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GREASES CONTAINING AMIDOUREA THICKENERS

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ABSTRACT OF THE DISCLOSURE

High temperature greases comprising a lubricating oil base and as a thickener therefor, an amido or imido substituted polyurea of from 1 to 3 hydrocarbyl urea groups.

This patent application relates to grease compositions and thickening agents therefor, which compositions are characterized by their extreme high temperature stability and outstanding penetration characteristics. More particularly, the application relates to greases thickened with novel carboxylic acid-ureido derivatives which may be characterized as amides and imides of alkyl and aryl ureas.

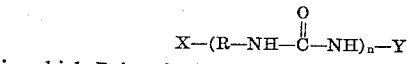
Recently, the demand has increased for greases capable of providing effective lubrication at high temperatures. The demand has been stimulated by development of modern equipment operating at high speeds, etc., and is evidenced by the many industrial and military specifications which provide minimum dropping point requirements of 400+° F. In many applications, operating temperatures of over 500° F. are encountered, and a consequent requirement has resulted for greases able to operate at these temperatures. Among the factors contributing to these demands are the increased driving power of automobiles and aircraft, etc., and reduction in size of gears and other parts resulting from streamlining and other like design factors. An example of such streamlining is the reduction in total diameter of transmission and power train equipment in modern automobiles for the purpose of reducing clearances necessary for floors, etc. This results in reduction of gear diameters with a consequent increase in speed and temperature.

Among the materials that have been employed to produce high melting point greases are the salts of certain fatty and other carboxylic acids. Examples of such materials of this type which are commonly employed are the lithium salts of various fatty acids. However, these salts, in common with other materials of this general type, while providing greases of high melting points, contribute oxidation-promoting metal ions to the grease composition. These ions thus effect corrosion of the parts which the greases are designed to lubricate. It is, therefore, particularly desirable to provide high temperature stable greases which are, in addition, ashless, i.e., do not contain metal ions.

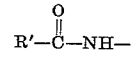
Although numerous non-metallic thickening agents have been proposed, these materials have generally failed to provide sufficiently high dropping points and consequent high temperature stabilities to be employed successfully in the aforementioned applications. Also, most of the ashless materials proposed have failed to provide proper stability characteristics, that is, such characteristics as are defined in tests as penetration, etc.

It is thus highly important to provide greases which have high dropping points, provide excellent lubrication for long periods at such high temperatures, are ashless and may be easily and economically prepared.

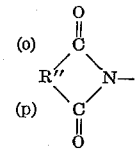
It has now been found that excellent high temperature greases result from the combination of an oil of lubricating viscosity and certain carboxylic acid-ureido compounds. Thus, the thickening agents of this invention comprise materials which may be represented by the formula:



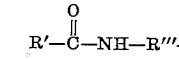
in which R is a hydrocarbylene radical of 1 to 30 carbon atoms, n is a cardinal number 1 to 3, and X is a radical selected from the group consisting of (a)



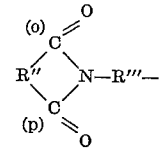
in which R′ is selected from the group consisting of alkyl radicals of 10 to 30 carbon atoms and aryl radicals of 6 to 16 carbon atoms, and (b)



in which R″ is selected from the group consisting of arylene radicals of 6 to 16 carbon atoms and alkyl groups of 2 to 30 carbon atoms and wherein bonds o and p are separated through R″ by 2 carbon atoms, and Y is selected from the group consisting of (a′)



in which R′ is as previously defined and R‴ is hydrocarbylene of 1 to 30 carbon atoms, and (b′)

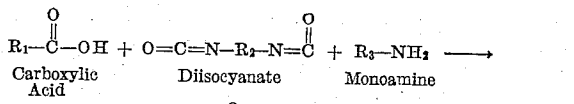


in which bonds o and p, R″ and R‴ are as previously defined, and (c) hydrocarbyl radicals of 1 to 30 carbon atoms.

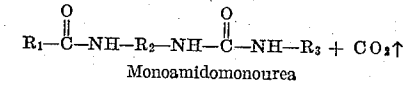
A preferred species of the invention is a grease thickened by a diamidodiurea derived from two molecules of stearic acid, two molecules of tolylene diisocyanate and one molecule of p-phenylene diamine.

Thus, the additives of this invention may be described as amides and imides of mono-, di- and triureas. These materials are formed by reacting in certain proportions suitable carboxylic acids or internal carboxylic anhydrides, diisocyanates and amines or diamines. The following reactions illustrate the formation of the various amidoureas of this invention.

Monoamidomonoureas are prepared by reacting one molecule of a diisocyanate with one molecule each of a carboxylic acid and a monoamine. Correspondingly, monoimidomonoureas are formed by reacting one molecule of a cyclic anhydride, one molecule each of a diamine and a monoisocyanate. The following equations using a monoamido compound as an example illustrate these reactions:



Carboxylic Acid — Diisocyanate — Monoamine



Monoamidomonourea

In the preparation of a monoimidourea, the anhydride reacts with one amine group of a diamine, and the other amine group reacts with the isocyanate, thus no CO_2 is released.

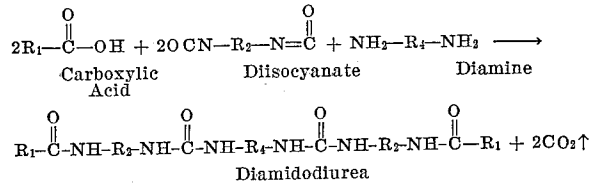
Suitable carboxylic acids from which R_1 is derived include aliphatic carboxylic acids of from about 11 to 31 carbon atoms and aromatic carboxylic acids of from 7 to 17 carbon atoms. Examples of suitable acids include aliphatic acids such as lauric, myristic, palmitic, margaric, stearic, arachidic, behenic, lignoceric acid, etc.; and aromatic acids, such as benzoic acid, 1-naphthoic acid, 2-naphthoic acid, phenylacetic acid, hydrocinnamic acid, cinnamic acid, mandelic acid, etc. Suitable anhydrides which may be employed are those derived from dibasic acids which form a cyclic anhydride structure, for example, succinic anhydride, maleic anhydride, phthalic anhydride, etc. Substituted anhydrides, such as alkenyl succinic anhydrides of up to 30 carbon atoms are further examples of suitable materials.

Examples of suitable diisocyanates, from which R_2 is derived, include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 3,3'-bi-tolylene diisocyanate, diphenylmethane-4,4'-diisocyanate, etc.

Suitable monoisocyanates and monoamines for the production of monoamido- and monoimidomonoureas include phenyl isocyanate and tolyl isocyanate, and are preferably derived from aliphatic radicals of 2 to 30 carbon atoms or aromatic radicals of 6 to 16 carbon atoms.

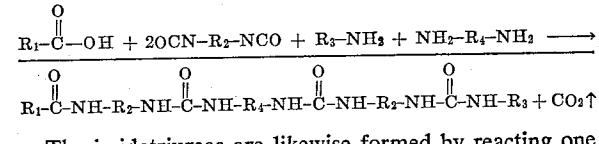
The diamines are preferably aliphatic diamines of 2 to 30 carbon atoms or aromatic diamines of 6 to 16 carbon atoms. Examples of suitable diamines are ethylene diamine, propylene diamine, butylene diamine, phenylene diamine, tolylene diamine, etc.

In the formation of diamidodiureas, two molecules of the acid, two molecules of the diisocyanate and one molecule of a diamine are reacted according to the following equation:



The acids, anhydrides, diisocyanates, monoamines and diamines are the same as employed in producing the monourea materials. Since the anhydride will not react directly with the isocyanate, diimidodiureas are produced by reacting two molecules of the anhydride with two molecules of the diamine and one molecule of the diisocyanate.

The monoamidotriureas are formed by the reaction of one molecule of the carboxylic acid, two molecules of the diisocyanate, and one molecule each of the diamine and monoamine according to the following reaction:



The imidotriureas are likewise formed by reacting one molecule of the anhydride, two molecules of the diamine, and one molecule each of the diisocyanate and the monoamine.

The thickeners may be easily prepared in situ, i.e., in the lubricant base, or may be prepared separately and then added to the base. The materials may be prepared by blending the several reactants together in a reaction vessel and heating them at temperatures ranging from 70° F. to about 600° F. for a time sufficient to cause formation of the desired thickener. For example, in the formation of a diamidodiurea, two moles of carboxylic acid, two moles of diisocyanate and one mole of a diamine may be blended together to form a uniform mixture, then heated at temperatures within the range prescribed. However, since the diisocyanate reacts with amines at a more rapid rate than with acids, a higher yield of the diamidodiurea may be obtained if the reaction is carried forth in separate steps. For example, it is preferable to react the diisocyanate first with the acid and then add the amine material. Correspondingly, in the case of diamido- and imidoureas, it is also preferable to conduct the acid-diisocyanate or anhydride-diamine reaction first. In either case, the reaction may be carried out simply by mixing the reactants together as described, or a basic catalyst may be employed to hasten the reaction. Typical bases which may be employed as catalysts are electron-rich nitrogen bases, such as triethylamine and triethylene diamine. The use of a mild catalyst and a somewhat elevated temperature for the reaction is preferable to the use of strong catalysts and lower temperatures. Strong bases, such as sodium hydroxide or an alkoxide, should not be used, as a possibly resulting uncontrolled reaction may lead to an explosion.

The following examples illustrate the preparation of the various carboxylic acid-urea type derivatives and greases which contain them. The examples are only illustrative and are not intended to be limiting of the invention.

Example I.—Preparation of diimidodiurea grease in single-step reaction

16.9 g. (0.0677 mole) of diphenylmethane-4,4'-diisocyanate in 50 ml. of methyl ethyl ketone, 14.7 g (0.135 mole) of p-phenylene diamine in 50 ml. of methyl ethyl ketone and 20.9 g. (0.135 mole) of hexahydrophthalic anhydride were mixed in a reaction vessel. To this mixture was added 146 g. of pentaerythritol tetracaproate and 4 g. of trimethyl dihydroquinoline oxidation inhibitor. The methyl ethyl ketone was then removed by distillation from the mixture. The mixture was then heated to 400° F. and stirred to yield a grease consisting of 25% thickener in the synthetic oil and having the following properties:

Penetration, initial (P_0)	256
Penetration, after 60 strokes (P_{60})	314
ASTM dropping point, ° F. (DP)	522

Example II.—Preparation of diamidodiurea grease employing mineral oil

85.2 g. (0.30 mole) of stearic acid was placed in a metal beaker and mixed with 300 g. of a paraffinic oil having a viscosity of 480 SSU at 100° F. The beaker was placed on a hotplate with a stirring motor attached and the mixture was heated and stirred at 150° F. until it was dissolved. 2.0 g. of triethylamine was added. 52.2 g. (0.30 mole) of 2.4-tolylene diisocyanate was then added to the mixture and the material was heated at 175° F. for twenty minutes until evolution of CO_2 ceased. 17.0 g. (0.15 mole) of m-phenylene diamine was mixed with 200 g. of the base oil and heated on a steamplate at 300° for thirty minutes. This solution was then stirred to suspend the liquified m-phenylene diamine and was added to the reaction beaker. There was no reaction at 175° F. The mixture was then heated to 295° F. with rapid stirring, and a very heavy gel formed. 235 g. of additional oil was added; stirring was continued. The grease was then heated to 400° F. for thirty minutes. 7.0 g of phenyl-alpha-naphthylamine oxidation inhibitor was added. The material was then cooled and milled in a 3-roll mill. To 890 g. of the grease, 50 g. of additional oil was added and hand mixed. The mixture was then passed once more through the 3-roll mill, giving a grease having a P_0 of 240, P_{60} of 284, a dropping point (DP) of 552° F. and containing 16.2% of the thickener.

Example III.—Preparation of monoamidourea and mixture of synthetic and mineral oil

300 g. of an oil blend comprising 50% of a paraffinic base oil having a viscosity of 150 SSU at 100° F. and 50% of dipropylene glycol dipelargonate and 102.2 g. (0.36 mole) of stearic acid were placed in a large flask equipped with heating jacket and stirring device. The mixture was stirred and heated to 150° F. for thirty minutes. All the

material dissolved. 5.0 g. of triethylamine was added, and the mixture was stirred an additional five minutes. 62.6 g. (0.36 mole) of an 80:20 isomeric mixture of 2,4- and 2,6-tolylene diisocyanate was added to the mixture. Foaming began and continued for thirty minutes. A solution of 38.5 g. (0.36 mole) of p-toluidine and 200 g. of the oil base which had been heated to 150° F. was added to the mixture. The mixture became cloudy and somewhat thick. The material was then heated to 240° F., and 5.0 g. of phenyl-alpha-naphthylamine oxidation inhibitor was added. Heating was continued. A heavy gel formed at about 250° F. The grease was then heated to 350° F., held for thirty minutes, cooled and transferred to beakers and heated in a 350° F. oven for three and one-half hours with occasional hand stirring. The grease was then cooled and milled in a 3-roll mill. 150 g. of the oil base was added to 650 g. of the grease, and the grease was then milled once more through the 3-roll mill. The grease, which contained 22.9% thickener, had a dropping point (DP) of 453° F., a P_0 of 229 and a P_{60} of 250.

Example IV.—Preparation of monoamidotriurea grease

17.0 g. (0.15 mole) of m-phenylene diamine and 16.0 g. (0.15 mole) of p-toluidine were mixed with 200 g. of a blend of 40% of a mineral lubricating oil having a viscosity of 480 SSU at 100°, 45% of pentaerythritol tetracaproate and 15% of dioctyl azelate. The mixture was placed on a hotplate and stirred to effect solution. 42.6 g. (0.15 mole) of stearic acid and 300 g. of the oil base were placed in a metal breaker and heated to 160° F. with stirring. 52.2 g. (0.30 mole) of tolylene diisocyanate was added to the mixture and stirred for five minutes. 2.0 g. of triethylamine was added to the mixture. The mixture was heated to 150° F. and stirred for thirty minutes until foaming ceased. The first and second solutions were mixed and heated to 300° F. At this temperature, gelation began, and the mixture continued to gel to a heavy grease at 350° F. The grease was heated to 400° F. and held for one hour. The grease was cooled and milled twice through a 3-roll mill. 150 g. of additional base oil was blended with 590 g. of the grease, yielding a grease containing 15.9% by weight thickener and having a dropping point of 540° F., P_0 of 246 and P_{60} of 290.

Greases containing carboxylic-urea derivatives were prepared according to the procedures enumerated above, and data on ASTM unworked penetration (P_0), ASTM worked penetration after 60 strokes in the ASTM worker (P_{60}), and ASTM dropping points in ° F. are included in the following table. Work breakdown penetration ($P_{100,000}$) is also included for certain samples of the greases.

The base oils which were employed are described as follows:

(A) California paraffinic-base petroleum oil having a viscosity of 480 SSU at 100° F.
(B) Mixture of 50% California paraffinic-base petroleum oil having a viscosity of 150 SSU at 100° F. and 50% dipropylene glycol dipelargonate
(C) Mixture of 40% (A), 45% pentaerythritol tetracaproate and 15% diisooctyl azelate
(D) Pentaerythritol tetracaproate

The anhydrides and the carboxylic acids which were employed are as follows:

(1) Stearic acid
(2) Oleic acid
(3) Hydrogenated fish acid
(4) 12-hydroxystearic acid
(5) Phthalic anhydride
(6) Hexahydrophthalic anhydride

The diisocyanates are as follows:

(7) 2,4-tolylene diisocyanate
(8) 80:20 isomeric mixture of 2,4,2,6-tolylene diisocyanate
(9) 3,3'-bi-tolylene diisocyanate
(10) Diphenylmethane-4,4'-diisocyanate

The dimaines employed are as follows:

(11) m-Phenylene diamine
(12) Ethylene diamine
(13) p-Phenylene diamine

The monoamines which were employed are as follows:

(14) p-Toluidine
(15) Tall oil fatty amines
(16) Rosin amine

The materials in the following table were prepared by the methods set forth previously and illustrated in the preceding examples. The materials were each inhibited with about 0.5% of phenyl-alpha-naphthylamine.

TABLE I

Sample No.	Thickener Type	Reactants					Thickener, percent	Oil	ASTM D.P., ° F.	P_0	P_{60}	$P_{100,000}$
		Anhydride	Acid	Diisocyanate	Diamine	Monoamine						
1	Diamidodiurea		4	8	11			A	(1)			
2	do		1	7	11		16.2	A	552	240	284	316
3	do		1	8	12		13.3	A	470	223	269	
4	do		1	7	11		15.0	C	511	225	284	
5	do		1	9	11		15.7	C	550	240	301	
6	do	1		7	11		25.0	A	550		268	
7	do	1		7	12		20.0	A	540		249	
8	Diimidodiurea	6		10	13		25.0	D	522	256	314	
9	do	5		10	13		20.0	D	406	305	359	
10	Monoamidourea		1	8		14	22.9	B	453	229	250	345
11	do		1	10		14	16.9	C	486	225	278	
12	do		2	8		14	28.7	B	496	275	351	
13	do		1	9		14	15.3	C	560	252	296	
14	do		1	9		14	15.9	C	546	248	305	
15	do		1	7		14	15.4	A	481	260	285	388
16	do		2	8		15	27.5	A		260	344	
17	do		1	8		15	32.7	A	439	212	280	
18	do		3	8		15	32.7	A	441	215	278	
19	do		1	8		16	34.7	A	<300	Fluid		
20	do		1	8		14	16.4	A	496	214	284	
21	Monoamidotriurea		1	8	11	14	15.9	C	540	246	290	330
22	do		1	8	11	14	17.2	C	513	232	285	
23	do		2	8	11	14	20.2	C	543	195	248	
24	do		3	8	11	14	19.7	B		208	275	

[1] Fluid at Room Temp.

As can be seen from the extensive data embodied in the above table, greases which are prepared from mineral oils, synthetics, and mixtures of mineral and synthetic oils when thickened by the diamido, diimido, monoimido, urea, etc., of this invention display high dropping points and excellent unworked (P_0) and worked (P_{60}) penetrations. Of special significance are the relatively small differences between the worked and unworked penetrations. Additionally, the work breakdown penetration ($P_{100,000}$) of selected samples shows excellent resistance to shear for these greases. Note that the grease of Example I which employed 12-hydroxystearic acid as the amide-forming unit was, however, fluid at room temperature. Also, it may be noted that Example 18 in which thickener employed was prepared from a mixed abietyl amine had an ASTM dropping point of less than 300° F. and was essentially fluid in the penetration test. Thus, amines of this type are not suitable for the preparation of grease thickeners.

In addition to dropping point, penetration, and aging tests, greases thickened by monoamido-monoureas were subjected to high speed bearing performance tests. The particular test employed 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 twenty-two hours at 350° F. The apparatus was then cooled to room temperature during a period of two hours. The procedure of operating at 10,000 r.p.m. at the noted temperature of cooling was repeated until there was bearing failure. The "Bearing Life" is the number of hours to bearing failure.

The thickeners employed in this test are as follows: X designates monoamidourea derived from stearic acid, 2,4-tolylene diisocyanate and p-toluidine. Y designates monoamidourea derived from stearic acid, diphenylmethane-4,4-diisocyanate and p-toluidine. Each sample contained 0.4% phenyl-alpha-naphthylamine and 2.0% dioctyldiphenylamine as corrosion and oxidation inhibitors. The oils employed in the tests are the same as referred to in Table I. Table II embodies the results of these tests:

TABLE II

Sample	Base Oil	Navy High Speed Bearing Life, 10,000 r.p.m., 350° F., hrs.	
		Run I	Run II
X	A	172	130
Y	C	379	347

As noted in the table, the mineral oil base grease had a bearing life of 172 and 130 hours respectively. This performance under 350° F. temperature is remarkable for a mineral oil. One hundred and fifty hours performance at 350° F. is equivalent to between 2,000 and 3,000 hours at 250°. The "Bearing Life" of the synthetic oil-based grease was also very good.

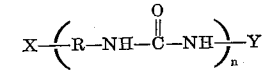
Lubricating oils which can be used as base oils for the greases of this invention include a wide variety of oils, for example, naphthenic base, paraffin base, and mixed-based mineral lubricating oils; synthetic oils, such as polymers of propylene, butylene, etc.; propylene oxide polymers; dicarboxylic acid esters, such as those which are prepared by esterifying azelaic acid with 2-ethylhexyl alcohol; and silicon esters, such as tetraethyl silicate, hexa(4-methyl-2-pentoxy)-disiloxane, etc. Also, mixtures of synthetic and mineral lubricating oils may be employed.

The thickeners described in this specification are employed in amounts sufficient to thicken the oils to the consistency of grease, that is, in amounts ranging from 5 to 50% by weight, or preferably in amounts from 10 to 30% by weight.

While the character of this invention has been described in detail with numerous examples, this has been done by way of illustration only and without limitation of the invention. It will be applied to those skilled in the art that numerous modifications and variations of the illustrative examples may be made in the practice of the invention within the scope of the appended claims.

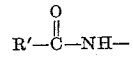
We claim:

1. 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 carboxylic-ureido derivative of the formula:



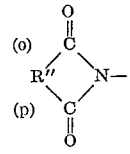
in which R is a hydrocarbylene radical of 1 to 30 carbon atoms, n is a cardinal number 1 to 3, and X is a radical selected from the group consisting of

(a)



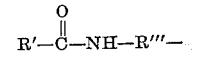
in which R′ is selected from the group consisting of alkyl radicals of 10 to 30 carbon atoms and aryl radicals of 6 to 16 carbon atoms, and

(b)



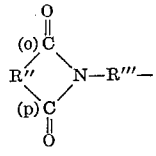
in which R″ is selected from the group consisting of arylene radicals of 6 to 16 carbon atoms and alkylene groups of 2 to 30 carbon atoms and wherein bonds o and p are separated through R″ by 2 carbon atoms, and Y is selected from the group consisting of

(a′)



in which R′ is as previously defined and R‴ is hydrocarbylene of 1 to 30 carbon atoms, and

(b)



in which R″ and R‴ and the bonds (o) and (p) are as previously defined, and (c) hydrocarbyl radicals of 2 to 30 carbon atoms.

2. The composition of claim **1** in which R is an arylene radical of 6 to 16 carbon atoms, n is 2, X is (a) in which R′ is an alkyl group of 10 to 30 carbon atoms and Y is (a′) in which R′ is an alkyl radical of 10 to 30 carbon atoms and R‴ is an arylene radical of 6 to 16 carbon atoms.

3. The composition of claim **2** in which R′ is alkyl of 12 to 24 carbon atoms.

4. The composition of claim **3** in which R and R‴ are tolylene radicals.

5. The composition of claim **3** in which R and R″ are 3,3′-bitolylene and R′ is the alkyl radical from stearic acid.

6. The composition of claim **1** in which n is 1 and Y is an alkyl radical of 10 to 30 carbon atoms.

7. The composition of claim **6** in which X is (a) and Y is an alkyl radical of 10 to 30 carbon atoms.

8. The composition of claim **1** in which n is 3 and Y is an alkyl radical of 10 to 30 carbon atoms.

9. The composition of claim **1** in which the oil of lubricating viscosity is a synthetic oil.

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9

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