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3,846,315

GREASE THICKENED WITH POLYUREA METAL SALTS AND ALKALINE EARTH METAL ALIPHATIC MONOCARBOXYLATE

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15 Claims

ABSTRACT OF THE DISCLOSURE

An improved grease composition is disclosed comprising a major portion of a lubricating oil containing (1) a polyurea metal salt wherein the polyurea portion of the molecule is prepared by reacting a diisocyanate, a polyamine with a monoisocyanate or monoamine and the metal salt portion is prepared by introducing into the above reaction product an acid group, such as a carboxylic or a sulfonic acid group, and neutralizing the terminal acid group with a basic metal compound, and (2) an alkaline earth metal aliphatic monocarboxylate having from 1 to 3 carbons.

BACKGROUND OF THE INVENTION

This invention relates to a novel grease composition. More particularly, this invention concerns grease composition containing a novel metal-containing polyurea thickening agent.

Modern technology is currently supplying the general public and the process industries with machinery which is designed to operate under a wider range of temperatures and under greater loads than previously available. In addition, most of the newer machines are designed to operate at extremely high speeds. Many of these machines require certain specific lubricating properties which are not available in the conventional lubricants. Thus, modernization of high speed and high temperature equipment has strained the petroleum industry for the development of a second generation of lubricants capable of satisfying the requirements of the new machines. Recently, for example, there has been an increased demand for grease lubricants capable of performing well at temperatures above 300° F. in high speed bearings and gears for periods in excess of 500 hours. In addition, with the further development of the high speed sealed bearings, the grease must be able to endure for the life of the bearing.

There have been numerous grease compositions developed which satisfy most of the new more stringent requirements. Many of these compositions, however, are entirely too expensive for commercialization or only meet some of the lubricating requirements and fail in others. One type of lubricant currently available is the ubiquitous lithium greases. These greases are simply a mixture of a hydrocarbon base oil and a lithium hydroxy stearate thickener with minor amounts of other additives. Although these greases exhibit good lubricating properties and perform well at moderate temperatures, their application in high temperature and high speed machinery has not been entirely successful. The lithium greases tend to deteriorate in these machines at high temperatures, particularly at temperatures above 300° F. The deterioration leads to a rapid loss of lubrication and ultimately failure of the equipment.

Another type of grease composition which has excellent lubricating properties at the higher temperatures is comprised of a lubricating oil (natural or synthetic) containing a polyurea thickener. This type of lubricant is dis-

closed in U.S. Pat. Nos. 3,242,210; 3,243,372; 3,281,361; 3,284,357; 3,346,497; and 3,401,027, all assigned to the Chevron Research Company. The polyurea thickener imparts a significant high temperature stability to the grease and, in fact, effects a mild anti-thixotropic property, i.e., increase in viscosity with increasing shear, to the lubricant. This property of the lubricant is advantageous to prevent the segregation or loss of grease from the moving parts of the machine.

Another type of grease which has excellent lubricating properties is comprised of a lubricating oil containing a polyurea metal salt thickener. This type of grease is disclosed in U.S. application Ser. No. 259,053, filed June 2, 1972, now Pat. No. 3,769,212. While the above polyurea greases have solved most of the problems associated with the older lubricants, they are handicapped by the requirement of large amounts of polyurea or polyurea metal salt (between 8 and 20 weight percent) and its relatively high costs. In addition, the polyurea or polyurea metal salts do not impart extreme pressure properties to the lubricant and, accordingly, E.P. additives must be added in applications involving high contact pressures. A need therefore still exists for an improved grease thickener which, when incorporated into a grease composition, can be used for longer periods at elevated temperatures, that exhibits good stability over prolonged periods, that exhibits both extreme pressure and anti-wear properties and that is relatively inexpensive to make.

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

It is another object of this invention to provide an improved grease composition having improved lubricating properties at high temperatures for prolonged periods.

It is another object of this invention to provide a relatively inexpensive grease composition capable of performing well at high temperatures in high speed applications and which exhibits good Extreme Pressure properties.

It is another object of this invention to provide a method of making an improved grease composition.

SUMMARY OF THE INVENTION

The foregoing objects and their attendant advantages can be realized with a grease composition containing (1) an alkali or alkaline earth metal salt of a polyurea compound having a minimum of two ureido groups and having a molecular weight between about 250 and 2500 and preferably between about 300 and 2000 and (2) an alkaline earth metal aliphatic monocarboxylate having from 1 and 3 carbons. The polyurea salts can be prepared by two different reaction schemes. In the first, a diisocyanate, a polyamine (preferably a diamine) and a monoisocyanate or monoamine are reacted with an amino acid metal salt or an amino carboxylic acid which is thereafter reacted with a basic metal compound capable of hydrolyzing the carboxylic acid group. In the second reaction scheme, a diisocyanate and a polyamine (preferably a diamine) are reacted with a monoamine or monoisocyanate to form an intermediate polyurea. When the terminal group is an isocyanate, it is then contacted with water in the presence of a caustic to form the corresponding polyurea amine and by-product carbon dioxide. The polyurea amine is then reacted with an anhydride, lactone or sultone and thereafter saponified with a basic metal compound to form the polyurea metal salt.

By incorporating an alkaline earth metal carboxylate within the grease composition, we have found that the polyurea content may be reduced by 50 percent of that required in the prior polyurea lubricants for the same dropping point and other physical properties. Moreover, the presence of the metal carboxylate imparts good ex-

molar part of a monoamine. This reaction product will have a free terminal isocyanate group which can be hydrolyzed to a free terminal amine group by reaction with an aqueous base. When $n+1$ molar parts of polyamine and n molar parts of diisocyanate are employed and a monoisocyanate is used in place of the monoamine above, the resulting polyurea compound has a terminal amine group and, hence, the hydrolysis step is not necessary. The polyurea reaction products having a free terminal amine group is then further reacted with an anhydride, lactone or sultone having from 2-24 carbons to form a polyurea having one or more free carboxylic acid or sulfonic acid groups. The polyurea metal salt is formed by reacting the polyurea carboxylic or sulfonic acid with a metal base. Polyurea metal salts having structures set forth by Formula 2 are prepared when a monoamine is employed. When a monoisocyanate is used, the polyurea metal salts will have structures as set forth in Formula 3.

In another reaction scheme, the carboxylic or sulfonic acid group is attached "in situ" during the reaction of the polyurea precursors. In this embodiment, the compounds prepared have structures as shown in Formulae 1 and 4. These compounds are prepared by reacting n or n_1 molar parts of a polyamine with $n+1$ or n_1 molar parts of a diisocyanate, one molar part of a monoamine or monoisocyanate and one molar part of an amino carboxylic acid, amino sulfonic acid or a metal salt thereof. The reaction product having a free carboxylic or sulfonic acid group is then reacted with a metal base to form polyurea metal salt.

Preferred Reaction Scheme

In the preferred preparation, salts defined by formulae 1 and 4, the desired reactants (diisocyanate, polyamine, carboxyl group source and monoamine or monoisocyanate) are admixed within a suitable reaction vessel in the proper proportions and preferably within an inert liquid reaction medium. The reaction may proceed without the presence of a catalyst and is initiated by merely contacting the reactants under conditions conducive for the reaction. Typical reaction temperatures range from 200 to 300° F. and preferably between about 150 and 260° F. Elevated pressures as well as reduced pressures may be employed. In many cases, the reaction will be exothermic and the temperature will rise during the course of the reaction. External heating or cooling, however, may be employed as required. The reaction conditions are maintained for a period sufficient to produce the intermediate polyurea with a free terminal carboxyl or sulfonic acid group. The reaction time is dependent upon the process conditions, reactants, presence of a catalyst, etc., but generally varies between about 0.5 and 4 hours.

After formation of the intermediate polyurea compound, i.e., formation of a polyurea compound having a terminal sulfonic acid, or carboxylic acid, or ester thereof, the reaction vessel is charged with a basic metal compound, preferably within an aqueous or alcoholic solution. The metal base reacts to form the terminal carboxyl or sulfonic acid groups to produce the polyurea metal salt and by-product water, or alcohol. The reaction may also proceed without the presence of a catalyst and is initiated by merely contacting the intermediate polyurea with the basic metal compound under conditions conducive for the reaction. Typical reaction temperatures range from 200 to 350° F. and preferably between about 250 and 320° F. The reaction is preferably conducted at atmospheric pressure; however, it may be advantageous to conduct the reaction at subatmospheric pressures so that the by-product water, or alcohol may be continuously removed from the system as soon as it is formed. If the by-products are not stripped during the reaction, they may be removed from the system on completion of the reaction by heating the products to about 200° F. to 340° F. for approximately 30 to 120 minutes.

The reactions of the material described above are conducted preferably within an inert organic liquid medium,

typically a hydrocarbon oil and preferably the oil to be thickened. The entire volume of oil to be thickened may be present, or, alternatively, a concentrate of thickened material containing up to 60 weight percent of the polyurea metal salt composition may be formed and this may subsequently be diluted to the desired concentration of the thickener.

The reaction of the basic metal compound and the intermediate polyurea, may be avoided by replacing the carboxyl or sulfonic-acid group source reactant with a metal salt of an amino acid in the initial reaction. In this embodiment, the polyurea metal salt is formed directly by reacting the polyurea precursors (diisocyanate, polyamine, and monoisocyanate or monoamine) with an amino acid metal salt. The reaction conditions are the same as described above, i.e., temperatures of 150 to 300° F., etc.

The molar ratio of diisocyanate and polyamine present within the reaction medium during the initial reaction will control the size of the polyurea component. The ratio of monoamine, monoisocyanate and carboxylic group source or amine carboxylate salt present to the diisocyanate, on the other hand, will control the point at which the polyurea polymer chain is terminated. Thus, an excess of the latter reactants will terminate the polyurea chain early and result in low molecular weight products, whereas, an excess of the former reactants will result in long chain or high molecular weight products. The amounts of the various reactants within the reaction medium are set forth in the following Table II and expressed in terms of mol percent based on the mols of reactants present.

TABLE II
Concentration of Ingredients

Ingredient	Mol percent	
	Broad range	Preferred range
Diisocyanate.....	25-40	15-20
Polyamine ¹	5-30	9-20
Monoisocyanate ¹	9-20	14-20
Monoamine ¹	10-25	15-20
Amino carboxylate salt ¹	10-25	15-20
Carboxylic group source ¹	10-25	15-20
Basic metal compound ¹	10-25	15-20

¹ When employed.

The monoamine or monoisocyanate used in the formulation of the polyurea salt will form one of the terminal end groups. As already indicated, these terminal end groups will have from 1 to 30 carbon atoms, but are preferably from 5 to 28 carbons, and more desirably from 12-18 carbon atoms.

Illustrative of various monoamines are phenylamine, hexylamine, heptylamine, octylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, eicosylamine, dodecenyamine, hexadecenyamine, octadecenyamine, octadecadienyamine, abietylamine, aniline, toluidine, naphthylamine, cumylamine, bornylamine, fenchylamine, tertiary butyl aniline, benzylamine, beta-phenethylamine, etc. Particularly preferred amines are those made from natural oils or fats or from the straight chain acids derived therefrom. These starting materials may be converted to amides by reactions with ammonia and the amides can then be dehydrated to give nitriles. The nitriles are then reduced, preferably catalytically, 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 hexylisocyanate, decylisocyanate, dodecylisocyanate, tetradecylisocyanate, hexadecylisocyanate, phenylisocyanate, cyclohexylisocyanate, xylylisocyanate, cumenylisocyanate, abietylisocyanate, cyclooctylisocyanate, etc.

The polyamines which form one of the internal hydrocarbon bridges between the ureido groups preferably contain from 2 to 30 carbon atoms, more preferably from 2 to

20 carbon atoms, and more desirably from 2 to 10 carbon atoms. Exemplary polyamines include ethylenediamine, propylenediamine, butylenediamine, hexylenediamine, dodecylenediamine, octylenediamine, hexadecylenediamine, cyclohexylenediamine, cyclooctylenediamine, phenylenediamine, tolylenediamine, xylylenediamine, dianiline methane ditoluidinemethane, bis(aniline), bis(toluidine), piperazine, diethylene triamine, tert-N-methyl diethylene triamine, triethylene tetramine, dipropylene triamine, N-methyl-imino-bis(propyl amino) tetraethylene pentamine, etc.

Representative examples of diisocyanates include hexylenediisocyanate, decylenediisocyanate, octadecylenediisocyanate, phenylenediisocyanate, tolylenediisocyanate, diphenyldiisocyanate, methylene bis(phenylisocyanate), etc. The aromatic diisocyanates, such as tolylenediisocyanate are preferred.

The carboxyl or sulfonic acid group source as referred to herein must be capable of reacting with an isocyanate to form a ureido group and must have a terminal carboxyl or sulfonic acid group (acid or ester) capable of being reacted with a basic metal compound to form the corresponding metal salt. Carboxyl and sulfonic acid group sources which may be employed in the practice of this invention include amino acids, amino esters, lactams, and amino sulfonic acids and esters. The preferred carboxyl or sulfonic acid group source is selected from an amino carboxylic acids, an amino ester, a lactam or mixtures thereof. The most preferred carboxylic acid group source is a lactam.

The amino monocarboxylic acid or amino dicarboxylic acid and the C₁-C₃ esters thereof will contain a primary (preferred) or secondary amino group. The amino acids or esters, must have at least one active hydrogen atom on the nitrogen, i.e., the tertiary amines cannot be used in the practice of this invention. The amino acids will have from 2 to 31 carbon atoms (including the carboxylated carbon atoms), preferably from 6 to 20 carbon atoms and more preferably from 6 to 12 carbon atoms. The esters of the above will contain from 1 to 6 carbon atoms and preferably 2 carbon atoms in the ester group.

Typical amino monocarboxylic acids which may be used in this invention include 4-aminobenzoic acid, 4-amino-*o*-toluic acid, 4-amino-*m*-toluic acid, 4-amino-*p*-toluic acid, 4-amino-salicylic acid, anthranilic acid, 3-aminobenzoic acid, *p*-amino- α -toluic acid, 1-ethyl-3-aminobenzoic acid, 1-ethyl-4-amino-benzoic acid, glycine, β -alanine, 5-amino-valeric acid, 6-amino-caproic acid, 8-minocaprylic acid, 10-aminocaproic acid, 12-aminolauric acid, 14-aminomyristic acid 16-aminopalmitic acid, 18-aminostearic acid, 18-aminooleic acid, 18-aminolinoleic acid, 18-aminolinolenic acid, 4-aminocyclohexane carboxylic acid, (*p*-aminophenyl)acetic acid, 6-aminolauric acid, 4-aminocaprylic acid, 12-aminopalmitic acid, 6-(*N*-methylamino)myristic acid, etc.

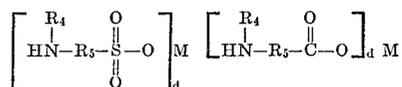
Typical aminodicarboxylic acids which may be suitable for use in this invention include aspartic acid, 3-aminoglutaric acid, 3-aminoadipic acid, 4-aminosuberic acid, 5-aminosebacic acid, 2-aminoterephthalic acid, etc. Other types include nitrilo diacetic acid, nitrilo dibenzoic acid, nitrilo dipropionic acid, etc. Exemplary amino diesters include diethyl 3-amino-glutamate, diethyl 3-aminoadipate, methylethyl 5-aminosebacate, etc.

Exemplary aminocarboxylic mono and diesters include methyl *p*-aminobenzoate, ethyl *p*-aminobenzoate, propyl *p*-aminobenzoate, ethyl 4-amino-*p*-methylbenzoate, propyl-6-aminocaproate, ethyl anthranilate dipropyl aspartate, dipropylglutamate, etc. Esters of the mono carboxylic acids are preferred.

Amino amides which may be used as reactants will have from 2 to 30 carbon atoms and preferably 3 to 12 carbon atoms. Typical amino amides which may be employed herein are the aminoacyclic amides such as 6-aminocapryl amide, 8-aminocapryl amide, 12-aminolauryl amide, *p*-

aminophenylacetamide, etc. The most preferred carboxyl group source is the cyclic amides and preferably the lactams having from 5 to 8 members in the heterocyclic structure. Typical lactams which may be used herein include 2-pyrrolidone, 5-methyl-2-pyrrolidone, 3,3-dimethyl-2-pyrrolidone, 2-piperidone, 3-methyl-2-piperidone, gamma-caprolactam, etc. Caprolactam is the most preferred.

The metal salt of an amino carboxyl or sulfonic acid which may be employed in the practice of this invention typically have one of the following general formulae:



wherein

R₄ is selected from hydrogen or a hydrocarbyl having from 1 to 20 carbons and preferably from 2 to 12 carbons;

R₃ is a hydrocarbylene having from 1 to 20 carbons and preferably from 6 to 16 carbons;

M is a metal atom described supra; and

d is an integer from 1 to 2 and sufficient to make the compound electro-neutral.

Exemplary metal salt include sodium-*p*-aminobenzoate, potassium *p*-aminobenzoate, lithium *p*-aminobenzoate, sodium aminoacetate, monosodium glutamate, monopotassium glutamate, disodium glutamate, sodium 4-amino-*p*-methylbenzoate, potassiumpiperidinate, monosodium aspartate, monosodium *p*-aminoisophthalate, sodium *p*-aminobenzyl sulfonate, sodium amino ethyl sulfonate, etc. The preferred amino metal salts are the alkali metal salts of monocarboxylic acids and preferably aromatic monocarboxylic acids.

The metal salts of amino carboxyl and sulfonic acids are generally highly insoluble within the typical lubricating oil reaction medium. In the event that solubility is problematic, a mutual solvent having appreciable solubility for the polyurea precursors and for the amino metal salt may be employed.

The basic metal compounds which may be employed in the practice of this invention to form the polyurea metal salt are hydroxides, oxides, carbonates and alcoholates of Groups I and II metals of the Periodic Table. These include hydroxides, oxides, carbonates and alcoholates of the alkaline (Group I) metals, such as lithium, potassium, sodium, rubidium, and cesium; the alkaline earth metals (Group II) such as beryllium, magnesium, calcium, strontium and barium. The preferred compounds are the alkali metal hydroxides, and most preferred are those of the low molecular weight alkali metals, such as, lithium, sodium and potassium, and particularly sodium. Typical compounds which may be employed herein include NaOH, KOH, LiOH, Ca(OH)₂, CaO, CaHCO₃, CaCO₃, Mg(OH)₂, Ba(OH)₂, etc.

Second Reaction Scheme

In this reaction scheme, a series of separate reaction steps are employed to prepare the compounds illustrated by Formulae 2 and 3. In the process, an intermediate polyurea compound having a terminal amine group is prepared. These may be prepared in substantially the same manner as described supra with the deletion of the carboxyl or sulfonic acid group source and by employing an excess of the polyamine reactant. If a polyurea having a terminal isocyanate group is prepared, this group may be hydrolyzed by an aqueous base to form a polyurea having a terminal amine group. The polyurea amine intermediate is then reacted with an anhydride, lactone or sulfonate to form a polyurea having a terminal carboxyl or sulfonic acid group. This polyurea acid is then saponified with a basic metal compound, described supra, to form the polyurea metal salt product. More specifically, in this preparation the desired reactants (diisocyanate,

polyamine, and monoamine or monoisocyanate) are mixed 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 reactants under conditions conducive for the reaction. Typical reaction temperatures range from 100 to 300° F. and preferably from 150 to 260° F. In most cases, the reaction will be exothermic and the temperature will rise during the course of the reaction. Regardless of the exothermicity of the reaction, external heating or cooling may be used as required. The reaction, as before, is preferably carried out within an inert solvent and typically the lubricating oil to be thickened. It is also necessary to agitate the mixture during the reaction to provide intimate contacting of the reactants. The reaction time is not critical but will generally range from 30 to 120 minutes; however, longer times (more than 3 hours) may be employed.

Upon completion of the polyurea reaction and when a free terminal isocyanate group is present, a dilute aqueous solution of an alkali metal hydroxide is charged to the reaction vessel and intimately contacted with the polyurea compound. The temperature of the reaction vessel is preferably maintained from 200 to 360° F. and more preferably to 200 to 320° F. during the reaction. The presence of the dilute caustic effects a decarbonation of the polyurea compound to form a polyurea amine from the terminal isocyanate group. The reaction is conducted until the diisocyanate is completely consumed.

At the completion of the reaction and the formation of the polyurea amine, the reaction medium is dehydrated and the vessel charged with an anhydride, lactone or sultone having from 3 to 24 carbons and preferably from 4 to 12 carbons. The anhydride, lactone or sultone reacts with one of the hydrogen atoms on the amine group forming a secondary amine having a free carboxylic or sulfonic acid group. The reaction may proceed without the presence of a catalyst and is initiated by merely contacting the anhydride, lactone or sultone with the polyurea amine under conditions conducive for the reaction. Typical reaction temperatures vary from 100 to 300° F. and more preferably from 150 to 200° F. The reaction is conducted at substantially atmospheric pressure; however, elevated pressures may be employed. At the completion of the reaction, generally between about 30 and 120 minutes, the polyurea acid is contacted with a basic metal compound and converted to the polyurea metal salt.

The amount of lactone, anhydride or sultone employed in the above reaction should be the stoichiometric amount, i.e., one mol of reactant per mol of polyurea amine present. In the neutralization step, the amount of basic metal compound employed varies depending upon how many carboxyl or sulfonic acid groups are present on the polyurea compound and on the valence of the basic metal compound. Generally, however, the amount of metal base is present in an amount from 1 to 10 percent excess over that stoichiometrically required to produce the polyurea metal salt.

Exemplary anhydrides which may be employed in the practice of this invention include malonic anhydride, succinic anhydride, glutaric anhydride, adipic anhydride, pimelic anhydride, maleic anhydride, phthalic anhydride, 3,3',4,4'-benzophenonetetracarboxylic anhydride, etc. Exemplary lactones include gamma-butyrolactone, gamma-valerolactone, β -propiolactone, delta-valerolactone, etc. Exemplary sultones which may be employed include propane sultone, butane sultone, naphthalsultone, etc.

The polyurea metal salt compositions are useful as grease thickeners, to produce greases with good lubricating properties. They are also useful as gellants for a variety of fluids, particularly hydrocarbons, of low viscosity to form fire starters, paints, and the like.

When used as grease thickeners, the compositions described herein are used in oils of lubricating viscosity in amount sufficient to thicken the oil to the consistency of grease when combined with the alkaline earth metal carboxylate. Generally, the amount ranges from 2 to 15

weight percent, preferably from 3 to 10 weight percent based on the weight of the final grease composition.

Alkaline Earth Metal Aliphatic Monocarboxylate

The second component of the grease composition is an alkaline earth metal aliphatic monocarboxylate having from 1 to 3 carbon atoms. 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 3 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 carboxylate present within the grease composition may vary depending upon the lubricating property desired, the particular polyurea constituent selected, the type of alkaline earth metal carboxylate 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 carboxylate to the 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 polyurea and preferably from 3 to 7 parts per part of polyurea.

Base Oil

The third component which must necessarily be present in the composition of this invention is a liquid base oil. The base oils which may be employed herein include a wide variety of lubricating oils such as naphthenic-base, paraffin-base, and mixed-base lubricating oils. Other hydrocarbon oils include lubricating oils derived from coal products and synthetic oils, e.g., alkylene polymers (such as, polymers of propylene, butylene, etc., and mixture thereof), alkylene oxide-type polymers (e.g., alkylene oxide polymers prepared by polymerizing alkylene oxide, e.g., propylene oxide polymers, etc., in the presence of water or alcohols, e.g., ethyl alcohol), carboxylic acid esters (e.g., those which were prepared by esterifying such carboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, alkenyl succinic acid, fumaric acid, maleic acid, etc., with the alcohols such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, pentaerythritol, etc.), liquid esters of acids of phosphorus, alkyl benzenes, polyphenols (e.g., biphenols and terphenols), alkyl biphenol ethers, polymers of silicon, e.g., tetraethyl silicate, tetraisopropyl silicate, tetra(4-methyl-2-tetraethyl)silicate, hexyl(4-methyl-2-pentoxy)disilicate, poly(methyl) siloxane, and poly(methyl-phenol)siloxane, etc. The base oils may be used individually or in combinations, whenever miscible or whenever made so by use of mutual solvents.

Preparation of Grease Composition

The greases exhibiting the superior properties of this invention can be prepared by the in situ production of the polyurea metal salt within a lubricating oil. In this embodiment, the lubricating oil is charged to a grease mixer along with the polyurea precursors, i.e., the reactants which combine to form the polyurea salt. The mixer contents are agitated and the process conditions and steps conducted in a manner discussed supra for the preparations of the polyurea metal salt.

The polyurea metal salts produced within the lubricating oil are generally mixtures of compounds, wherein n and n_1 in the Formulae vary from 0 to 3 and polyureas with different degrees of polymerization exist within the grease composition at the same time. For example, the grease composition may concurrently contain metal salts of diurea, triurea, tetraurea, pentaurea, hexaurea, octaurea, etc. In fact, particularly good results have been

realized when the polyurea compound is comprised of a combination of diurea salts and tetraurea salts of the 3 ureido groups. Moreover, while it is not shown by the formulas, cross-linking between polymer chains through a divalent or trivalent metal atom may also be present in minor amounts within the reaction mixture.

After the formation of the polyurea metal salt the grease mixer 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 mixer 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 carboxylic acid. During the reaction water is released and is removed from the system by heating above 212° F. or alternatively applying a slight vacuum on the mixer of 20 to 29 inches of mercury and heating to about 212° F. and higher.

The grease composition can be further processed by subjecting it to shear hardening. Shear hardening is performed by milling the grease in an extrusion of stator rotor mill under elevated pressures. The milling improves the dispersion of the polyurea metal salt 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, and now abandoned, discloses a preferred method of shear hardening a grease which can be successfully employed for the composition of this invention.

In addition to the polyurea metal salt, other additives may be successfully employed within the grease composition of this invention without affecting its high stability and 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 bearings. Typical antioxidants are organic compounds containing sulfur, phosphorus or nitrogen, such as organic amines, sulfides, hydroxy sulfides, phenols, etc., alone or in combination with metals like zinc, tin or barium. 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-acyl-phenothiazines, alkylphenol-formaldehyde-amine.

Another additive which may be incorporated into the grease composition of this invention is an anti-corrodant. The anti-corrodant is employed to suppress attack by acidic bodies 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 an alkali metal nitrite, preferably sodium nitrite. When an alkali metal nitrite is employed, it is used at a concentration ranging from 0.1 to 5 weight percent and preferably from 0.2 to 2 weight percent.

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 limitations upon the scope of the invention.

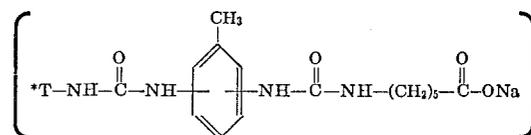
EXAMPLE 1

In this example, a diureido and a tetraureido sodium salt thickening agent and a grease containing the same are prepared. A 45 liter stainless steel mixer equipped with a stirrer is charged with 10,000 grams of 480 neutral oil, 1780 grams of tall oil fatty amine and 740 grams of caprolactam. The mixture is stirred at 210° F. to disperse the amine and caprolactam within the neutral oil. Thereafter, it is cooled to 150° F. and 188 grams of ethylene diamine are added to the mixture.

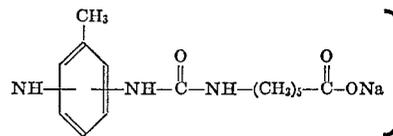
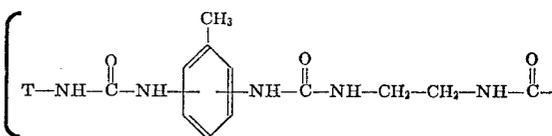
The mixture is then charged with a blend of 1712 grams of tolylene diisocyanate in 8000 grams of 480 neutral oil. The diisocyanate-oil blend is added slowly to the previously prepared mixture over a period of 45 minutes. On contacting of the toluene diisocyanate with the fatty amine and caprolactam an exothermic reaction occurs causing a rise in the system temperature. During the course of the reaction, the reaction mixture is diluted with an additional 10,000 grams of neutral oil to reduce the degree of thickening. The mixture is stirred and recycled in the mixer for a period of two hours.

To the mixture is then added 528 grams of a 50 weight percent aqueous sodium hydroxide solution. The mixture is heated to 320° F. for 1 hour with stirring to remove water. The mixture is cooled to 170° F. and milled in a 3 Manton-Gaulin mill. It is diluted with oil to produce a final thickener content of 11 weight percent. The grease is tested under ASTM Test Method D 217 and after 60 strokes has a worked penetration (P_{60}) of 291.

A sample of the grease is calculated to contain 11 weight percent of thickening agent and has a theoretical content of about 54 weight parts of diureido sodium salt



and about 46 weight parts of tetraureido sodium salt



EXAMPLE 2

This example is presented to demonstrate the effectiveness of a representative grease to this invention containing the polyurea metal salt in long term performance as compared to a typical lithium stearate grease and a typical polyurea grease. The polyurea metal salt grease to be tested is prepared by the method of Example 1. The lithium grease is a commercially available grease and is composed essentially of the following:

LITHIUM GREASE COMPOSITION

Component:	Amount, wt. percent
Lithium hydroxy stearate.....	9
Lubricating oil.....	83
Commercial E.P. agent.....	7.5
Commercial rust inhibitor.....	0.4

The lithium grease has an ASTM work penetration after 60 strokes (P_{60}) of 320.

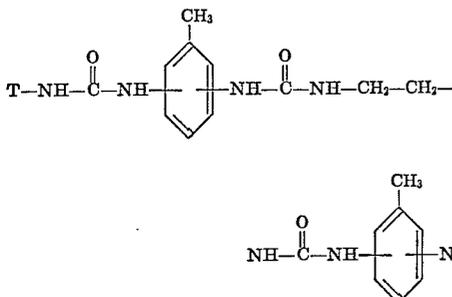
*T is tall oil fatty amine radical.

The second comparison is with a representative polyurea grease composed essentially of the following:

POLYUREA GREASE COMPOSITION

Component:	Amount, wt. percent
Polyurea ¹	5
Polyurea ¹	9
Lubricating oil	89.5
Commercial antioxidant	0.5
Commercial rust inhibitor	1.0

¹ The polyurea compound is:



wherein T is tall oil fatty amine radical.

The polyurea grease has an ASTM work penetration after 60 strokes (P_{60}) of 280.

The three greases are subjected to a high-speed bearing life test to determine the maximum bearing life of each of the greases. The test procedure is set forth in Federal Test Method 331.1 (Navy High Speed Bearing Test) and conducted at a temperature of 325° F. and at 10,000 r.p.m. The results from this test are set forth in the following Table III.

TABLE III

High Speed Bearing Test At 325° F.

Test Grease:	Bearing life, hrs.
Polyurea	1700
Lithium	300
Polyurea metal salt	2600

The bearing life test revealed the antiwear and lubricating characteristics of the grease and demonstrates the overall performance which can be expected from the particular grease composition. It can be seen from the above table that the polyurea metal salt greases illustrate a 845 percent increase in bearing life over the lithium grease and a 65 percent increase in bearing life over the polyurea grease.

EXAMPLE 3

This example is presented to demonstrate the preparation of polyurea metal salts having structures presented in Formula 2. In the preparation of a 22 liter stainless steel mixer is charged with a 600 neutral petroleum oil and varying amounts of tall oil fatty amine and a carboxyl group source. The mixture is stirred at 210° F. to disperse the amine and carboxyl group source within the oil. Following the dispersion of the amine and carboxyl group source, varying amounts of a diamine are added to the mixture.

A mixture of a diisocyanate in a 480 neutral oil is slowly added to the above reaction mixture over a 30-minute period. During the course of the reaction, the reaction mixture is diluted with additional oil to reduce the degree of thickening. The mixture is stirred and recycled in the reaction vessel for an additional 1-2 hours.

To the mixture is then added an aqueous 50 percent metal hydroxide solution. The mixture is thereafter heated to 320° F. for 1 hour with stirring to remove the water. The mixture is then cooled and milled.

The following table illustrates the preparation of the polyurea metal salts of this invention and of the greases using them as thickeners.

TABLE IV
Polyurea Metal Salt Greases

Grease	Reactants ¹										Grease characteristics			
	Diamine		Diisocyanate		Monoamine		Carboxyl source		Metal hydroxide		No. of ureido groups ²	Thickener (wt. percent)	ASTM (P_{60})	Bearing life (hrs.) ³
	Type	Mols	Type	Mols	Type	Mols	Type	Mols	Type	Mols				
1.....	EDA	4.7	TDI	9.4	TOFA	4.7	BZC	4.7	NaOH	4.1	4	18.0	296	681, 534
2.....	EDA	4	TDI	8	TA	4	CPLT	4	NaOH	3.8	4	16.9	313	-----
3.....	EDA	0.05	TDI	0.1	TOFA	0.05	CPLT	0.05	NaOH	0.05	4	20	-----	-----
4.....	XDA	2.57	TDI	7.75	TOFA	5.16	BZC	5.16	NaOH	5.16	3	10	293	213
5.....	EDA	2.7	PAPI	5.4	TOFA	2.7	BZC	2.7	NaOH	2.7	4	21.5	298	-----
6.....	EDA	3.5	BPM	7.0	TOFA	3.5	BZC	3.5	NaOH	3.5	4	24	293	-----
7.....	PPZ	0.06	TDI	0.12	TOFA	0.06	BZC	0.06	NaOH	0.06	4	19.6	237	-----
8.....	PPZ	4	TDI	8	TOFA	4	BZC	4	NaOH	4	4	21.7	344	-----
9.....	DTH	4	TDI	8	TOFA	4	BZC	4	NaOH	4	4	23.4	340	-----
10.....	DTH	4	TDI	8	TOFA	4	BZC	4	NaOH	4	4	17.0	292	-----
11.....	HDA	4	TDI	8	TOFA	4	BZC	4	NaOH	4	4	20	300	-----
12.....	HDA	0.07	TDI	0.14	TOFA	0.07	BZC	0.07	NaOH	0.07	4	16	267	-----
13.....	EDA	4	TDI	8	TOFA	4	CPLT	4	LiOH	4	4	18	290	608; 1,161
14.....	EDA	0.8	TDI	2.5	TA	1.6	CPLT	1.6	NaOH	6.55	3	11	291	2,874; 2,436
15.....	EDA	2.0	TDI	6.2	TA	4.1	CPLT	4.1	NaOH	4.1	-----	14	307	-----
16.....	MPDA	4.7	TDI	9.4	ODA	4.7	BZC	4.7	NaOH	4.7	4	22	284	-----
17.....	None	-----	BPM	4.8	ODA	4.8	BZC	4.8	NaOH	4.8	2	16	306	278, 369
18.....	EDA	0.92	BPM	2.85	TOFA	1.9	CPLT	1.9	NaOH	1.9	3	13	326	-----
19.....	MPDA	1.4	TDI	4.34	TOFA	2.9	CPLT	2.9	NaOH	2.9	3	15	302	-----
20.....	EDA	0.62	TDI	1.87	TOFA	1.25	DAIP	1.25	NaOH	2.5	3	10.4	300	-----
21.....	EDA	0.025	TDI	0.075	TOFA	0.05	DPA	0.05	NaOH	0.1	3	12	300	-----
22.....	EDA	0.025	TDI	0.075	TFFA	0.05	AAA	0.05	NaOH	0.05	3	11.1	330	-----
23.....	EDA	1.0	TDI	3.1	TOFA	2.06	PYD	2.06	NaOH	2.06	3	10	296	-----

¹ The reactants of Table IV are abbreviated as follows:

AAA = p-Amino-acetanilide.
BPM = Bis(p-phenylisocyanate)methane.
BZC = Benzocaine (ethyl ester of p-aminobenzoic acid).
CPLT = ϵ -Caprolactam.
DPA = Dipropyl aspartate.
DTH = 1,6-diamino-2,2,4-trimethylhexane.
DAIP = Dimethyl 5-aminoisophthalate.
EDA = Ethylene diamine.
HDA = 1,6-hexanediamine.
MPDA = Metaphenylene diamine.

NaOH = Sodium hydroxide.

ODA = Octadecylamine.

PAPI = Polyethylene polyphenyl diisocyanate (M.W. = 381-400).

PPZ = Piperazine.

PYD = 2-pyrrolidone.

TA = Tallow amine.

TDI = Toluene diisocyanate.

TOFA = Tall oil fatty amine.

XDA = Xylene diamine.

² The average number of polyurea groups in entire composition.

³ Conducted at 10,000 r.p.m. at 350° F.

The above table demonstrates the practice of the instant invention in the preparation of numerous representative polyurea metal salts and corresponding greases containing the salts. The 27 compositions amply illustrate the broad range of diamines, diisocyanates, monoamines and carboxyl group sources which can be successfully employed to prepare the polyurea salts. Also illustrated is the wide range of concentrations for the various reactants as well as for the total thickener content which may be employed.

EXAMPLE 4

This example is presented to demonstrate the practice of this invention wherein a variety of metal moieties can be used in the preparation of the polyurea salt. In the preparation, a process identical to that described in Example 1 is used with the exception that LiOH, Ba(OH)₂ or Ca(OH)₂ is substituted for NaOH in the neutralization of the polyurea caprolactam adduct. The properties of the various greases are given in the following Table V. A sample of the lithium and sodium greases are tested under Federal Test Methods Standards 791a, Method 331, and the bearing life determined. The following Table V also presents the results from this test.

TABLE V
Grease Characteristics

Type	Thickener (percent)	Ureido groups (No.)	P ₆₀	Bearing life (hrs.) ¹	Dropping point ASTM D-2265
Calcium salt	18	4	(3)	-----	-----
Barium salt	18	4	301	-----	499; 492
Lithium salt	18	4	290	1,161; 608	484
Sodium salt ²	11	3	291	2, 436; 2, 874	460; 483

¹ Test conducted at 350° F. at 10,000 r.p.m.

² Bearing life test conducted at 325° F. at 10,000 r.p.m.

³ Very soft.

The above table illustrates the preparation of various metal salts and the effectiveness of greases containing these metal salts in lubricating bearings at elevated temperatures. Also illustrated is the improvement resulting from the employment of the alkali metal salts.

EXAMPLE 5

This example is presented to illustrate the preparation of polyurea metal salts having the structure presented in Formula 2 of the specification and the effectiveness of these compositions as thickening agents for grease compositions. In the preparation, a 22 liter stainless steel mixer is charged with 7212 grams of a 600 neutral oil, 1088 grams (4 mols) of a tall oil fatty amine and 120 grams (2 mols) of a diamine. The contents of the mixer are stirred and heated to a temperature of 150° F. to uniformly disperse the reactants within the oil reaction medium. Thereafter, the solution of 3376 grams of the above neutral oil containing 1044 grams (6 mols) of tolylene diisocyanate are charged to the mixer over a period of 45 minutes. Contents of the mixer are vigorously agitated at a temperature of 165-170° F. for a period of 1 hour to produce the polyurea compound within the lubricating oil. At the end of the reaction the mixture is heated to a temperature of 190° F. and 216 grams of 10 percent sodium hydroxide solution are charged to the mixer and intimately contacted with the polyurea compound. The contents of the mixer are maintained at these conditions for 45 minutes. Thereafter, the mixture is dehydrated at a temperature of 310° F.

After the contents of the mixer have been dehydrated, 4 mols of a lactone or anhydride and 1650 grams of 600 neutral oil are charged to the mixer and intimately contacted with its contents. The contents of the mixer are maintained at a temperature of 190° F. for a period of 1 hour to effect the carboxylation of the polyurea amine compound. After approximately 1.5 hours, a 50 percent aqueous solution of sodium hydroxide is charged to the mixer and intimately contacted with the carboxylated polyurea. The temperature of the system is maintained at 190° F. during this period and the contents vigorously agitated. After approximately 0.5 hour, the temperature of the system is increased to 310° F. to strip the grease composition of water.

An additional 1889 grams of 600 neutral oil is charged to the mixer and the contents milled at 4500 p.s.i. Grease characteristics are then measured and reported in the following table. The bearing life on the greases tested is conducted in accordance with Federal Test Methods Standard 791a, Method 331 at a temperature of 350° F. and at 10,000 r.p.m.

TABLE VI
Polyurea Metal Salt Greases

Grease	Reactants					Grease characteristics				
	EDA (mols)	TDI (mols)	Lactone or anhydride Type ¹	(Mols)	TOFA (mols)	NaOH (mols)	No. of ureido group	Thickener (wt. percent)	ASTM (P ₆₀)	Bearing life (hrs.) ²
1	1.5	4.5	SA	3.0	3.0	3.0	3	13	294	-----
2	2.0	6.0	BL	4.0	4.0	4.0	3	11.5	300	700
3	1.75	5.25	PL	3.5	3.5	3.5	3	10	290	-----
4	0.025	0.075	PA	0.05	0.05	0.05	3	14	296	-----
5	0.025	0.075	MA	0.05	0.05	0.05	3	13	296	-----
6	0.025	0.075	BTCA	0.05	0.05	0.05	6	15	294	-----

¹ SA=Succinic anhydride; BL=Gamma-butyrolactone; PL=Beta-propiolactone; PA=Phthalic anhydride; MA=Maleic anhydride; BTCA=3,3,4,4-benzophenone tetra carboxylic anhydride.

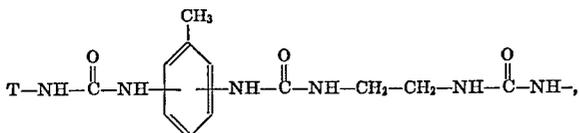
² Operated at 10,000 r.p.m. at 350° F.

The compositions illustrated in the above Table VI are calculated to have the following structures:

and the contents vigorously agitated at a temperature of 165-170° F. for a period of 1 hour. At the end of the

Grease	Polyurea metal salt structure
1.....	
2.....	
3.....	
4.....	
5.....	
6.....	

wherein triurea has the structure



and T represents a tall oil fatty amine radical.

This example thus illustrates the preparation of various representative polyurea metal salts having the structure set forth in Formula 2 and the effectiveness of these compositions in thickening a lubricating oil to the consistency of grease. Also illustrated is the excellent bearing life of one of the representative greases.

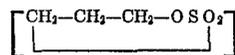
EXAMPLE 6

This example is presented to demonstrate the preparation of a polyurea metal salt having the structure presented in Formula 2 and prepared from neutralizing a polyurea sulfonic acid with sodium hydroxide.

In the preparation, a 600 ml. glass beaker is charged with approximately 100 grams of a 600 neutral oil, 0.05 mol of tall oil fatty amine and 0.025 mol of ethylene diamine. The contents of the beaker are stirred and heated to a temperature of about 150° F. to uniformly disperse the reactants within the oil reaction medium. Thereafter, approximately 65 grams of 600 neutral oil and 0.075 mol of tolylene diisocyanate are charged to the glass beaker

reaction, the beaker is heated to 190° F. and 25 grams of 10 percent sodium hydroxide solutions are admixed with the beaker contents. The admixture is agitated at the above temperature for a period of 45 minutes and thereafter dehydrated at a final temperature of 310° F.

After the contents of the beaker have been dehydrated, 0.05 mol of propane sultone



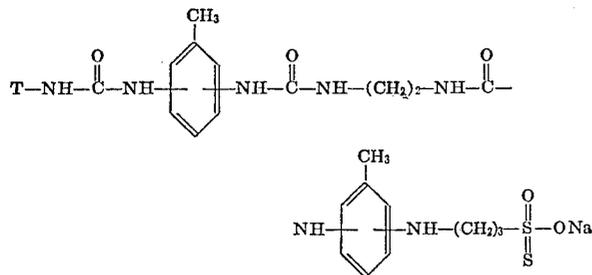
are charged to the beaker. The contents are mixed for a period of 1 hour at 190° F.

After approximately 1.5 hours, a 50 percent aqueous solution of sodium hydroxide (0.05 mol) is charged to the beaker and intimately contacted with polyurea sulfonic acid. The temperature is maintained at 190° F. for a period of approximately 30 minutes. At the end of the reaction, the water is stripped from the system by heating to a temperature of about 310° F.

An additional 128 grams of 600 neutral oil is charged to the beaker and the contents milled in a 3-roll mill. The ASTM work penetration after 60 strokes is 294.

The polyurea metal salt is calculated to have the following structure and is present within the oil in an amount

of 11 weight percent based on the weight of total grease composition.



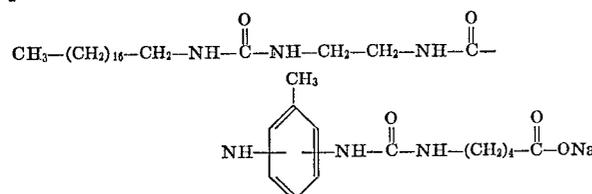
wherein T is a tall oil fatty amine radical.

EXAMPLE 7

This example is presented to demonstrate the preparation of a representative polyurea metal salt having the structure presented in Formula 4.

A 600 ml. flask is charged with 100 grams of 600 neutral oil and 5.65 grams of caprolactam. The contents are heated to 150° F. and 3 grams of ethylene diamine with 5 grams of oil are charged to the flask. Thereafter, 23 grams of 600 neutral oil and 8.7 grams of tolylene diisocyanate and 14.75 g. of octadecylisocyanate are admixed with the flask contents. During the reaction, the temperature of the flask rises to 180° F. and is stirred for 90 minutes. An additional 0.9 grams of EDA are added to insure that all of the diisocyanate has reacted.

The contents of the flask are transferred to a 600 ml. glass beaker and 4 grams of sodium hydroxide in 4 grams of water are charged to the beaker. The oil in the beaker is calculated to contain 21 weight percent of polyurea sodium salt. The ASTM work penetration (P₆₀) is measured to be 294. The structure of the polyurea compound is calculated to be as follows:



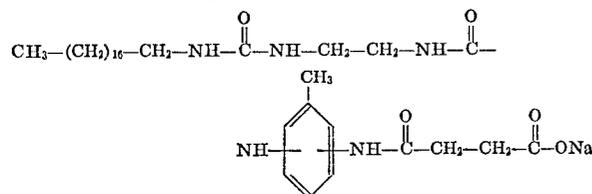
EXAMPLE 8

This example is presented to demonstrate the preparation of a representative polyurea metal salt having the structure presented in Formula 4.

The processing steps are the same as shown in Example 6 except that the following reactants and amounts are employed.

Components	Amounts	
	Mols	Gram
1. Octadecyl isocyanate.....	0.05	14.75
2. Ethylene diamine.....	0.05	3.0
3. Tolylene diisocyanate.....	0.05	8.7
4. Succinic anhydride.....	0.05	5.0
5. 600 neutral oil.....		123
6. NaOH (10%).....		5
7. NaOH (50%).....	0.05	4.0

The grease exhibits an ASTM worked penetration after 60 strokes of 261. The polyurea metal salt is calculated to have the following structure:



It is apparent that many widely different embodiments

of this invention may be made without departing from the scope and spirit thereof; and these embodiments are considered to be within the scope of this invention.

EXAMPLE 9

This example is presented to illustrate the preparation of a grease containing a polyurea metal salt and alkaline earth metal aliphatic monocarboxylate. A grease mixer is charged with 14,000 grams of 600 neutral mineral oil, 1200 grams of tall oil fatty amine, 500 grams of caprolactam and 132 grams of ethylene diamine. The mixer is cooled to 140° F. and charged with 1148 grams of tolylene diisocyanate in 6000 grams of 600 neutral mineral oil. The lines are flushed and the mixer charged with an additional 1000 grams of 600 neutral oil. After about 2 hours and a reaction temperature of 190° F., an additional 10 grams of ethylene diamine are added to the mixer to assure the elimination of any unreacted isocyanate groups. Thereafter 176 grams of sodium hydroxide in 180 grams of water are charged to the mixer and the temperature raised to 310° F. to remove the water. An additional 1000 grams of 600 neutral oil are charged to the mixer followed by 2440 grams of hydrated lime and flushed with 1000 grams 600 neutral oil. The contents are cooled to 140° F. Thereafter 2757 grams of acetic acid are charged to the mixer along with 1000 grams of 600 neutral mineral oil. Then, 197 grams of sodium nitrite and 197 grams of water are charged and the temperature raised to 300° F. to dehydrate the product. Thereafter, 394 grams of an oxidation inhibitor is charged to the mixer and the contents cooled. An additional 1800 grams of 600 neutral oil are added and the product milled at 5500 p.s.i.

The product has an ASTM worked penetration after 60 strokes (P₆₀) of 287 and an ASTM dropping point of 465. The product contains about 9 wt. percent of polyurea metal salt of the formula shown in Example 1, and 15 wt. percent of calcium acetate.

The product was further subjected to an ASTM (D-2509) Timken Test. The Timken load had passed 70 lbs. with no failure before the test was discontinued. This illustrates an excellent extreme pressure property. The Timken load for a similar polyurea calcium acetate grease is 50 pounds.

The product was further subjected to a modified ASTM D-1743 rust test in 3% synthetic sea water (ASTM 665) and 97% distilled water. The rust rating is 0 no rust and 5 very rusty with intermediate values between 0 and 5 representing increasing degrees of rust. The rating system is more fully described in IP 220 (British Institute of Petroleum). The ratings as determined after the bearing is stored for 1 day at 77° F. The rust rating for the above product (polyurea metal salt-calcium acetate) is 0 and at 5% synthetic sea water and 95% distilled water is 0. Similar polyurea and polyurea calcium acetate greases containing these additives will not pass these sea water tests.

EXAMPLE 10

In this example the preparation of a polyurea calcium salt-calcium acetate grease is illustrated. The steps of Example 9 are followed except that lime is used in place of the sodium hydroxide. The following amounts are used:

	Amount (grams)
65 Tall oil fatty amines	1200
E-Caprolactam	500
Ethylene diamine	132
Tolylene diisocyanate	1192
Hydrated lime	2656
70 Acetic acid	2800
Oxidation inhibitor	400
Sodium nitrite	200
600 neutral mineral oil	30,920
Total	40,000

The product contains about 8 wt. percent of a calcium polyurea salt and about 13 wt. percent of calcium acetate. The product has an ASTM worked penetration (P_{60}) of 272 and a dropping point of 450.

What is claimed is:

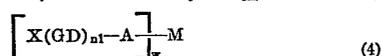
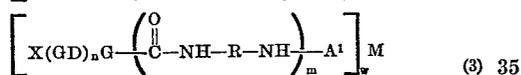
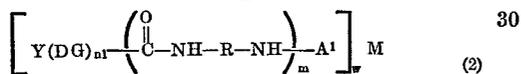
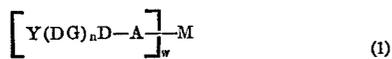
1. A grease composition comprising a major portion of a lubricating oil and minor grease thickening portions of (1) an alkali or alkaline earth metal salt of a polyurea sulfonate or carboxylate compound having at least 2 ureido groups and having a molecular weight between about 250 and 2500 and (2) an alkaline earth metal aliphatic monocarboxylate having from 1 to 3 carbons.

2. The grease defined in Claim 1 wherein said polyurea compound is a tetraurea and said alkaline earth metal aliphatic monocarboxylate is calcium acetate.

3. The grease defined in Claim 1 wherein a corrosion inhibiting amount of an alkali metal nitrite is also present.

4. The grease defined in Claim 3 wherein said alkali metal nitrite is sodium nitrite.

5. A composition of matter comprising a major portion of a lubricating oil and an amount sufficient to thicken said oil to the consistency of grease of (1) an alkaline earth metal aliphatic carboxylate having from 1 to 3 carbon atoms, and (2) a polyurea metal salt having a structure presented in one of the following formulae:

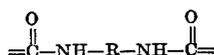


wherein

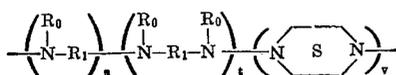
Y is C_2-C_{30} hydrocarbylamino group

X is a C_2-C_{30} hydrocarbylcarbamoyl group

D is a dicarbamoyl hydrocarbylene of the formula:



G is a divalent polyamino group of the formula:



M is a metal selected from Groups I and II of the Periodic Table;

n is an integer from 0 to 3;

n_1 is an integer from 1 to 3;

m is an integer from 0 to 1;

w is an integer from 1 to 2 and sufficient to make the compound electroneutral;

z is an integer from 0 to 2;

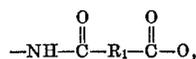
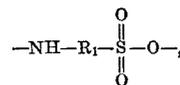
v is an integer from 0 to 1;

t is an integer equal to 1 when v is 0 and 0 when v is 1; R is the same or different hydrocarbylene having from 2 to 30 carbons;

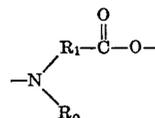
R_1 is the same or different hydrocarbylene having from 2 to 12 carbons;

R_0 is the same or different components selected from hydrogen or a C_1-C_3 alkyl;

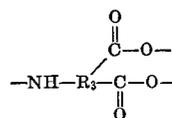
A is a divalent radical selected from the group consisting of:



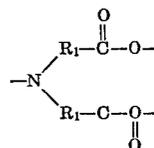
and



or a trivalent radical selected from the group consisting of:



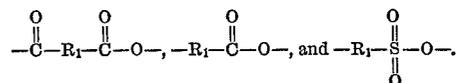
and



wherein

R_2 is the same or different trivalent hydrocarbon radical having from 1 to 30 carbons; and

A^1 is a divalent radical selected from:



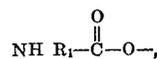
6. The composition defined in Claim 5 wherein n is 1 and n_1 is 2.

7. The composition defined in Claim 5 wherein M is an alkali metal.

8. The composition defined in Claim 5 wherein said polyurea metal salt has a structure defined by Formula 1 or 2.

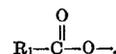
9. The composition defined in Claim 8 wherein said n is 1, n_1 is 1, m is 1, A is

55



and A^1 is

60



10. The composition defined in Claim 9 wherein y is a C_{12} to C_{24} hydrocarbylamino, G is an alkylene diamino, D is tolylene dicarbamoyl and R_1 is an alkylene having from 2 to 6 carbons.

11. The composition defined in Claim 10 wherein said alkylene diamino is ethylene diamino.

12. The composition defined in Claim 11 wherein said metal aliphatic monocarboxylate is calcium acetate.

13. The composition defined in Claim 12 wherein said metal aliphatic carboxylate is present in an amount from 4 to 15 weight percent of calcium acetate and (2) from present in an amount from 3 to 10 weight percent of the final grease composition.

14. The composition defined in Claim 13 wherein from

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0.1 to 5 weight percent of an alkali metal nitrite is also present in said composition of matter.

15. A composition of matter comprising a major portion of a lubricating oil and an amount sufficient to thicken said oil to the consistency of grease of (1) from 4 to 15 weight percent of calcium acetate and (2) from 3 to 10 weight percent of a polyurea metal salt prepared by reacting one molar part of ethylene diamine with two molar parts of tolylene diisocyanate, one molar part of a C₁₂ to C₂₄ monoamine and one molar part of caprolactam followed by saponification of the reaction product with sodium hydroxide.

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References Cited

UNITED STATES PATENTS

2,892,778	6/1959	Carter et al.	252—33.6
2,947,696	8/1960	Nelson et al.	252—33.6

PATRICK P. GARVIN, Primary Examiner

I. VAUGHN, Assistant Examiner

U.S. Cl. X.R.

252—17, 25, 33, 33.6

UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No. 3,846,315 Dated November 5, 1974

Inventor(s) GARTH M. STANTON AND JOHN L. DREHER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, line 46 (4th formula) should read $--[X(GD)_{n_1}-A-]_wM--$

Col. 5, line 44, "temeprature" should read --temperature--

Col. 7, line 48, "8-minocaprylic" should read --8-aminocaprylic--

Col. 7, line 50, "acid 16" should read --acid, 16--

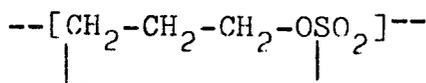
Col. 7, line 61, "dipropione" should read --dipropionic--

Col. 11, line 22, "extrusion of" should read --extrusion or--

Col. 12, line 4, "staniless" should read --stainless--

Col. 12, line 57, "to this invention" should read --of this invention--

Col. 18, line 58, " $[CH_2-CH_2-CH_2-OSO_2]_2$ " should read

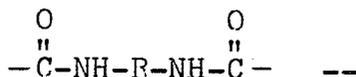


Col. 19, line 12, end of formula " $\overset{O}{\parallel}S$ " should read $--\overset{O}{\parallel}S--$

Col. 20, line 23, "grams 600 neutral" should read --grams of 600 neutral--

Col. 21, line 23, "aliphatic carboxylate" should read --aliphatic monocarboxylate--

Col. 21, line 48, " $\overset{O}{\parallel}C-NC-R-NH-\overset{O}{\parallel}C$ " should read--



PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

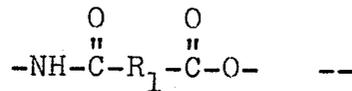
Patent No. 3,846,315 Dated November 5, 1974

Inventor(s) GARTH M. STANTON AND JOHN L. DREHER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Page 2 of Certificate of Correction:

Col. 22, line 7, " $\text{-NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}_1-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}$ " should read --



Col. 22, line 71, "aliphatic carboxylate" should read
--aliphatic monocarboxylate--

Col. 22, line 72, "4 to 15 weight percent of calcium acetate and (2) from" should read --4 to 15 weight percent and said polyurea metal salt is--.

Signed and sealed this 15th day of April 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks