

1

3,242,210
POLYUREAS

John L. Dreher, Berkeley, and Judson E. Goodrich, San Rafael, Calif., assignors to Chevron Research Company, a corporation of Delaware
No Drawing. Filed Mar. 16, 1965, Ser. No. 440,282
17 Claims. (Cl. 260-553)

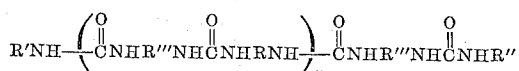
This application is a continuation-in-part of application Serial Nos. 84,511, filed Jan. 24, 1961; 109,827, filed May 15, 1961, both now abandoned; 210,559, filed July 17, 1962 and 312,357, filed Sept. 30, 1963, all now abandoned.

This invention concerns novel polyureas and their use as grease thickening agents. More particularly, this invention concerns novel polyureas of at least 4 urea groups having hydrocarbon terminal end members and their use as grease thickening agents.

There has been an increasing need for grease thickening agents 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.

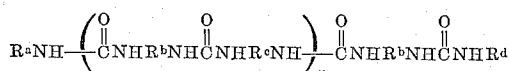
Pursuant to this invention, grease thickening agents having relatively high melting points (relatively high dropping points for the greases) are provided which are polyureas of the following formula:



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., alkaryl, 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 polyureas of this invention find use as grease thickeners providing greases which 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. Moreover, the polyureas are thickeners or gellants in a variety of fluids, particularly hydrocarbons, of low viscosity to form fire starters, paints, and the like.

The preferred compositions of this invention have 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, dodecenyamine, hexadecenyamine, octadecenyamine, octadecadienyamine, abietyamine, aniline, toluidine, naphthylamine, cumylamine, bornylamine, fenchylamine, tert-butyl aniline, benzylamine, β -phenethylamine, etc.

Illustrative of monoisocyanates are hexylisocyanate, decylisocyanate, dodecylisocyanate, tetradecylisocyanate, hexadecylisocyanate, phenylisocyanate, cyclohexylisocyanate, 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.

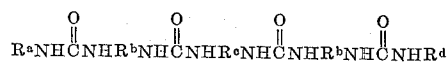
Illustrative of various diamines are ethylenediamine, propanediamine, butanediamine, hexanediamine, dodecanediamine, octanediamine, hexadecanediamine, cyclohexanediamine, cyclooctanediamine, phenylenediamine, toluenediamine, xylenediamine, dianilinmethane, ditoluidine-methane, bisaniline, bistoluidine, etc.

Illustrative of diisocyanates are hexanediisocyanate, decanediisocyanate, octadecanediisocyanate, phenylene-diisocyanate, 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.

Preferably, the polyureas will 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 of this invention have the following formula:



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

The polyureas of this invention can be used as thickening agents to form greases in a wide variety of oils of lubricating viscosity. Various base oils include naphthenic base, paraffin base and mixed base mineral lubricat-

ing 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-pentoxy)disiloxane, etc.

When used as grease thickeners, the compounds described herein are used in 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 compositions of this invention may also be used with a wide variety of hydrocarbon solvents as gellants. These include both aromatic solvents such as benzene, toluene, xylene, or mixtures thereof as well as aliphatic solvents, such as heptane, hexane, octane, nonane, decane, etc. or mixtures thereof. When used as a gellant, the polyureas will be present in amount of at least about 0.5 weight percent, more usually from about 1 to 5 weight percent.

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 1,200 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 diisooctylazelate 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 had 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 diisooctylazelate 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:

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

EXAMPLE 3.—PREPARATION OF HEXAUREA

A mixture of 10.8 g. (0.10 mole) of metaphenylene diamine, 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.

EXAMPLE 4.—PREPARATION OF OCTAUREA

A mixture of 16.2 g. (0.15 mole) of metaphenylene diamine 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.

EXAMPLE 5.—PREPARATION OF TETRAUREA

A mixture of 3.6 g. of ethylenediamine, 30 g. of Armeen T¹, and 7 g. of an antioxidant was heated at 140° F. for 10 minutes, forming a homogenous 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 on 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

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

many instances, the ASTM Dropping Point in degrees F. are reported.

Base oil "L" was a mixture of dipropylene glycol dipelargonate and a polypropylene oxide capped with an

Table I

Ex. No.	Tetraurea Characteristics				Grease Composition		Grease Properties		
	Diisocyanate	R'	R''	R	Base Oil	Thickener ¹ (Weight Percent)	P ₀	P ₅₀	Dropping Point, °F.
		Derived From—							
6	A	(1)	(3)	(6)	H	17.5	216	275	530+
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	228.5	197	296	
20	A	(2)	(2)	(7)	H	218.8	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, Ill.;

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

(3) p-toluidine;

n-butyl group and a hydroxyl radical and having a molecular weight of about 500;

30 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);

35 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 weight percent	MoS ₂ Weight percent	Grease Properties		
		Derived From—			Base Oil	Weight percent Thickener ¹			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 ²	14	2.2	-----	238	300	443
25	E	5	3	8	Q/K ²	13	1.4	5	236	288	450

¹ Included in this composition were from 1.4 to 2.1 weight percent of commercial antioxidants and dyes.

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

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

(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 tetracaproate;

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 grease 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 material 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 (weight percent)	Base Oil	Oxidation Inhibitor (weight percent)	Grease Properties			
				P ₀	P ₆₀	Bearing Life	
						Temp., ° F.	Hours ¹
(1)-----	A (20.0)-----	J-----	2.0	819	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

¹ 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 as described as follows:

- (1) "Armeen HT" is 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 (weight percent)	Grease Properties		
R'	R''	R		P ₀	P ₆₀	Dropping Point, ° F.
Derived From—						
(1)	(1)	(3)				
(2)	(2)	(4)	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 polyureas as grease thickeners. 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-tolylidiisocyanate and 2,6-tolylidiisocyanate.

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.

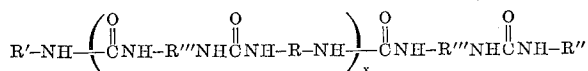
To demonstrate the use of the polyureas as gellants, a tetraurea was prepared at 0.7 weight percent in a commercial thinner. A 0.1 weight percent solution of 1,3-propane diamine (163 ml.), 11.85 ml. of a 10 weight percent solution of tall oil fatty amine and 75.2 ml. of a 1 weight percent solution of tolylene diisocyanate (as previously described) (the solvent in each case was the

thinner) was mixed and 50 additional ml. of thinner added. Penetration following the ASTM method, but using a 23 g. cone, was 331. The composition was a stable gel.

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 polyurea of the formula

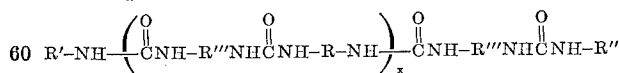


wherein x is a number having a value from 1 to 3, R, R' and R'' are hydrocarbon radicals containing from 1 to 30 carbon atoms, and R''' is a hydrocarbon radical containing from 2 to 30 carbon atoms.

2. A polyurea as described in claim 1 wherein x=1.

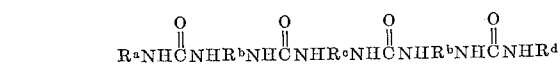
3. A polyurea as described in claim 1 wherein x=1 and the ratio of carbon atoms to the number of urea groups is at least about 6:1.

4. 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, R''' and R are hydrocarbon radicals of from 2 to 26 carbon atoms.

5. A tetraurea of the formula



wherein R^a and R^d are hydrocarbonyl of from 5 to 28 carbon atoms, and R^b and R^e are hydrocarbonylene of from 2 to 26 carbon atoms.

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

9

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

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

9. A tetraurea according to claim 5 wherein the ratio of carbon atoms to urea groups is at least 6:1.

10. A tetraurea 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.

11. A tetraurea 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, the sum of the carbon atoms of all of the R^b and R^c is in the range of 12 to 40 and the ratio of carbon atoms to urea groups is at least 6:1.

12. A tetraurea according to the formula



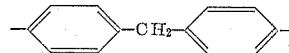
wherein R^a and R^d are hydrocarbyl of from 5 to 28

10

carbon atoms, R^c is aliphatic of from 2 to 18 carbon atoms and R^b is aromatic of from 6 to 18 carbon atoms.

13. A tetraurea according to claim 12 wherein R^b is tolylene.

5 14. A tetraurea according to claim 12 wherein R^b is of the formula



10 15. A tetraurea according to claim 12 wherein R^b is tolylene and R^c is ethylene diamine.

16. A tetraurea according to claim 12 wherein R^a and R^d are aliphatic of from 10 to 20 carbon atoms and R^b is tolylene.

15 17. A tetraurea according to claim 12 wherein the ratio of carbon atoms to urea groups is at least 6:1.

No references cited.

NICHOLAS S. RIZZO, *Primary Examiner*.