde with between 2 and 4 molar parts of said amine for each part of said phenol.

4. The grease composition defined in claim 3 wherein said amine is diethanolamine.

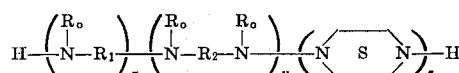
5. A grease composition comprising (1) a major portion of an oil of lubricating viscosity, (2) from 3 to 30 weight percent of an alkaline earth metal aliphatic monocarboxylate having from 1 to 3 carbons, (3) from 0.5 to 20 weight percent of a mono or polyurea thickener prepared by reacting

a. a diisocyanate having the formula



wherein R is a hydrocarbylene having from 2 to 30 carbons;

b. a polyamine having the formula



wherein R₀ is selected from the group consisting of hydrogen, a C₁-C₄ alkyl or mixtures thereof;

R₁ and R₂ are the same or different type of hydrocarbylene having from 1 to 20 carbons;

x is an integer from 0 to 2;

z is an integer from 0 to 1; and

y is an integer equal to 1 when z is 0 and 0 when z is 1;

c. a monofunctional compound selected from the group consisting of C₁-C₃₀ monoisocyanate, C₁-C₃₀ monoamines or mixtures thereof; and (4) from 0.1 to 10 weight percent of a Mannich Base prepared by reacting phenol with formaldehyde and an amine selected from the class consisting of diethanolamine, N,N-diethanol alkylenediamine and diethylamine, the molar ratio of formaldehyde to amine to phenol being between about 0.5 and 5:0.5 and 5:1.

6. The grease composition defined in claim 5 wherein said diisocyanate is tolylene diisocyanate, said poly-

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amine is ethylene diamine and said monofunctional compound is a C₁₀ to C₂₄ monoamine.

7. The grease composition defined in claim 6 wherein 2 molar parts of said diisocyanate are reacted with 1 molar part of said polyamine and 2 molar parts of said monoamine.

8. The grease composition defined in claim 7 wherein said amine is diethanolamine.

9. The grease composition defined in claim 7 wherein the Mannich Base is prepared by reacting 2 to 4.4 molar parts of formaldehyde and 2 to 4 molar parts of

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diethanol amine with each molar part of said phenol.

10. The grease composition defined in claim 5 wherein said alkaline earth metal aliphatic monocarboxylate is calcium or barium acetate.

11., The grease composition defined in claim 1 wherein said alkaline earth metal aliphatic monocarboxylate is calcium acetate.

12. The grease composition defined in claim 10 wherein said alkaline earth metal aliphatic monocarboxylate is calcium acetate.

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