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3,082,170

POLYORGANO SILOXANE THICKENED TO A GREASE CONSISTENCY WITH A DIAZO COMPOUND AND AN ARYLUREA

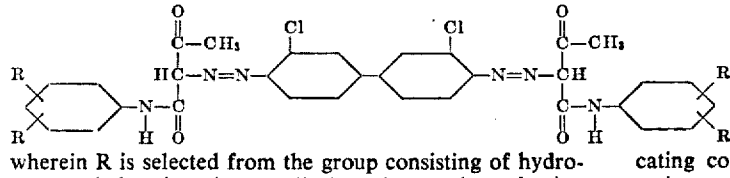
Paul R. McCarthy, Allison Park, and Thomas R. Orem, Pittsburgh, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

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8 Claims. (Cl. 252—49.6)

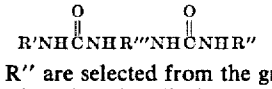
This invention relates to improved lubricating compositions and more particularly to lubricants suitable for high temperature lubrication.

The trend in design of modern aircraft has accentuated the need for greases which will lubricate anti-friction bearings operating at high rotational speeds and high temperatures. While considerable progress has been made in recent years in producing improved aircraft greases some difficulty has been encountered in producing a grease which will effectively lubricate bearings operating at high rotational speeds and high temperatures for prolonged periods of time. Conventional aircraft greases currently available have failed to meet the stringent requirements on such a lubricant.

We have discovered that a lubricating composition having improved lubricating characteristics for an extended period of time when used to lubricate bearings operating at an elevated temperature under high rotational speeds can be obtained by incorporating into a lubricating oil in oil thickening proportions a mixture of a diazo compound having the following structural formula



wherein R is selected from the group consisting of hydrogen, methyl and methoxy radicals and an arylurea having the general formula



wherein R′ and R″ are selected from the group consisting of aryl and substituted aryl radicals containing no more than 12 cyclic carbon atoms, and R‴ is selected from the group consisting of arylene and substituted arylene radicals containing no more than 12 cyclic carbon atoms, the weight ratio of the diazo compound to the arylurea being about 1:4 to about 4:1. The substituted aryl and substituted arylene radicals can contain substituents such as alkyl, aryl, hydroxy, alkoxy, carboxy, halogen, nitro, carboalkoxy, cyano, and the like. The aryl and arylene radicals can be mononuclear and/or polynuclear. By way of example and not limitation, the unsubstituted aryl radicals thus include phenyl, diphenyl, naphthyl, etc. The unsubstituted arylene radicals include phenylene, biphenylene, naphthylene, diphenylmethane, etc. Thus, the improved lubricating composition of our invention comprises a dispersion in a lubricating oil of a sufficient amount to thicken the lubricating oil to a grease consistency of a mixture of a diazo compound and an arylurea of the type designated by the above structural formulae wherein the weight ratio of the diazo compound to the arylurea is about 1:4 to about 4:1. A preferred range of the diazo compound to the arylurea obtained from an aryl diisocyanate and a mixture of aryl monoamines is about 1:1 to about 3:1.

The amount of the combined diazo compound and the arylurea which we use is an amount sufficient to thicken the lubricating oil to a grease consistency. In general, this amount comprises about 10 to about 40 percent by

weight of the total composition. The weight ratio of the diazo compound to the arylurea will vary depending upon the characteristics desired in the ultimate composition. In general, however, the ratio of diazo compound to the arylurea is between about 1:4 and about 4:1.

The diazo compounds are available commercially. Therefore, neither the compounds per se nor their method of preparation constitutes any portion of the invention. These compounds are familiarly known as Benzidine Yellows. Particularly suitable compounds of the class represented by the structural formula as designated hereinabove are bis(acetyl-N-phenylcarbamylmethyl)4,4′-diazo-3,3′-dichlorodiphenyl; bis(acetyl-N-o-tolylcarbamylmethyl)4,4′ - diazo-3,3′-dichlorodiphenyl; bis(acetyl-N-p-tolylcarbamylmethyl)4,4′ - diazo - 3,3′ - dichlorodiphenyl; bis (acetyl - N-o-methoxyphenylcarbamylmethyl)4,4′ - diazo-3,3′-dichlorodiphenyl; and bis(acetyl-N-m-xylylcarbamylmethyl)4,4′-diazo-3,3′-dichlorodiphenyl.

The amount of the diazo compound used may vary over wide limits depending upon the particular oil with which the diazo compound is to be blended and upon the properties desired in the final lubricating composition. While as much as 20 percent by weight of the total composition may comprise the diazo compound, we prefer to use smaller amounts, that is, in the order of about 5 to 15 percent by weight. It should be understood, however, that depending upon the consistency of the composition desired and upon the arylurea compound used in combination therewith, less than 5 percent or even more than 20 percent of the diazo compound may be employed.

The arylurea compound which we employ in the lubricating composition of this invention is prepared by reacting, preferably in the lubricant vehicle, an aryl isocyanate with an aryl amine or mixture of aryl amines. Thus, for example, an especially outstanding thickener may be prepared by reacting 3,3′-dimethylbiphenylene-4,4′-diisocyanate with a mixture of p-toluidine and p-chloroaniline in a molar ratio of 1:1:1 respectively. Examples of the aryl isocyanates which can be employed are 1,4-diisocyanato benzene; 1,3,5-triisocyanato benzene; 2,4-tolylene diisocyanate; 2,6-tolylene diisocyanate; p,p′-diisocyanate biphenyl; 3,3′-dimethylbiphenylene-4,4′-diisocyanate; methylene di(p-phenylene isocyanate); naphthylene diisocyanate; mixtures thereof; etc. Examples of the amines are p-aminobenzoic acid; p-biphenylamine; benzidine; p-anisidine; o-tolidine; p-aminophenol; p-amino-benzonitrile; p-phenylenediamine; m-phenylenediamine; o-phenylenediamine; aniline; p-chloroaniline; p-fluoroaniline; diaminodurene; p-toluidine; N-ethyl-o-toluidine; menthanediamine; triaminobenzene; benzoguanamine; 2,5-dichloroaniline; mixtures thereof; etc. The amount of the arylurea compound employed may vary over wide limits depending upon the particular compound employed, the particular oil with which the arylurea compound is blended and the properties desired in the ultimate composition. While the arylurea compound may comprise as much as 20 percent by weight of the total composition, we prefer to use smaller amounts, that is, in the order of about 5 to about 15 percent by weight. It should be understood, however, that depending upon the consistency of the composition desired and upon the diazo compound content of the composition less than 5 percent or more than 20 percent of the arylurea compound can be employed.

The arylurea compound is readily prepared by heating a mixture of the aryl isocyanate and the aryl amine at a temperature within the range of room temperature (about

70° F.) to about 350° F. The aryl isocyanate can comprise a mixture of aryl isocyanates. Also, the aryl amine can comprise a mixture of aryl amines. The aryl isocyanate and the aryl amine are preferably employed in amounts so that the ratio of cyano radicals to amino radicals is about 1 to 1. Thus, if an aryl diisocyanate is reacted with an aryl monoamine, the molar ratio of aryl diisocyanate to monoamine is preferably 1 to 2. If an equimolar mixture of two aryl monoamines is employed, the molar ratio of aryl diisocyanate to each monoamine is preferably 1 to 10.

The lubricating oil in which the diazo compound and the arylurea compound are incorporated is preferably a lubricant of the type best suited for the particular use for which the ultimate composition is designed. Since many of the properties possessed by the lubricating oil are imparted to the ultimate lubricating composition, we advantageously employ an oil which is thermally stable at the contemplated lubricating temperature. Some mineral oils, especially hydrotreated mineral oils, are sufficiently stable to provide a lubricating base for preparing lubricants to be used under moderately elevated temperatures. Where temperatures in the order of 400° F. and above are to be encountered, synthetic oils form a preferred class of lubricating bases because of their high thermal stability. The synthetic oil can be an organic ester which has a majority of the properties of a hydrocarbon oil of lubricating grade such as di-2-ethylhexyl sebacate, dioctyl phthalate and dioctyl azelate. Instead of an organic ester, we can use polymerized olefins, copolymers of alkylene glycols and alkylene oxides, polyorgano siloxanes, poly-aryl ethers and the like.

The liquid polyorgano siloxanes and certain poly-aryl ethers because of their exceedingly high thermal stability form a preferred group of synthetic oils to which the diazo compound and arylurea are added. The polyorgano siloxanes are known commercially as silicones and are made up of silicon and oxygen atoms wherein the silicon atoms may be substituted with alkyl, aryl, alkaryl, aralkyl and cycloalkyl radicals. Exemplary of such compounds are the dimethyl silicone polymers, diethyl silicone polymers, ethyl-phenyl silicone polymers and methyl-phenyl silicone polymers. Exemplary of an exceedingly good polyaryl ether is a polyphenyl ether, i.e., m-bis(m-phenoxyphenoxy)-benzene.

If desired, a blend of oils of suitable viscosity may be employed as the lubricating oil base instead of a single oil by means of which any desired viscosity may be secured. Therefore, depending upon the particular use for which the ultimate composition is designed, the lubricating oil base may be a mineral oil, a synthetic oil, or a mixture of mineral and/or synthetic oils. The lubricating oil content of the compositions prepared according to this invention comprises about 60 to about 90 percent by weight of the total composition.

In compounding the compositions of the present invention, various mixing and blending procedures may be used. In a preferred embodiment of the invention, the aryl isocyanate is dispersed in about one half of the lubricating oil at about 350° F. After all of the aryl isocyanate is added, the mixture is cooled to and held at about 180° to 190° F. with continuous stirring. The aryl amine or mixture of amines is dispersed in the other half of the lubricating oil at about 180° F. The oils containing the isocyanate and amine respectively are then pumped simultaneously through a Premier colloid mill set at a stator-rotor clearance of 0.0015 inch. Mixing and reaction of the isocyanate with the amine occurs in the mill whereupon an arylurea grease is obtained. The arylurea grease is then transferred from the mill to a grease kettle where the grease is heated and stirred under nitrogen to 450° F. in about 3 hours and then held at this temperature for an additional hour. The grease is then cooled to about 150° F. while stirring is continued. The diazo compound together with conventional lubricant additives, if desired, are then added to the cooled arylurea grease while stirring is continued. The mixture thus formed is then passed twice by means of a pump, through a Premier colloid mill set at a stator-rotor clearance of 0.0015 inch. Maximum thickening occurs on the second pass through the mill.

The lubricating composition of this invention can contain conventional lubricant additives, if desired, to improve other specific properties of the lubricant without departing from the scope of the invention. Thus, the lubricating composition can contain a filler, a corrosion and rust inhibitor, an extreme pressure agent, an antioxidant, a metal deactivator, a dye, and the like. Whether or not such additives are employed and the amounts thereof depend to a large extent upon the severity of the conditions to which the composition is subjected and upon the stability of the lubricating oil base in the first instance. Since the polyorganosiloxanes, for example, are in general more stable than mineral oils, they require the addition of very little, if any oxidation inhibitor. When such conventional additives are used they are generally added in amounts between about 0.01 and 5 percent by weight based on the weight of the total composition.

In order to illustrate the lubricating characteristics at an elevated temperature and high rotational speeds, grease compositions of the invention were subjected to a test procedure similar to that outlined by the Coordinating Research Council Tentative Draft (July, 1954), "Research Technique for the Determination of Performance Characteristics of Lubricating Grease in Antifriction Bearings at Elevated Temperatures," CRC Designation L–35. According to the procedure used to evaluate the compositions, 3 grams of the grease to be tested are placed in a bearing assembly containing an eight-ball SAE No. 204 ball bearing. In general, bearings fabricated from high speed tool steel and ball retainers fabricated from silver-plated beryllium-copper (MRC204S–17) are used as both test and outboard bearings. The bearing assembly which is mounted on a horizontal spindle is subjected to a radial load of 5 pounds. The portion of the spindle upon which the test bearing assembly is located is encased in a thermostatically controlled oven. By this means the temperature of the bearing can be maintained at a desired elevated temperature which in the tests reported hereinafter was 400° F. The spindle is driven by a constant belt-tension motor drive assembly, capable of giving spindle speeds of 20,000 revolutions per minute. The spindle is operated on a cycling schedule consisting of a series of periods, each period consisting of 20 hours running time and 4 hours shutdown time. The test continues until the lubricant fails. The lubricant is considered to have failed when any one of the following conditions occurs, (1) spindle input power increases to a value approximately 300 percent above the steady state condition at the test temperature; (2) an increase in temperature at the test bearing of 20° F. over the test temperature during any portion of a cycle; or (3) the test bearing locks or the drive belt slips at the start or during the test cycle.

The oil used in preparing the lubricating compositions summarized in Table I was a synthetic oil known commercially as DC 550 Fluid. DC 550 Fluid is marketed by Dow-Corning Corporation and is a methylphenyl-siloxane polymer having as typical characteristics a viscosity at 100° F. of 300 to 400 SUS, a viscosity-temperature coefficient of 0.75, a freezing point of −54° F., a flash point of 600° F. and a specific gravity 25° C./25° C. of 1.08.

In order to illustrate the increased performance life of grease compositions of the invention (compositions F, G and H), comparative grease compositions were prepared using only the arylurea compound (compositions A and B) or the diazo compound (composition C) as the oil thickening agent. Other grease compositions (compositions D and E) were prepared in which the ratio of diazo compound to arylurea compound was above 4 to 1. The thickened lubricating compositions had the following approximate make-up and properties.

TABLE I

Composition, Percent By Weight	A	B	C	D	E	F	G	H
Lubricating Oil: DC 550 Fluid	89.39	79.05	80	79.9	79.86	79.67	79.52	79.8
Diazo Compound:								
Bis(acetyl-N-phenylcarbamylmethyl)4,4'-diazo-3,3'-dichlorodiphenyl					17		8.78	
Bis(acetyl-N-o-methoxyphenylcarbamylmethyl)-4,4-diazo-3,3'-dichlorodiphenyl			20	17		13	1.22	15
Arylurea Compound Prepared From:								
Aryl Isocyanate—								
3,3'-Dimethylbiphenylene-4,4'-diisocyanate	5.65	11.15		1.7	1.67	3.90	5.58	2.8
Aryl Amine—								
p-Toluidine	2.27	4.48		0.6	0.67	1.57	2.24	1.1
p-Chloroaniline	2.69	5.32		0.8	0.80	1.86	2.66	1.3
Ratio of diazo compound to arylurea compound				5.5:1	5.4:1	1.8:1	0.95:1	2.9:1
Inspection:								
Penetration (ASTM D217-52T)—								
Unworked	297	333	257	271	297	264	320	279
Worked	357	340	294	309	302	279	331	305
Dropping Point, ° F. (ASTM D566-42)	450+	450+	450+	450+	450+	450+	450+	450+
Performance Life, Hrs.—Pope Spindles, 20,000 r.p.m. at 400° F	321	375	221	56	338	530+	596+	517+

The long performance life of the compositions of the invention (compositions F, G and H) at a high rotational speed and a high temperature is self-evident from the above data. It will be noted that even though compositions D and E contained all of the components of a grease composition of the invention, the weight ratio of the diazo compound to the arylurea compound was above the maximum required to give an optimum performance life.

In addition to the shorter performance life obtained with the arylurea greases (compositions A and B), these greases tended to gum during operation in the bearing at 400° F., thus increasing the torque required for rotation of the bearing. Composition C containing only the diazo compound did not exhibit the gumming tendency of compositions A and B, but the composition lacked the lubricating ability of the arylurea greases at high speeds under load. Compositions D and E which contained an excess of the diazo compound also lacked the lubricating ability of greases of the invention.

Other lubricating compositions within the scope of the invention are illustrated in Table II. G. E. Silicone 81717 is marketed by General Electric Company and is a water-white to amber liquid polymer of the general formula

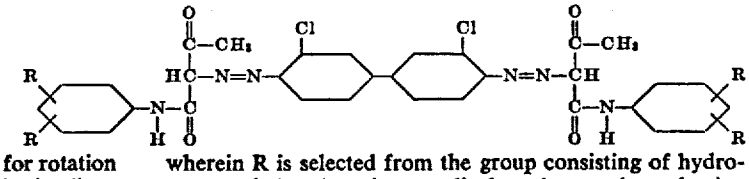
$$[—Si(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2O—]_x$$

It has a viscosity at −65° F. of 3487 centistokes, at 0° F. of 390 centistokes, at 100° F. of 71.3 centistokes, at 210° F. of 22 centistokes and at 700° F. of 1.9 centistokes.

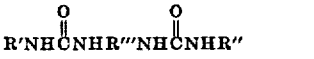
While our invention has been described with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such examples and embodiments and may be variously practiced within the scope of the claims hereinafter made.

We claim:

1. A lubricating composition comprising a dispersion in a liquid polyorgano siloxane of a sufficient amount to thicken the polyorgano siloxane to a grease consistency of a mixture of a diazo compound having the following structural formula



wherein R is selected from the group consisting of hydrogen, methyl and methoxy radicals and an arylurea having the general formula



wherein R' and R'' are selected from the group consisting of aryl and substituted aryl radicals containing no more than 12 cyclic carbon atoms, and R''' is selected from the group consisting of arylene and substituted arylene radicals containing no more than 12 cyclic carbon atoms, the weight ratio of the diazo compound to the arylurea being about 1:4 to about 4:1.

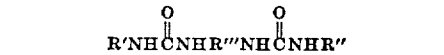
2. The lubricating composition of claim 1 wherein the combined diazo compound and arylurea comprises about 10 to about 40 percent by weight of the total composition.

3. A lubricating composition comprising a liquid poly-

TABLE II

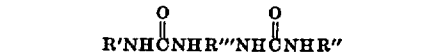
Composition, Percent By Weight	I	J	K	L	M	N	O	P	Q	R
Lubricating Oil:										
DC 550 Fluid	60		80		76.6	76.2	75.1	70.1	80	90
G.E. Silicone 81717		73.8								
m-Bis(m-phenoxyphenoxy)benzene				75						
Diazo Compound:										
Bis(acetyl-N-phenylcarbamylmethyl)4,4'-diazo-3,3'-dichlorodiphenyl	20			20					15	
Bis(acetyl-N-o-tolylcarbamylmethyl)4,4'-diazo-3,3'-dichlorodiphenyl		17.5								
Bis(acetyl-N-o-methoxyphenylcarbamylmethyl)-4,4'-diazo-3,3'-dichlorodiphenyl			10		13	13	5	15		5
Arylurea Compound Prepared From:										
Aryl Isocyanate—										
2,4-Tolylene diisocyanate	7.3	2.0					6.5			
2,6-Tolylene diisocyanate		1.0								
3,3'-Dimethylbiphenylene-4,4'-diisocyanate				2.6	7.4	5.7		7.9	2.6	2.6
Methylene di(p-phenylene isocyanate)			7.0							
Aryl Amine—										
p-Phenylenediamine	3.3		3.0		3.0					
N-Ethyl-o-toluidine	9.4									
p-Toluidine		2.8		1.1		2.3	6.1	3.2	1.1	1.1
p-Chloroaniline				1.3		2.8	7.3	3.8	1.3	1.3
p-Fluoroaniline		2.9								
Ratio of diazo compound to arylurea compound	1:1	2:1	1:1	4:1	1.3:1	1.2:1	1:4	1:1	3:1	1:1

organo siloxane thickened to a grease consistency with about 10 to about 40 percent by weight, based on the weight of the total composition, of a mixture of bis(acetyl-N - phenylcarbamylmethyl)4,4' - diazo - 3,3' - dichlorodiphenyl and an arylurea having the general formula



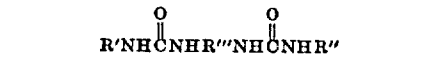
wherein R' and R'' are selected from the group consisting of aryl and substituted aryl radicals containing no more than 12 cyclic carbon atoms and R''' is selected from the group consisting of arylene and substituted arylene radicals containing no more than 12 cyclic carbon atoms, wherein the weight ratio of the bis(acetyl-N-phenylcarbamylmethyl)4,4'-diazo-3,3'-dichlorodiphenyl to the arylurea is about 1:4 to about 4:1.

4. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 40 percent by weight, based on the weight of the total composition, of a mixture of bis(acetyl-N - o - tolylcarbamylmethyl)4,4' - diazo - 3,3' - dichlorodiphenyl and an arylurea having the general formula



wherein R' and R'' are selected from the group consisting of aryl and substituted aryl radicals containing no more than 12 cyclic carbon atoms and R''' is selected from the group consisting of arylene and substituted arylene radicals containing no more than 12 cyclic carbon atoms, wherein the weight ratio of the bis(acetyl-N-o-tolylcarbamylmethyl)4,4'-diazo-3,3'-dichlorodiphenyl to the arylurea is about 1:4 to about 4:1.

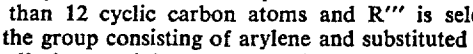
5. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 40 percent by weight, based on the weight of the total composition, of a mixture of bis(acetyl-N - o - methoxyphenylcarbamylmethyl)4,4' - diazo - 3,3'-dichlorodiphenyl and an arylurea having the general formula



wherein R' and R'' are selected from the group consisting of aryl and substituted aryl radicals containing no more than 12 cyclic carbon atoms and R''' is selected from the group consisting of arylene and substituted arylene radicals containing no more than 12 cyclic carbon atoms,

wherein the weight ratio of the bis(acetyl-N-o-methoxyphenylcarbamylmethyl)4,4' - diazo - 3,3' - dichlorodiphenyl to the arylurea is about 1:4 to about 4:1.

6. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 40 percent by weight, based on the weight of the total composition, of a mixture of bis(acetyl-N - o - methoxyphenylcarbamylmethyl)4,4' - diazo - 3,3'-dichlorodiphenyl and an arylurea having the general formula

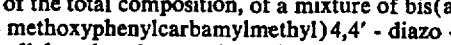


wherein the weight ratio of the bis(acetyl-N-o-methoxyphenylcarbamylmethyl)4,4' - diazo - 3,3' - dichlorodiphenyl to the arylurea is about 1:1 to about 3:1.

7. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 40 percent by weight, based on the weight of the total composition, of a mixture of bis(acetyl-N - o - methoxyphenylcarbamylmethyl)4,4' - diazo - 3,3'-dichlorodiphenyl and an arylurea having the general formula

wherein the weight ratio of the bis(acetyl-N-o-methoxyphenylcarbamylmethyl)4,4' - diazo - 3,3' - dichlorodiphenyl to the arylurea is about 1:1 to about 3:1.

8. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 40 percent by weight, based on the weight of the total composition, of a mixture of bis(acetyl-N - o - methoxyphenylcarbamylmethyl)4,4' - diazo - 3,3'-dichlorodiphenyl and an arylurea having the general formula



wherein the weight ratio of the bis(acetyl-N-o-methoxyphenylcarbamylmethyl)4,4' - diazo - 3,3' - dichlorodiphenyl to the arylurea is about 1:1 to about 3:1.

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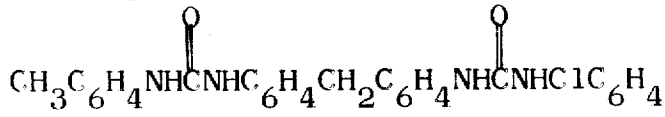
CERTIFICATE OF CORRECTION

Patent No. 3,082,170 March 19, 1963

Paul R. McCarthy et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 11, for "1 to 10" read -- 1 to 1 --; column 8, line 38, the formula should appear as shown below instead of as in the patent:



Signed and sealed this 1st day of October 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

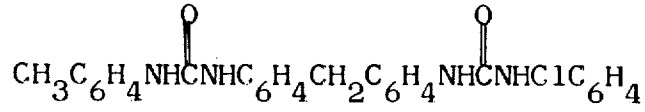
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