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3,243,372

GREASES THICKENED WITH POLYUREA

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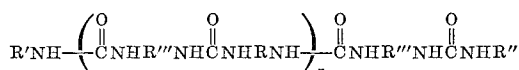
This application is a continuation-in-part of applications Serial Nos. 84,511, filed January 24, 1961; 109,827, filed May 15, 1961, and 210,559, filed July 17, 1962, all now abandoned.

This invention concerns novel greases thickened with polyureas. More particularly, this invention concerns novel greases thickened with polyureas of at least 4 urea groups having hydrocarbon terminal end members.

There has been an increasing need for greases which are operable at elevated temperatures, that is, temperatures above 350° F. and preferably temperatures above 400° F. The need is a result of the increasing speed and energy requirements of the jet age. Gears, bearings, and other moving parts are required to operate at greater speed and higher loads than have heretofore been required. This has resulted in ever-increasing temperatures occurring in the area of the moving parts.

For the most part, high temperature grease thickening agents have been fatty acid salts. Illustrative of such thickeners which provide relatively high melting point grease compositions are the lithium soaps of various fatty acids. However, these fatty acid salts catalyze the oxidation of the lubricant. At the higher temperatures of operation, the rapid oxidative degradation of the lubricant increases the frequency with which the old lubricant must be removed and new grease lubricant applied to the moving surface.

Pursuant to this invention, greases having relatively high dropping points are provided which have, in an amount sufficient to provide thickening to a grease, polyureas of the following formula:



wherein x is an integer of from 1 to 3, R and R'' may be the same or different and are hydrocarbylene of from 2 to 30 carbon atoms (hydrocarbylene is a divalent organic radical composed solely of carbon and hydrogen which may be aliphatic, alicyclic or aromatic or combinations thereof, e.g., alkaryl, aralkyl, etc., having its two free valences on different carbon atoms); R' and R'' may be the same or different and are hydrocarbyl of from 1 to 30 carbon atoms (hydrocarbyl is a monovalent organic radical composed solely of carbon and hydrogen which may be aliphatic, aromatic, or alicyclic or combinations thereof, e.g., aralkyl, alkaryl, etc.).

The polyureas of the above formula are readily prepared by mixing diisocyanates and diamines with monoisocyanates or monoamines in the proper proportions to form the desired polyurea. The greases thickened with the polyureas are useful at temperatures from about -100° F. to 500° F. and remain unctuous after long use, not becoming hard or brittle. The grease compositions thus formed are extremely resistant to emulsification in water.

The preferred greases are thickened by compositions of the following formula:



2

wherein x is an integer of from 1 to 3, preferably, 1, R^a and R^d are the same or different and are hydrocarbyl of from 5 to 28 carbon atoms, preferably of from 6 to 25 carbon atoms and R^b and R^c may be the same or different and will be hydrocarbylene of from 2 to 26 carbon atoms, more usually of from 2 to 18 carbon atoms. It is further preferred that in the tetraureas, the sum of the carbon atoms of R^a and R^d is in the range of 10 to 30 and the sum of the carbon atoms of R^b and R^c is in the range of 12 to 40.

The monoamine or monoisocyanate used in the formation of the polyurea will form the terminal end group. As already indicated, these terminal end groups will be of from 1 to 30 carbon atoms, but are preferably of from 5 to 28 carbon atoms and more desirably of from 6 to 25 carbon atoms. As already indicated, the substituent on the nitrogen is a hydrocarbon radical which may be aliphatic, aromatic or alicyclic, may be aliphatically saturated or unsaturated, or may be combinations of the various types of hydrocarbon radicals.

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, tert-butyl aniline, benzylamine, β -phenethylamine, etc.

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

The preferred aromatic terminal end groups are those of from 6 to 12 carbon atoms. The preferred aliphatic terminal end groups are those of from 10 to 20 carbon atoms.

The diamines and diisocyanates which form the internal hydrocarbon bridges between the ureas are, as indicated, of from 2 to 30 carbon atoms, preferably from 2 to 26 carbon atoms and more desirably of from 2 to 18 carbon atoms.

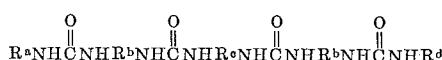
Illustrative of various diamines are ethylenediamine, propanediamine, butanediamine, hexanediamine, dodecanediamine, octanediamine, hexadecanediamine, cyclohexanediamine, cyclooctanediamine, phenylenediamine, toluenediamine, xylenediamine, dianilinemethane, ditoluidinemethane, bisaniline, bistoluidine, etc.

Illustrative of diisocyanates are hexanediisocyanate, decanediisocyanate, octadecanediisocyanate, phenylenediisocyanate, toluenediisocyanate, bis(diphenylisocyanate), methylene bis(phenylisocyanate), etc.

The aromatic hydrocarbylene or bridging groups will generally be of from about 6 to 18 carbon atoms. The aliphatic hydrocarbylene or bridging groups will generally be of from about 2 to 10 carbon atoms.

The polyurea grease thickeners have a polar/nonpolar balance. That is, there will be at least about 6 carbon atoms per urea group and more usually about 8 carbon atoms per urea group, but fewer than 20 carbon atoms per urea group and more usually fewer than 16 carbon atoms per urea group.

The tetraureas used in this invention have the following formula:



wherein R^a , R^b , R^c and R^d are as defined previously.

The greases of this invention are formed with a wide variety of oils of lubricating viscosity. Various base oils include naphthenic base, paraffin base and mixed base mineral lubricating oils; synthetic oils, such as polymers of propylene, butylene, etc., propylene oxide polymers, carboxylic acid esters, e.g., isooctyl azelate, pentaerythritol caproate or dipropylene glycol dipelargonate; silicon esters, such as tetraethyl silicate, hexa-(4-methyl-2-pent-oxy)disiloxane, etc.

The greases have the polyureas in the oils of lubricating viscosity in amounts sufficient to thicken the oil to the consistency of grease, that is, in amounts ranging from 5% to 50% by weight, preferably, in amounts from 6 to 25% by weight.

The greases will generally have dropping points in excess of 400° F. and more usually in excess of 450° F.

As indicated when preparing the polyureas, the monoamines or isocyanates are merely brought together with the diisocyanates and diamines in the proper proportion, preferably in the presence of an inert diluent. Usually, the vehicle to be thickened or gelled will be the preferred diluent. It is not necessary that the diluent be a solvent for all the reactants. With a heterogeneous system, efficient stirring helps to insure smooth reaction between the various reactants.

The temperature of the reaction will generally vary from about 20° C. to about 100° C., more usually from about 20° C. to 75° C. The reaction itself is exothermic and by starting at room temperature, elevated temperatures are obtained. However, external heating or cooling may be desirable. The concentration of polyurea in the final product may vary from about 1 to 50 weight percent, depending on the various reactants, the particular product desired, etc.

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLE 1.—PREPARATION OF TETRAUREA

A mixture of 177.8 g. (0.711 mole) of diphenylmethane, 4,4'-diisocyanate and 350 ml. of methylethylketone (MEK) was heated to 150° F. This mixture was blended with 1200 g. of pentaerythritol caproate (Hercoflex 600). To this blend was added an MEK solution of 38.5 g. (0.356 mole) of p-phenylenediamine, 98 g. (0.364 mole) of Armeen 18-D, which is described hereinbelow, and 37.8 g. (0.353 mole) p-toluidine in 350 ml. of hot MEK with agitation. The whole blend was heated to 300° F., at which temperature was added 49.7 g. of commercial oxidation inhibitors and 402.3 g. of pentaerythritol caproate. The temperature was increased to 400° F., after which the composition was pan cooled, then milled twice at 4000 p.s.i. The resulting thickened composition was useful as a grease and had an ASTM unworked penetration (P_0) of 237 and a dropping point of 500+° F.

EXAMPLE 2.—PREPARATION OF TETRAUREA

A solution of 141.5 g. (0.566 mole) of diphenylmethane, 4,4'-diisocyanate in 350 ml. of methylethylketone (MEK) was blended with 1089 g. of diisooctylazolate with agitation. To this blend was added a solution of 56.1 g. (0.283 mole) of methylene dianiline, 152.2 g. (0.566 mole) of Armeen 18-D in 350 ml. of warm MEK. After this blend has been heated to 300° F., there was added 36.8 g. of commercial oxidation inhibitors. The mixture was heated to 400° F., and 364 g. of diisooctylazolate was added. After pan cooling, the resulting thickened composition was milled at 4000 p.s.i., yielding a grease thickened with 19% tetraurea, and having a P_{60} of 275 and a dropping point of 500+° F.

A sample of the tetraurea grease thickener of Example 2 hereinabove was isolated by placing 50.34 g. of the grease for Example 2 in a Soxhlet extractor for 72 hours with refluxing MEK. The cup was then dried in vacuo,

and on analysis the extract solid was found to contain the following:

C, wt. percent	76.21
H, wt. percent	7.74
N, wt. percent	10.74
O, wt. percent	5.31
(by difference)	100.00

10 EXAMPLE 3.—PREPARATION OF HEXAUREA

A mixture of 10.8 g. (0.10 mole) of metaphenylenediamine, and 30.0 g. (0.10 mole) of a mixture of primary amines having an average molecular weight of 300, was heated at 300° F. until a solution was obtained. This amine solution was added quickly with rapid agitation to a mixture consisting of 41.7 g. (0.15 mole) of diphenylmethane, 4,4'-diisocyanate and 300 g. of a California paraffinic base oil having a viscosity of 500 SSU at 100° F. The resulting mixture was stirred in a high speed Waring Blendor for 15 minutes, then heated in an oven at 350° F. for 3 hours, with an occasional mixing by hand. The mixture was cooled to ambient temperatures, then milled through an extrusion-type mill at 5600 p.s.i. After the addition of 75 g. of the same oil described hereinabove, the thickened grease-type composition was milled twice at 5600 p.s.i.

The resulting grease, which contained 15.6% of the hexaurea, had an ASTM worked penetration (P_{60}) of 294, and an ASTM dropping point of 473° F.

30 EXAMPLE 4.—PREPARATION OF OCTAUREA

A mixture of 16.2 g. (0.15 mole) of metaphenylenediamine and 300 g. (0.10 mole) of the same amine described in Example 3 hereinabove, was heated at 300° F. until solution occurred. This hot amine solution was added quickly with violent agitation to a blend consisting of 55.6 g. (0.20 mole) of diphenylmethane, 4,4'-diisocyanate and 372 g. of a California paraffin base oil having a viscosity of 500 SSU at 100° F. The resulting blend was stirred at high speed for 30 minutes, then heated in an oven at 350° F. for 3 hours, with a mixing by hand every 30 minutes. The grease was cooled to ambient temperature, then milled twice through an extrusion-type mill at 5600 p.s.i.

The finished grease, which contained 19.9% of the octaurea, had an ASTM worked penetration (P_{60}) of 303, and an ASTM dropping point of 496° F.

50 EXAMPLE 5.—PREPARATION OF TETRAUREA

A mixture of 3.6 g. of ethylenediamine, 30 g. of Armeen T,¹ and 7 g. of an antioxidant was heated at 140° F. for 10 minutes, forming a homogeneous solution. This solution was added quickly to a lubricating oil blend consisting of 223 g. of a California base oil having a viscosity of 480 SSU at 100° F., and 17.4 g. of an isocyanate (an 80/20 mixture of 2,4-toluenediisocyanate and 2,6-toluenediisocyanate) with vigorous agitation in a Waring Blendor. A gel formed immediately. The resulting grease was removed from the blender, hand mixed, and milled at 8000 p.s.i.

The final grease which contained 12.5% thickening agent, had an ASTM worked penetration (P_{60}) of 290 and an ASTM dropping point of 505° F.

The following table illustrates a number of tetraureas prepared as described in the prior examples. The tetraureas were formed in a variety of oils of lubricating viscosity with varying chemical nature. The ASTM Unworked Penetration (P_0), the ASTM Worked Penetration after 60 strokes in the ASTM worker (P_{60}), and in many instances, the ASTM Dropping Point in degrees F. are reported.

¹ Armeen T is principally an octadecenyl amine sold by the Armour Company, Chicago, Ill.

Table I

Ex. No.	Tetraurea Characteristics				Grease Composition		Grease Properties		
	Diisocyanate	R' Derived From—	R'' Derived From—	R Derived From—	Base Oil	Thickener ¹ (Wt. Percent)	P ₀	P ₅₀	Dropping Point, °F.
6.....	A	(1)	(3)	(6)	H	17.5	216	275	580+
7.....	A	(1)	(3)	(6)	H	17.4	237	326	-----
8.....	A	(1)	(1)	(7)	J	20.0	189	289	-----
9.....	A	(1)	(1)	(7)	H	16.0	220	291	560
10.....	B	(1)	(1)	(7)	H	15.8	198	282	520
11.....	C	(1)	(1)	(7)	H	18.0	208	277	520
12.....	D	(1)	(1)	(7)	H	18.0	227	300	460
13.....	E	(1)	(1)	(7)	H	18.0	220	338	525
14.....	A	(1)	(3)	(7)	K	15.4	254	330	-----
15.....	A	(1)	(3)	(7)	K	20.5	263	332	-----
16.....	A	(1)	(1)	(7)	K	19.0	216	275	-----
17.....	A	(2)	(2)	(7)	L	20.0	218	277	-----
18.....	A	(2)	(2)	(7)	M	21.0	214	275	-----
19.....	A	(2)	(2)	(7)	N	² 28.5	197	296	-----
20.....	A	(2)	(2)	(7)	H	² 18.8	246	299	580+
21.....	A	(4)	(4)	(7)	H	16.0	252	387	-----
22.....	A	(1)	(1)	(7)	O	22.7	265	305	-----

¹ In addition to the thickener, these greases contained from 1.4% to 2.1% by weight of an oxidation inhibitor

² No antioxidants were used.

It is evident from the above table, that excellent greases are obtained having low penetrations and high dropping points.

The diisocyanates used in the preparation of the polyureas of Table I are described as follows:

"A" diphenylmethane 4,4'-diisocyanate;

"B" 3,3'-dimethyldiphenylmethane 4,4'-diisocyanate,

"C" 3,3'-bitolylene 4,4'-diisocyanate;

"D" m-xylylene diisocyanate;

"E" 2,4, 2,6-toluenediisocyanate (80/20).

The monoamines from which the R' and R'' radicals were derived are described as follows:

(1) Octadecylamine sold as "Armeen 18D" by the Armour Company, Chicago, Illinois;

(2) A mixture of monoamines sold as "Armeen HT" by the Armour Company, Chicago, Illinois, containing 25% hexadecylamine, 70% octadecylamine and 5% octadecenylamine;

(3) p-Toluidine;

(4) Rosin Amine (abietyl derived amine sold by Hercules Chemical Company;

Base oil "L" was a mixture of dipropylene glycol dipelargonate and a polypropylene oxide capped with an n-butyl group and a hydroxyl radical and having a molecular weight of about 500;

Base oil "M" was dipropylene glycol dipelargonate;

Base oil "N" was a poly(methylphenyl)siloxane (DC 710);

Base oil "O" was a poly(methylphenyl)siloxane (DC 510);

Base oil "P" is a neutral petroleum oil having a viscosity of 130 SSU at 100° F.;

Base oil "Q" is a neutral petroleum oil having a viscosity of 150 SSU at 100° F.

The following table illustrates three greases prepared according to the prior examples wherein sodium metaborate or sodium metaborate and molybdenum disulfide are incorporated in the grease. The sodium metaborate is an extreme pressure agent, while the molybdenum disulfide provides dry lubricating properties. The ureas formed were tetraureas and the data demonstrate that they are compatible with and operative with the alkali metal metaborates as well as molybdenum disulfide.

Table II

	Diisocyanate	R'	R''	R	Grease Composition		Sodium Metaborate Octahydrate Wt. Percent	MoS ₂ Wt. Percent	Grease Properties		
		Derived From—			Base Oil	Wt. Percent ² Thickener			P ₀	P ₅₀	Dropping Point, °F.
23.....	E.....	5	3	9	P.....	15	1	-----	240	300	484
24.....	E.....	5	3	8	Q/K ¹	14	2.2	-----	238	300	443
25.....	E.....	5	3	8	Q/K ¹	13	1.4	5	236	288	450

¹ About 2 parts of Q per 5 parts of K.

² Included in this composition were from 1.4 to 2.1 weight percent of commercial antioxidants and dyes.

(5) Tall oil fatty amine; M.W.=286; N= 4.89%;

The R radicals were derived from diamines described as follows:

(6) p-Phenylene diamine;

(7) Methylene dianiline;

(8) Ethylene diamine;

(9) m-Phenylene diamine.

The base oils are described as follows:

Base oil "H" was pentaerythritol tetracaporate;

Base oil "J" was a California paraffinic base petroleum oil having a viscosity of 480 SSU at 100° F.;

Base oil "K" was diisooctylazelate;

In order to demonstrate the effectiveness of the greases prepared using the polyureas, the following tests were carried out.

The "bearing life" for a particular grease composition was determined by the following test procedure which is known as the Navy High Speed Bearing Test as described in Federal Test Method 331.1. In this test, a ball bearing was operated at 10,000 r.p.m. continuously for approximately 22 hours at the temperature noted in Table III. The apparatus was then cooled to room temperature during a period of 2 hours. This procedure of operating at 10,000 r.p.m. at the noted temperature and cooling was repeated until there was bearing failure. The bearing life is the number of hours to bearing failure.

The thickeners were tetraureas, prepared as previously described. The various materials used are described hereinafter.

The base oils are identified as the same base oils used in Table I hereinabove.

In thickener A, the R' and R'' were derived from octadecylamine identified hereinabove as Armeen 18D; the diamine was methylene dianiline; and the diisocyanate was diphenylmethane 4,4'-diisocyanate.

Thickener B was as follows: the R' and R'' were derived from the octadecylamine identified hereinabove as Armeen HT, the diamine was methylene dianiline, and the diisocyanate was diphenylmethane 4,4'-diisocyanate. Thickener C was prepared as follows: the R' and R'' radicals were derived from the octadecylamine described hereinabove as Armeen 18D, the diamine was methylene dianiline, and the diisocyanate was m-xylylene diisocyanate.

Table III

	Thickener (wt. percent)	Base Oil	Oxidation Inhibitor (wt. percent)	Grease Properties			
				P ₀	P ₆₀	Bearing Life	
						Temp., ° F.	Hours *
(1)-----	A (20.0)	J	2.0	189	289	350	216
(2)-----	A (16.0)	H	1.6	220	291	350	424
(3)-----	B (18.0)	H	1.6	227	300	350	710
(4)-----	C (28.5)	N	0.0	197	296	450	128
(5)-----	A (22.7)	O	2.0	265	305	450	117

*Geometric Mean of 2 tests.

Table IV below presents further data on the physical characteristics of grease compositions thickened with tetraureas.

In all instances, the diisocyanate was an 80/20 blend of 2,4-toluenediisocyanate and 2,6-toluenediisocyanate.

The monoamines from which the R' and R'' radicals were derived are described as follows:

- (1) "Armeen HT" as described hereinabove;
- (2) "Armeen T" as described hereinabove.

The R radicals were derived from diamines described as follows:

- (3) Meta-xylenediamine;
- (4) Meta-phenylenediamine;
- (5) Ethylenediamine.

The base oil was a California base petroleum oil having a viscosity of 480 SSU at 100° F.

Table IV

Urea Characteristics			Thickener ¹ (wt. percent)	Grease Properties		
R' Derived From—	R'' Derived From—	R Derived From—		P ₀	P ₆₀	Dropping Point, ° F.
(1)	(1)	(3)	13.3	240	297	500+
(2)	(2)	(4)	10.8	216	286	500+
(2)	(2)	(5)	12.5	245	290	500+

¹ In addition to the thickener, the greases contained from 1.4% to 2.1% by weight, of an oxidation inhibitor.

Table V hereinbelow presents additional data showing the effectiveness of the greases of this invention. As prepared, a polyurea was used in that amount sufficient to produce a grease having an ASTM worked penetration (P₆₀) of approximately 290. The data shows the diisocyanate/diamine mole ratio.

The diisocyanate which was used was an 80/20 mixture of 2,4-tolyldiisocyanate and 2,6-tolyldiisocyanate.

The diamine was ethylenediamine, and the monoamine was Armeen T defined hereinabove.

8
Table V

	Diisocyanate/ Diamine Ratio	Percent Thickener
(1)-----	(^a) 1.3	20.6
(2)-----	(^b) 1.5	10.8
(3)-----	(^c) 2.0	10.2

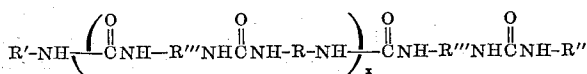
- (^a) Octaurea.
(^b) Hexaurea.
(^c) Tetraurea.

As will be evident to those skilled in the art, various modifications on this invention can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the following claims.

We claim:

1. A grease composition comprising an oil of lubricat-

ing viscosity and in an amount sufficient to thicken said oil to the consistency of a grease, a polyurea of the formula



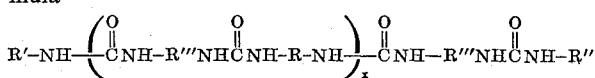
wherein x is a number having a value from 1 to 3, R' and R'' are hydrocarbon radicals containing from 1 to 30 carbon atoms, R and R''' are hydrocarbon radicals containing from 2 to 30 carbon atoms, wherein the ratio of carbon atoms to the number of urea groups is at least 6:1.

2. A grease composition according to claim 1 wherein said polyurea is present in an amount of from 5 to 50 percent by weight of said total composition.

3. A grease composition according to claim 1 wherein

said polyurea is present in an amount of from 6 to 25 percent by weight of said total composition.

4. A grease composition comprising an oil of lubricating viscosity and in an amount sufficient to thicken said oil to the consistency of a grease, a polyurea of the formula



wherein x is a number having a value of from 1 to 3, R'

and R'' are hydrocarbon radicals of from 5 to 28 carbon atoms, and R''' and R are hydrocarbon radicals of from 2 to 26 carbon atoms, wherein the ratio of carbon atoms to the number of urea groups is at least about 6:1.

5. A grease composition comprising an oil of lubricating viscosity and in an amount sufficient to thicken said oil to the consistency of a grease, a polyurea of the formula



wherein R^a and R^d are hydrocarbyl of from 5 to 28 carbon atoms, and R^b and R^c are hydrocarbylene of from 2 to 26 carbon atoms, wherein the ratio of carbon atoms to the number of urea groups is at least about 6:1.

6. A grease composition according to claim 5 wherein R^a and R^d are from 6 to 25 carbon atoms and R^b and R^c are from 2 to 18 carbon atoms.

7. A grease composition according to claim 5 wherein R^a and R^d are aliphatic of from 10 to 20 carbon atoms.

8. A grease composition according to claim 5 wherein R^a is an aliphatic radical of from 10 to 20 carbon atoms and R^d is an aryl radical of from 6 to 12 carbon atoms.

9. A grease composition according to claim 5 wherein the sum of the carbon atoms of R^a and R^d is in the range of 10 to 30.

10. A grease composition according to claim 5 wherein the sum of the carbon atoms of R^a and R^d is in the range of 10 to 30 and the sum of the carbon atoms of all of the R^b and R^c groups is in the range of 12 to 40.

11. A grease composition comprising an oil of lubricating viscosity and in an amount sufficient to thicken said

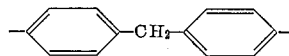
oil to the consistency of a grease, a polyurea of the formula



wherein R^a and R^d are hydrocarbyl of from 5 to 28 carbon atoms, R^c is an aliphatic hydrocarbon divalent radical of from 2 to 18 carbon atoms and R^b is an aromatic hydrocarbon divalent radical of from 6 to 18 carbon atoms, wherein the ratio of carbon atoms to the number of urea groups is at least about 6:1.

12. A grease composition according to claim 11 wherein R^b is tolylene.

13. A grease composition according to claim 11 wherein R^b is of the formula



14. A grease composition according to claim 11 wherein R^b is tolylene and R^c is ethylene.

15. A grease composition according to claim 11 wherein R^a and R^d are aliphatic of from 10 to 20 carbon atoms and R^b is tolylene.

16. A grease composition according to claim 11 wherein R^a is aromatic and R^d is aliphatic and the sum of the number of carbon atoms in R^a and R^d is in the range of 10 to 30.

References Cited by the Examiner

UNITED STATES PATENTS

2,832,739 4/1958 Swakon ----- 252—51.5

DANIEL E. WYMAN, *Primary Examiner*.

I. VAUGHN *Assistant Examiner*.