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(72) Inventeurs/Inventors:
WALLACE, WILLIAM G., US;
FRYE, RICHARD L., US;
WAYNICK, JOHN A., US

(73) Propriétaire/Owner:
AMOCO CORPORATION, US

(74) Agent: GOWLING LAFLEUR HENDERSON LLP

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A lubricating grease having superior penetration, dropping point, and shear stability properties is provided comprising a base oil, an additive package, a urea-containing thickener, and a lithium soap thickener.



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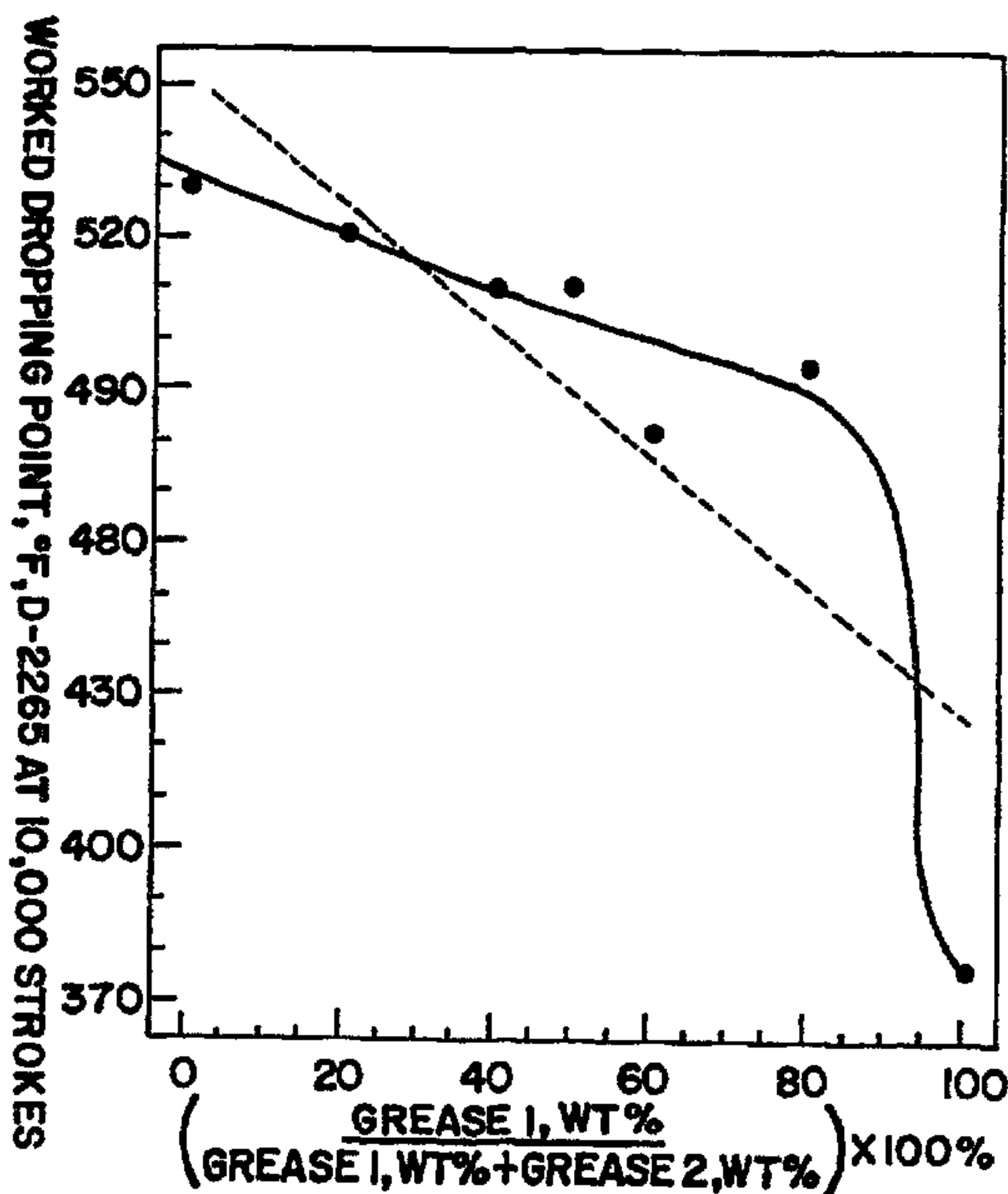
(30) Priority Data:
08/240,849 11 May 1994 (11.05.94) US(71) Applicant: AMOCO CORPORATION [US/US]; Law Dept.,
Mail Code 1907A, 200 East Randolph Drive, P.O. Box
87703, Chicago, IL 60680-0703 (US).(72) Inventors: WALLACE, William, G.; 418 Stonemill Lane,
Oswego, IL 60543 (US). FRYE, Richard, L.; 1549 Aztec
Circle, Naperville, IL 60563 (US). WAYNICK, John, A.; 1
North 210 Parkridge Drive, Wheaton, IL 60188 (US).(74) Agent: KRETCHMER, Richard, A.; Amoco Corporation, Law
Dept., Mail Code 1907A, 200 East Randolph Drive, P.O.
Box 87703, Chicago, IL 60680-0703 (US).(81) Designated States: CA, JP, MX, RU, UA, European patent
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(54) Title: LUBRICATING GREASE

(57) Abstract

A lubricating grease having superior penetration, dropping point, and shear stability properties is provided comprising a base oil, an additive package, a urea-containing thickener, and a lithium soap thickener.



LUBRICATING GREASE

Background Of The Invention

5 This invention relates to lubricants and greases possessing superior penetration, dropping point, and shear stability properties. More particularly, this invention relates to a lubricating grease which comprises urea-containing and lithium soap thickeners.

10 Early lubricating greases were thickened by metal soap salts of fatty acids of which the most commonly used metals were sodium, calcium, aluminum, and lithium. Fatty acids included various vegetable and animal fatty acids as well as those derived from petroleum sources. More recently, the preferred fatty acids have been hydroxylated stearic acids and more preferably, 12-hydroxystearic acid.

15 Metal soap salts of fatty acids for lubricating greases were generally provided by reacting the metal hydroxide, oxide, carbonate, or other metallic basic compound with the fatty acid to form the corresponding fatty acid soap. This thickener formation reaction usually occurred directly in the base oil which was to be thickened. Depending on the thickener being formed, water was often used as a reaction solvent or stabilizer. If a fatty acid derivative such as an ester was used
20 as the fatty acid source, water was added to hydrolyze the derivative and free the fatty acid which could then react with the basic reagent to form the fatty acid soap. If water was not required in the final product to stabilize the thickener system, the water was generally removed by heating the grease above 212°F.

25 Fatty acid soap thickeners such as those described above are generally referred to as simple soap thickeners. Depending on the metallic base used, greases thickened by such simple soaps have (ASTM D-2265) dropping points of about 200°F to about 380°F. Traditionally, the dropping point of these simple soap thickened products defined their highest operating temperature by the following qualitative relationship: the highest temperature of satisfactory
30 performance is 100°F less than the dropping point. For example, when using a lithium soap thickened grease with a dropping point near 400°F, the maximum useful operating temperature of that grease was only about 300°F.

35 As the severity of lubricating grease applications increased, the need for thickener systems having higher dropping points became apparent. This need resulted in the development of complex soap thickeners. The most commonly

used complex soap thickeners are calcium complex, lithium complex, and aluminum complex.

5 Lithium complex and aluminum complex greases generally have poor thermal and oxidative stability at sustained high temperatures, such as 350°F and higher. At such temperatures, the grease rapidly degrades to a lacquer-hard material which is devoid of lubricating properties. This lacquer-hard deposition is generally considered to be the result of catastrophic oxidation of the grease and is generally believed to be promoted by lithium and aluminum complex thickeners. The use of antioxidant additives can delay oxidation of the grease but cannot
10 prevent it. As such, high sustained temperatures adversely affect the performance of lithium complex and aluminum complex greases despite their generally higher dropping point properties.

 Calcium complex thickened greases can also severely harden under sustained high temperatures, although usually not to the lacquer-hard condition
15 exhibited by lithium and aluminum complex greases. However, calcium complex greases are vulnerable in other areas. For example, at temperatures as low as 75°F and in the presence of air, calcium complex greases generally begin to harden. The hardening begins at the grease/air interface and slowly extends further into the bulk of the grease with time. This phenomena is well known in the
20 art and is commonly referred to as skin/age hardening.

 This hardening characteristic of complex soap thickened greases presents numerous problems for many commercial applications. For example, in bearing applications where the bearing is moving only part of the time but experiences high temperatures during those times, hardening effects generally reduce bearing
25 life. In applications where fretting or oscillatory motions are experienced, long term grease hardening can cause catastrophic failure due to starvation of functional lubricant.

 Another problem commonly experienced by lithium and calcium complex greases is that of reduced thickening power. Simple lithium soap greases with an
30 NLGI No. 2 grade consistency can typically have a lithium soap content of 6 percent to 7 percent based on the weight of the grease. However, with lithium complex thickened greases of equivalent consistency, nearly twice the amount of thickener, 12 percent to 14 percent, based on the weight of the grease, is required. Calcium complex thickened greases show similar behavior. For
35 example, an NLGI No.2 grade calcium complex grease can typically require soap

levels of 16 percent to 18 percent, based on the weight of the grease, compared to about 8 percent for simple calcium soap thickened greases of equal consistency. Aside from the higher cost associated with the thickener component compared to the grease base oil, higher thickener levels can adversely affect the pumpability characteristics of the grease.

Another thickener system which has been used with significant success and as an alternative to the above complex soap thickeners is polyurea. Polyurea thickener has numerous fine qualities which make it a superior grease thickener for some applications compared to lithium, calcium, and aluminum complex thickeners. Polyurea does not exhibit high temperature lacquer deposition and generally has acceptable pumpability characteristics. The dropping point of polyurea is above 450°F, and often above 500°F. When polyurea thickened greases exhibit their dropping point, it is generally due to the thickener's inability to hold the oil and not due to the melting of the polyurea. This is in contradistinction to most complex soap thickeners which generally melt at their dropping points.

In spite of the many advantages of polyurea thickeners, polyurea thickeners possess several attributes that limit their usefulness as a lubricating grease thickener. Polyurea thickened greases retain their original consistency quite well when subjected to high shearing force, but can often soften significantly when subjected to lower shearing forces. For instance, in ASTM D-1403 Penetration tests at 100,000 strokes, polyurea greases usually soften by 60 to 100 points or more. Similar softening effects can occur when polyurea greases are subjected to ASTM D-1831 Roll Stability tests. Polyurea thickened greases can also have oil separation characteristics which significantly and undesirably increase as the application temperature increases. This is a characteristic which is also exhibited by many complex soap thickened greases. Moreover, polyurea thickeners are generally more expensive than complex soap thickeners providing large incentives to reduce or eliminate polyurea usage in lubricating greases.

Several U.S. Patents disclose grease compositions containing lithium-containing thickeners.

For example, U. S. Patent No. 2,397,956 to Fraser discloses a grease composition comprising a grease-forming lubricant base and a lithium soap of 12-hydroxystearic acid. The 12-hydroxystearic acid is provided in a quantity that

increases the ability of the grease to maintain its consistency when mechanically worked.

U. S. Patent No. 4,897,210 to Newsoroff discloses a lithium complex grease thickener comprising a lithium salt of 12-hydroxystearic acid or the alkyl esters thereof in combination with a dilithium salt derived from dialkyl esters of terephthalic acid in a molar proportion of about 0.5 to 15:1. The grease has high lubricating activity, shear stability, water resistance, and dropping point.

U. S. Patent No. 5,242,610 to Doner et al. discloses a grease composition comprising an alkali or alkaline earth metal or amine derivative of a hydroxy-containing or polyhydroxy-containing soap thickener such as 12-hydroxystearic acid and a borated derivative of an organic compound. The grease has strong dropping point characteristics.

Numerous other U.S. Patents disclose grease compositions containing urea-containing components.

For example, U. S. Patent No. 5,145,591 to Kinoshita et al. discloses a grease composition comprising diurea. The diurea grease maintains its consistency at high temperatures.

U. S. Patent No. 5,059,336 to Naka et al. discloses a grease composition comprising a synthetic lubricating base oil, a thickening agent consisting of an urea compound, sorbitan monooleate, barium sulfonate, and barium lanolate. The grease has rust-prevention properties and is particularly effective for use with high-speed roller bearings.

U. S. Patent No. 5,043,085 to Kinoshita et al. discloses a grease composition comprising a base oil, a thickener selected from the group consisting of urea compounds, urea-urethane compounds, and mixtures thereof, and an ingredient selected from the group consisting of oxidized paraffins, diphenylhydrogen phosphite, hexamethyl phosphoric triamide, and mixtures thereof. The grease provides improved properties for preventing fretting when applied to sliding or joining portions of parts for constraining relative motions or for bearing fine reciprocal movements.

U. S. Patent No. 5,011,617 to Fagan discloses a complex tolylene polyurea-thickened grease composition containing less than 7 parts per million 2, 4-diaminotoluene and a process for making such a grease. The process comprises reacting an isocyanate, a polyamine, and monoamine with a major portion of a lubricating oil and thereafter adding an alkaline earth metal oxide or

hydroxide and a carboxylic acid anhydride containing 2 to 20 carbon atoms to the mixture and thereafter milling to grease consistency. The grease is prepared in a manner so as to contain no detectable 2, 4-diaminotoluene which is stated by Fagan to cause cancer in laboratory animals.

5 U. S. Patent No. 4,692,255 to Matzat et al. discloses a grease composition comprising a polyurea thickener and a method for preparing the polyurea thickener. The thickener is the reaction product of isocyanate and at least three isocyanate groups in the molecule with a long-chain, straight-chain, or branched aliphatic monoamine. The thickened grease results in extended temperature and
10 wear properties.

U. S. Patent No. 3,846,314 to Dreher et al. discloses a grease composition comprising a mono or polyurea compound having from 1 to 8 ureido groups and having a molecular weight of between about 375 and 2500 and an alkaline earth metal aliphatic monocarboxylate having from 1 to 3 carbon atoms. The weight
15 ratio of the alkaline earth metal carboxylate to mono and polyurea compounds is from 1 to 15. The grease composition is particularly useful at high temperatures.

U. S. Patent No. 3,243,372 to Dreher et al. discloses a grease composition comprising polyurea of at least 4 urea groups having hydrocarbon terminal end members. The grease composition is particularly effective at high temperatures.

20 The prior art greases and thickener systems identified above have met with varying degrees of success, and have largely been subject to the various application limitations and constraints described previously.

The combination of a blended thickener package consisting of polyurea and calcium soap has also been taught in the art.

25 U. S. Patent No. 5,084,193 to Waynick discloses a grease composition having a blended thickener package consisting of polyurea and calcium soap. The polyurea and calcium soap thickener package reduces lacquer deposition, high temperature hardening, skin/age hardening, and has superior oil separation properties.

30 It has now been found that a lubricating grease comprising a thickener package comprising a lithium soap thickener and a urea-containing thickener provides synergistically superior performance than greases comprising either thickener individually or than the results expected from a mathematical blend of the thickener systems.

It has also been found that a grease comprising a thickener package comprising a lithium soap thickener and a urea-containing thickener provides synergistically superior performance over a wider and more cost-effective range of soap thickener to urea-containing proportions compared to identical greases wherein a calcium soap thickener was used in place of a lithium soap thickener.

It has also been found that adding a critically targeted amount of boric acid to a grease comprising a thickener package comprising a lithium soap thickener and a urea-containing thickener, provides superior results to that achieved without addition of boric acid.

It has also been found that grease preparation steps comprising heating the grease comprising a thickener package comprising a lithium soap thickener, a urea-containing thickener, and a critically targeted amount of boric acid to temperatures in excess of 200°F provides superior results to greases prepared from processing steps maintained at temperatures below 200°F.

It is therefore an object of the present invention to provide a lubricating grease that has superior oxidation stability, hardening, and dropping point characteristics to lubricating greases containing simple or complex metal soap salt of fatty acid thickeners alone.

It is another object of the present invention to provide a lubricating grease that has improved shear stability and oil separation properties, and cost advantages to greases containing urea-containing thickeners alone.

It is yet another object of the present invention to provide a lubricating grease that exhibits outstanding dropping point characteristics at high sustained operating temperature levels while maintaining excellent penetration properties.

Other objects appear herein

Summary Of The Invention

The above objectives can be achieved by providing a lubricating grease comprising a base oil, an additive package, a urea-containing thickener, and a lithium soap thickener.

In another embodiment, the above objectives can be achieved by providing a lubricating grease comprising a base oil, an additive package, and a blended thickener system comprising a urea-containing thickener and a lithium soap thickener wherein said lithium soap thickener comprises from about 30 percent to about 95 percent of said blended thickener system, calculated by weight.

In still another embodiment, the above objectives can be achieved by providing a lubricating grease comprising a base oil, an additive package, a blended thickener system comprising a urea-containing thickener and a lithium soap thickener wherein said lithium soap thickener comprises from about 30 percent to about 95 percent of said blended thickener system, calculated by weight, and boric acid in an amount ranging from about 0.1 weight percent to about 2.0 weight percent calculated as a percentage of the lubricating grease.

The lubricating grease in accordance with the present invention achieves numerous performance benefits not met by prior art lubricating greases. The lubricating grease provides improved shear stability, dropping point, oil separation over a wide range of temperatures, fretting wear, and thermal and oxidative stability.

The lubricating grease in accordance with the present invention maintains its thickening power and pumpability characteristics in contrast to prior art complex thickeners composed entirely of metal soap salts of fatty acids.

The lubricating grease in accordance with the present invention generally does not exhibit the lacquer deposition problems which are common with greases containing lithium or aluminum soap thickeners exclusively. Furthermore, greases thickened with the thickener system of the present invention exhibit substantially less severe high temperature hardening, a characteristic often associated with calcium complex thickened greases. Similarly, skin/age hardening is also reduced.

The lubricating grease in accordance with the present invention can be used as lubricating greases for a wide range of applications including, but not limited to, both extreme pressure and anti-wear conditions. Additives commonly used in soap and non-soap thickened greases can also be used in greases thickened by the improved thickener system of the present invention, thereby providing the grease formulator a high degree of flexibility by which improved products can be developed.

Brief Description of the Drawings

Figure 1 is a graph of Worked Dropping Point (ASTM D-2265) in °F at 10,000 Strokes compared to the percentage of Grease 1 (lithium soap thickener) expressed as a percentage of the total of Greases 1 and 2 (lithium soap and urea-containing thickeners).

Figure 2 is a graph of Worked Dropping Point (ASTM D-2265) in °F at 10,000 Strokes compared to the percentage of Grease 4 (calcium soap thickener) expressed as a percentage of the total of Greases 4 and 5 (calcium soap and urea-containing thickeners).

5 Figure 3 is a graph of Worked Dropping Point (ASTM D-2265) in °F at 10,000 Strokes compared to the weight percent of boric acid in the grease for Greases 16 through 20.

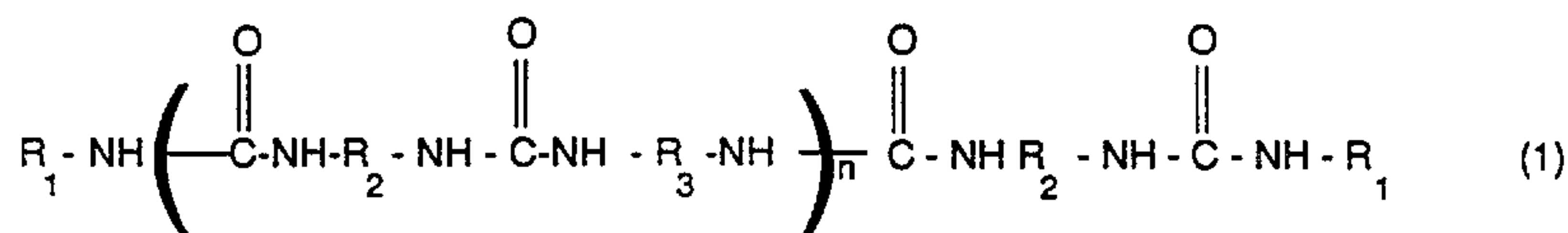
10 Figure 4 is a graph of Worked Dropping Point (ASTM D-2265) in °F at 10,000 Strokes compared to grease oven temperature in °F for Greases 21 through 26.

Brief Description of the Invention

15 A lubricating grease having superior shear stability, dropping point, oil separation over a wide range of temperatures, fretting wear, and thermal and oxidative stability is provided which is particularly useful for lubricating wheel bearings, steel mill bearings, constant velocity joints such as those found in front wheel drive automobiles, fifth wheels on semi-trailers, high-speed flexible couplings, universal joints, and other devices requiring the application of a superior performance grease. The lubricating grease comprises a base oil, an
20 additive package, a urea-containing thickener, and a lithium soap thickener.

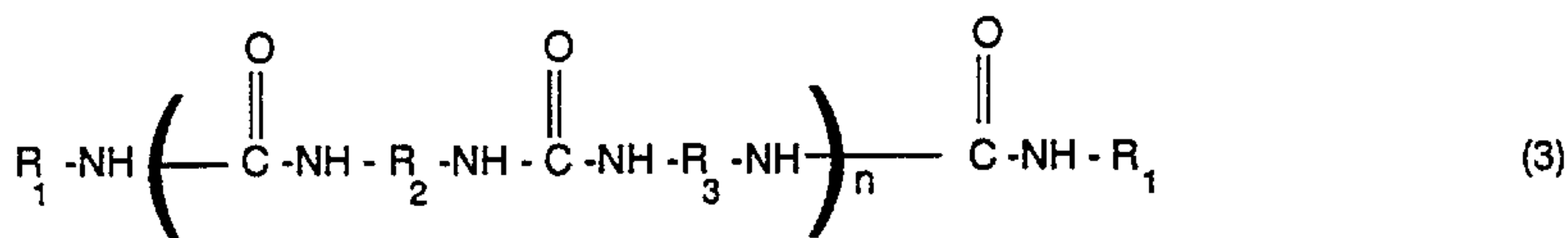
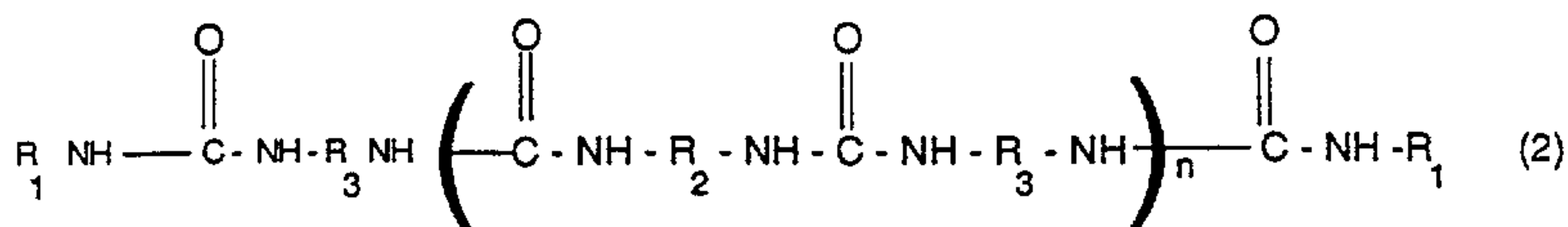
The urea-containing thickener component suitable for use with the present invention can be a monourea, diurea, triurea, or polyurea thickener component. The preferred urea-containing thickener is polyurea.

25 Mono- and polyurea compounds suitable for use with the present invention generally have structures defined by the following formulae:



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wherein n is an integer of from 0 to 3; R_1 is the same or a different hydrocarbonyl having from 1 to 30 carbon atoms and preferably from 10 to 24 carbon atoms; R_2 is the same or a different hydrocarbonylene having from 2 to 30 carbon atoms and preferably from 6 to 15 carbon atoms; and R_3 is the same or a different hydrocarbonylene having from 1 to 30 carbon atoms and preferably from 2 to 10 carbon atoms.

As referred to herein, the hydrocarbonyl group is a monovalent organic radical consisting essentially of hydrogen and carbon and can be aliphatic, aromatic, alicyclic, or combinations thereof. The hydrocarbonyl group can include, but is not limited to aralkyl, aryl, cycloalkyl, and alkylcycloalkyl, and can be saturated or olefinically unsaturated (one or more double-bonded carbons conjugated or non-conjugated). The hydrocarbonylene, as defined in R_2 and R_3 above, is a divalent hydrocarbon radical which can be aliphatic, alicyclic, aromatic, or combinations thereof such as alkylaryl, aralkyl, alkylcycloalkyl, and cycloalkylaryl and having its two free valences on different carbon atoms.

The mono- or polyureas having the structure presented in Formula (1) above are prepared by reacting $n+1$ moles of diisocyanate with 2 moles of a monoamine and n moles of a diamine. When n is equal to 0 in the above Formula (1), the diamine is eliminated. Mono- or polyureas having the structure presented in Formula (2) above are prepared by reacting n moles of a diisocyanate with $n+1$ moles of a diamine and 2 moles of a monoisocyanate. When n is equal to 0 in the above Formula (2), the diisocyanate is eliminated. Mono- or polyureas having the structure presented in Formula (3) above are prepared by reacting n moles of a diisocyanate with n moles of a diamine and 1 mole of a monoamine. When n is

equal to 0 in the above Formula (3), both the diisocyanate and diamine are eliminated.

In preparing the above mono- or polyureas, the reactants (diisocyanate, monoisocyanate, diamine, and monoamine) are generally mixed in a vessel as appropriate. The composition can be prepared with or without a catalyst and is generally initiated by contacting the reactants under processing conditions conducive to the reaction. Typical reaction conditions generally include a reaction temperature ranging from about 70°F to about 210°F at atmospheric pressure. The reaction is generally exothermic, and by initiating the reaction at room temperature, elevated temperatures are obtained. External heating or cooling can also be used to facilitate the reaction. The reaction can also be carried out in the presence of a solvent. Generally, a portion of the base oil to be used in the formation of the grease is used or functions as a solvent. In this manner, the polyurea thickener is generated within the base oil and a grease structure is obtained as the reaction proceeds.

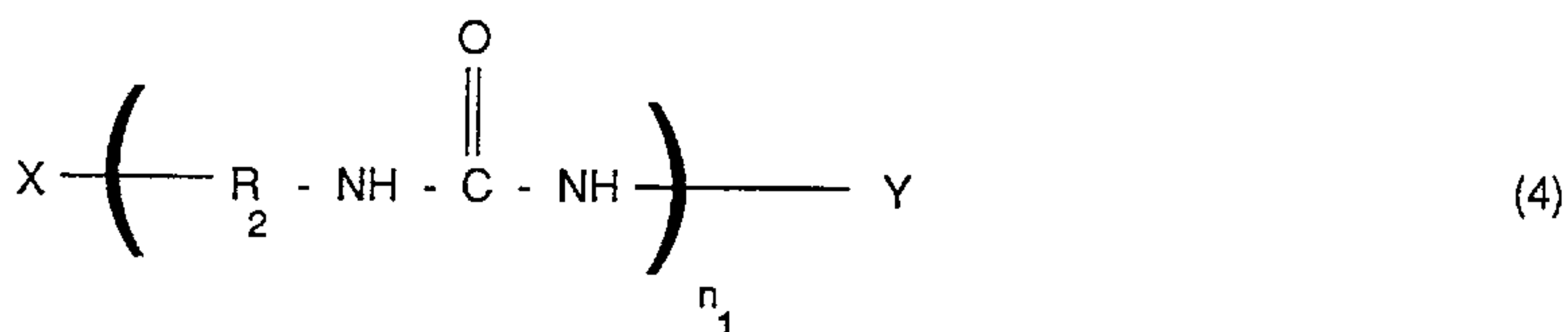
The monoamine or monoisocyanate used in the formulation of the mono- or polyurea can form terminal end groups. These terminal end groups can have from 1 to 30 carbon atoms, but preferably have from 5 to 28 carbon atoms, and more preferably from 10 to 24 carbon atoms for best results. Illustrative of the various monoamines include, but are not limited to: pentylamine, hexylamine, heptylamine, octylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, eicosylamine, dodecenylamine, hexadecenylamine, octadecenylamine, octadecadienylamine, abietylamine, aniline, toluidine, naphthylamine, cumylamine, bornylamine, fenchylamine, tertiary butyl aniline, benzylamine, and beta-phenethylamine. Preferred amines are prepared from natural fats and oils or the fatty acids obtained therefrom. These starting materials can be reacted with ammonia to provide amides and then nitriles. The nitriles are reduced to amines by catalytic hydrogenation. Exemplary amines prepared by the method include, but are not limited to: stearylamine, laurylamine, palmitylamine, oleylamine, petroselinylamine, linoleylamine, linolenylamine, and eleostearylamine. Unsaturated amines are particularly useful for preparing the urea-containing thickener. Illustrative of monoisocyanates are: hexylisocyanate, decylisocyanate, dodecylisocyanate, tetradecylisocyanate, hexadecylisocyanate, phenylisocyanate,

cyclohexylisocyanate, xyleneisocyanate, cumeneisocyanate, abietylisocyanate, and cyclooctylisocyanate.

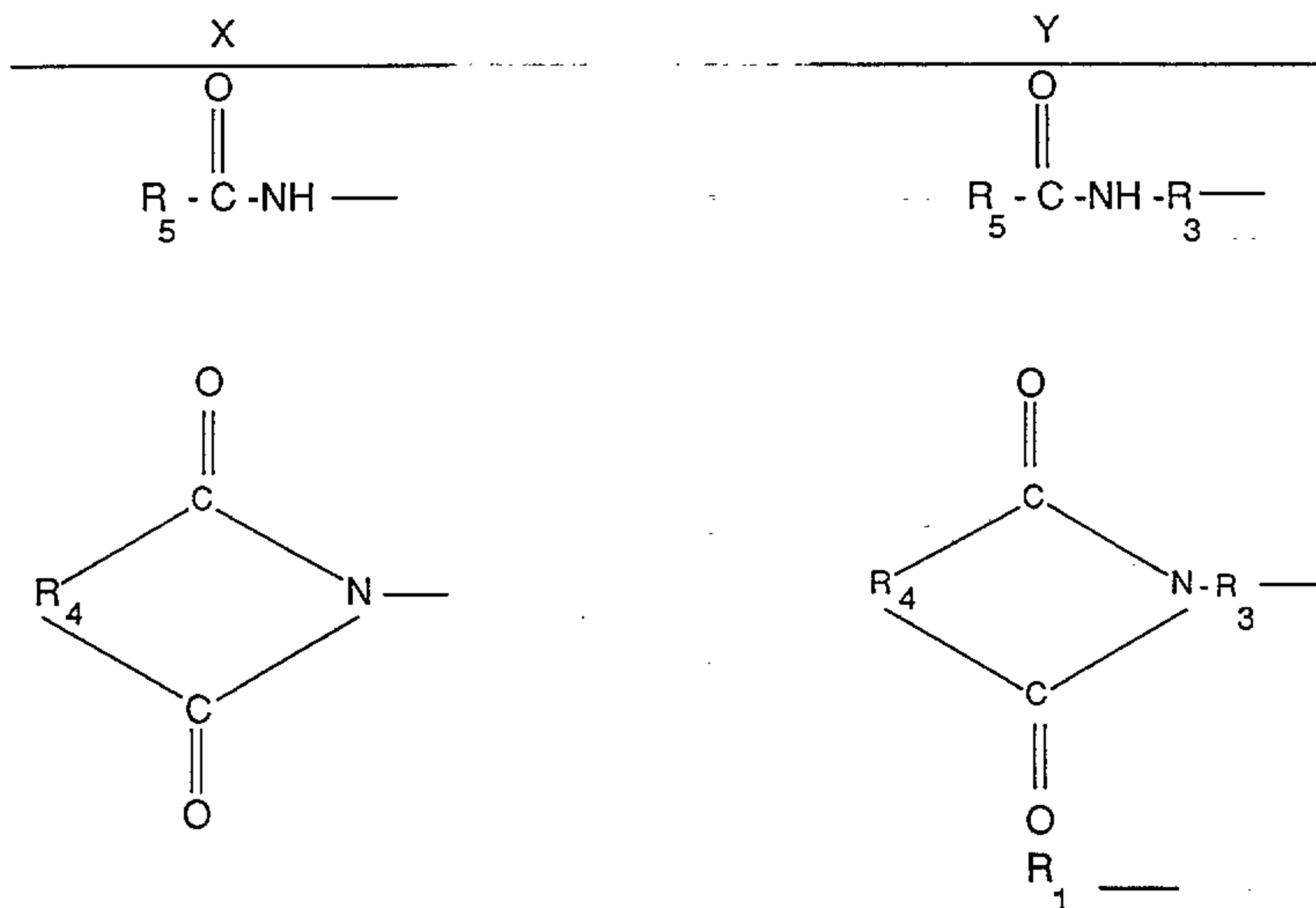
Polyamines which form the internal hydrocarbon bridges generally contain from 2 to 40 carbon atoms, preferably from 2 to 30 carbon atoms, and more preferably from 2 to 20 carbon atoms for best results. The polyamine generally has from 2 to 6 amine nitrogens, more preferably from 2 to 4 amine nitrogens, and most preferably 2 amine nitrogens. Such polyamines can include, but are not limited to the: diamines such as ethylenediamine, propanediamine, butanediamine, hexanediamine, dodecanediamine, octanediamine, hexadecanediamine, cyclohexanediamine, cyclooctanediamine, phenylenediamine, tolylenediamine, xylenediamine, dianiline methane, ditoluidinemethane, bis(aniline), bis(toluidine), and piperazine; triamines such as aminoethyl piperazine, diethylene triamine, dipropylene triamine, and N-methyldiethylene triamine; and polyamines such as triethylene tetraamine, tetraethylene pentaamine, and pentaethylene hexamine.

Representative examples of diisocyanate include: hexane diisocyanate, decanediisocyanate, octadecanediisocyanate, phenylenediisocyanate, tolylenediisocyanate, bis(diphenylenediisocyanate), and methylene bis(phenylisocyanate).

Other mono- or polyurea compounds which can be used comport with the formula:



where n_1 is an integer of 1 to 3, R_2 is defined supra, and X and Y are monovalent radicals selected from the following:



Where R_1 is defined supra, R_3 is defined supra, R_4 is selected from the groups consisting of arylene radicals having 6 to 16 carbon atoms and alkylene groups having 2 to 30 carbon atoms, and R_5 is selected from the group consisting of alkyl radicals having from 10 to 30 carbon atoms and aryl radicals having from 6 to 16 carbon atoms.

Mono- or polyurea compounds described by Formula (4) above can be characterized as amides and imides of mono-, di-, and triureas. These materials are generally formed by reacting suitable carboxylic acids or internal carboxylic anhydrides with a diisocyanate and a polyamine with or without a monoamine or monoisocyanate. The mono- or polyurea compounds are prepared by blending the reactants together in a vessel and heating the vessel to a temperature ranging from about 70°F to about 400°F for a period sufficient to cause formation of the compound. The time generally required for reaction can range from 5 minutes to 1 hour and the reactants can be added all at once or sequentially.

The above mono- or polyureas can be mixtures of compounds having structures wherein n or n_1 varies from 0 to 8, or n or n_1 varies from 1 to 8, existent within the grease composition at the same time. For example, when a monoamine, a diisocyanate, and a diamine are all present within a reaction zone,

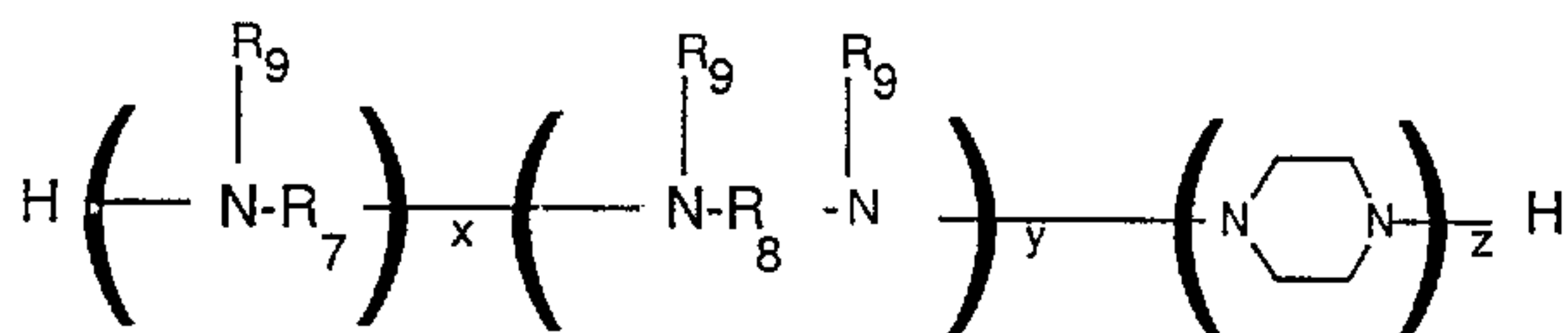
as in the preparation of ureas having the structure shown in Formula (2) above, some of the monoamine may react with both sides of the diisocyanate to form diurea (biurea). In addition to the formulation of diurea, simultaneous reactions can occur to form tri-, tetra-, penta-, hexa-, octa-, and higher polyureas.

5 Biurea (diurea) can also be used as thickener, but it is not as stable as polyurea and can shear and lose consistency when pumped. Triurea can also be used with or in lieu of the mono-, di, and polyureas disclosed herein.

The urea-containing thickener can also be prepared by eliminating the diamine or polyamine components described above and reacting the remaining
10 two components in the presence of water. The water reacts with the diisocyanate and generates a diamine component in situ. This method for formulating the urea-containing thickener is preferred since when properly implemented, the method results in a one step elimination of excess, unreacted isocyanate moieties from the final grease. When water is used as a reactant, reaction conditions are
15 similar to those set forth above. The reaction is preferably performed in at least a portion of the base oil used to formulate the grease.

An example of a urea-containing thickener suitable for use with the present invention and the method of preparation is provided below. The reactants for forming the urea-containing thickener include the following:

- 20 1. A diisocyanate or mixture of diisocyanate having the formula $\text{OCN-R}_6\text{-NCO}$, where R_6 is a hydrocarbylene having from 2 to 30 carbon atoms, preferably from 6 to 15 carbon atoms, and more preferably 7 carbon atoms.
2. A polyamine or mixture of polyamines having a total of 2 to 40
25 carbon atoms and having the formula:



where R_7 and R_8 are the same or different types of hydrocarbylenes
30 having from 1 to 30 carbon atoms, preferably from 2 to 10 carbon atoms, and more preferably from 2 to 4 carbon atoms; R_9 is selected from hydrogen or a C_1 to C_4 alkyl, and preferably hydrogen; x is an

integer of from 0 to 4; y is 0 or 1; and z is an integer equal to 0 when y is 1 and equal to 1 when y is 0.

3. A monofunctional component selected from the group consisting of monoisocyanate or a mixture of monoisocyanate having from 1 to 30 carbon atoms, preferably from 10 to 24 carbon atoms, and mixtures thereof.

The reaction can be carried out by contacting the three reactants in a suitable reaction vessel at a temperature ranging between 60°F and 320°F and preferably between 100°F and 300°F, for a period of 0.5 hours to 5 hours and preferably for a period of 1 to 3 hours. The molar ratio of the reactants present can vary from 0.1 - 2.0 moles of monoamine or monoisocyanate and 0.0 - 2.0 moles of polyamine for each mole of diisocyanate. When the monoamine is employed, the molar quantities can be m+1 moles of diisocyanate, m moles of polyamine, and 2 moles of monoamine. When the monoisocyanate is employed, the molar quantities can be m moles of diisocyanate, m+1 moles of polyamine, and 2 moles of monoisocyanate where m is a number from 0.1 to 10, preferably from 0.2 to 3, and most preferably 1.

The lithium soap thickener of the present invention can also be prepared in several ways. To make a lithium soap thickener generally requires a lithium-containing base and a fatty monocarboxylic acid, ester, amide, anhydride, or other fatty monocarboxylic acid derivative. When the two materials are reacted together, usually while slurried, dispersed, or otherwise suspended in a base oil to be used in the grease, a lithium carboxylate salt, or mixture of salts is formed in the base oil. The lithium salt or salts formed thicken the oil, thereby facilitating a grease-like texture. During the reaction, water may or may not be present to assist in the formation of thickener. Simple lithium soap thickeners generally comprise at least a minor portion of monocarboxylic acids or fatty acid derivatives with, preferably, a hydroxyl group on one or more of the carbon atoms of the fatty chain for better stability of grease structure.

The lithium base material used in the thickener can be lithium oxide, lithium carbonate, lithium bicarbonate, lithium hydroxide, or any other lithium-containing substance which, when reacted with a monocarboxylic acid or monocarboxylic acid derivative, provides a lithium carboxylate thickener. Lithium hydroxide monohydrate is the preferred lithium-containing substance.

Desirably, monocarboxylic fatty acids or their derivatives used in simple lithium soap thickeners have a moderately high molecular weight of from 7 to 30 carbon atoms, preferably from 12 to 30 atoms, and more preferably from 18 to 22 carbon atoms. Suitable monocarboxylic acids or derivatives thereof can include lauric, myristic, palmitic, stearic, behenic, myristoleic, palitoleic, oleic, and linoleic acids. Also, vegetable or plant oils such as rapeseed, sunflower, safflower, cottonseed, palm, castor, and corn oils and animal oils such as fish oil, hydrogenated fish oil, lard oil, and beef oil can be used as a source of monocarboxylic acids in simple lithium soap thickeners. Various nut oils or the fatty acids derived therefrom may also be used in simple lithium soap thickeners. These oils generally comprise the triacyclglycerides. Triacyclglycerides can be reacted directly with the lithium-containing base or the fatty acids may be cleaved from the triglyceride backbone, separated, and then reacted with the lithium-containing base as free acids.

Hydroxy-monocarboxylic acids are preferred in simple anhydrous lithium soap thickeners and can include any counterpart to the preceding acids. The most widely used hydroxy-monocarboxylic acids are 12-hydroxystearic acid, 14-hydroxystearic acid, 16-hydroxystearic acid, 6-hydroxystearic acid, and 9, 10-dihydroxystearic acid. Likewise, any fatty acid derivatives containing any of the hydroxy-carboxylic acids may be used. In general, the monocarboxylic acids and hydroxy-monocarboxylic acids can be saturated or unsaturated, straight or branched chain. Esters, amides, anhydrides, or any other derivative of these monocarboxylic acids can be used in lieu of the free acids in forming simple lithium soap thickeners. The preferred monocarboxylic and hydroxy-monocarboxylic acid derivative is free carboxylic acid for best results.

When preparing simple lithium soap thickeners by reacting the lithium base and the monocarboxylic acid, or a mixture of monocarboxylic acids or derivatives thereof, it is preferred that the lithium base be added in an amount sufficient to react with all the acids and/or acid derivatives. It is also generally advantageous to add an excess of lithium base to more easily facilitate a complete reaction. The amount of excess lithium base depends on the severity of processing which the base grease will experience. The longer the base grease is heated and the higher the maximum heat treatment temperature, the less excess lithium base is required.

In forming the simple anhydrous lithium soap thickener, the thickener forming reaction is usually carried out at elevated temperatures ranging from about 150°F to about 320°F. Water may or may not be added to facilitate a better or more complete reaction. Preferably, water added at the beginning of the processing as well as water formed from the thickener reaction is evaporated by heat, vacuum, or both. The thickener reaction is generally carried out after the addition of a portion of the base oil as previously described. After the thickener has been formed and any water removed, the resulting lithium soap thickener may optionally be heated to about 400°F, until the lithium soap melts. This will ensure complete reaction of the lithium-containing base and fatty acid. The melted grease is then cooled to reform the base grease.

The blended thickener system comprising the urea-containing and lithium soap thickeners can be produced through several methods. One such method for preparing the blended thickener system is to form each thickener component separately in different vessels and thereafter mix the resulting greases. The individual polyurea and lithium soap thickened greases may include sufficient base oil for the final grease product, or more base oil may be added during or after the two component thickeners are mixed. Generally, however, the urea-containing and lithium soap thickened greases are made so that the resulting grease containing the blended thickener has a consistency harder than required by the final grease. Then, additional additives and base oil can be added to soften the grease to its desired consistency.

Another process for making the blended thickener system comprising urea-containing and lithium soap thickeners is to sequentially form each thickener system in the same vessel. When this method is used, the first thickener component is formed and a base grease thickened by that component produced. The second thickener component is thereafter formed by reacting the appropriate components within the base grease thickened by the first thickener component. Sufficient base oil is added, either at the very beginning of the manufacturing process or after formation of the first thickener component, so that the formation of the second thickener component does not produce a urea-containing and lithium soap thickened grease that is too hard to stir in the reaction vessel.

When reacting the urea-containing and lithium soap thickeners sequentially in the same reaction vessel, each thickener is formed by the same procedures which are used when forming them in separate vessels. The order in

which the urea-containing and lithium soap thickeners are formed is not critical and both orders can produce favorable results. However, it is preferable that the urea-containing thickener be formed first for best results. If the lithium soap thickener is formed first and any free, unreacted acids remain, they may interfere with formation of the urea-containing thickener. Also, it has been discovered that polyurea acts as an excellent promoter in the reaction of carboxylic acids with lithium-containing bases. The presence of the urea-containing components mitigates the need for adding water to react the lithium-containing base with the carboxylic acid.

Once both thickener systems have been sequentially formed in the same kettle, the resulting urea-containing and lithium soap thickened base grease is dried by heat, vacuum, or both, followed by heat treatment. Maximum heat treatment temperatures of the urea-containing and lithium soap thickened grease, when made by sequential formation of thickeners in the same vessel, should generally not exceed 400°F, preferably not exceed 350°F, and more preferably not exceed 325°F for best results.

The urea-containing and lithium soap thickener system can comprise any proportion of the two thickener components providing that the lesser component comprises at least 1% by weight of the total thickener in the final grease. Lubricating greases thickened by the urea-containing and lithium soap thickener system should have a total thickener level of between from about 6% to about 20% by weight and more preferably from about 10% to about 16% by weight of the lubricating grease for best results. The preferred composition of the thickener system, as a percentage calculated by weight, is where the lithium soap thickener comprises from about 30% to about 95% of the total thickener and more preferably from about 60% to about 90% of the total thickener for best results. For purposes of developing, measuring, and identifying greases in accordance with the ranges set forth hereabove, the urea-containing and lithium soap thickeners are each prepared to substantially similar penetration levels such as those determined under testing procedure ASTM D-1403. While the compositional range set forth above is directed to urea-containing and lithium soap thickener components of similar penetration levels, equivalent compositional ranges can be determined to reflect equivalent ranges for urea-containing and lithium soap thickeners having disparate penetrations. While the above thickener composition is preferred for best results, if desired, other amounts of the urea-containing and

lithium soap thickeners can be used depending on the intended application and desired properties of the grease.

The qualities of the lubricating grease thickener system in accordance with the present invention can be further enhanced with the addition of a particularly
5 targeted amount of boric acid. The preferred amount of boric acid, calculated as a percentage of the lubricating grease, ranges from about 0.1 weight percent to about 2.0 weight percent and more preferably from about 0.2 weight percent to about 1.2 weight percent for best results. Boric acid can be added to the lubricating grease in the form of boron oxide, which reacts with water to form boric
10 acid. If desired, other boron-containing materials may be used in lieu of boric acid, such as the borate, metaborate, or pyroborate salts such as metaborate ($B_3O_3(OH)_3$). The preferred metals for use with any of the borate, metaborate, or pyroborate salts are sodium and potassium.

The performance of lubricating greases prepared in accordance with the
15 present invention, and further comprising the addition of boric acid, can be further enhanced by the particular grease formulation steps. It has been found that when boric acid is added to the lubricating grease formulation, the temperature that the heat treatment step is conducted at subsequent to boric acid addition can substantially affect the ASTM D-2265 dropping point characteristics of the grease.
20 The rate of increase in dropping point with heat treatment temperature accelerates at temperatures in excess of 200 °F and preferably in excess of 250°F. Therefore, a further increase in lubricating grease dropping point can be obtained through the proper addition of a critically targeted amount of boric acid.

Base oils used with the thickener system of the present invention can be
25 any of the many known base oils reported and commonly used in prior art lubricating greases. The base oil can comprise naphthenic, paraffinic, or aromatic hydrocarbon, or can be a synthetic oil such as a polyalphaolefin, polyester, polyolester, diester, polyalkyl ethers, polyaryl ethers, silicone polymer fluids, or combinations thereof. The viscosity of the base oil can range from about 50 to
30 about 10,000 SUS at 100°F.

Suitable base oils can also include: (a) oil derived from coal products, (b) alkylene polymers, such as polymers of propylene, butylene, etc., (c) alkylene oxide-type polymers, such as alkylene oxide polymers prepared by polymerizing alkylene oxide (e.g., propylene oxide polymers in the presence of water or
35 alcohols such as ethyl alcohol), (d) carboxylic acid esters, such as those which

are prepared by esterifying such carboxylic acids as adipic acid, azelaic acid, suberic acid, alkenyl succinic acid, fumaric acid, maleic acid with alcohols such as butyl alcohol, hexyl alcohol, and 2-ethylhexyl alcohol, (e) liquid esters of acid of phosphorus, (f) alkyl benzenes, (g) polyphenols such as biphenols and terphenols, (h) alkyl biphenol ethers, and (i) polymers of silicon, such as tetraethyl silicate, tetraisopropyl silicate, tetra (4-methyl-2-tetraethyl) silicate, hexyl (4-methyl-2-pentoxo) disilicone, poly(methyl)siloxane, and poly(methyl)phenylsiloxane.

Most additives used in prior art lubricating greases can be successfully used in lubricating greases thickened by the urea-containing and lithium soap thickener system of the present invention. The various types of additives available and their functions are generally well known to those skilled in the art.

The lubricating grease in accordance with the present invention has improved performance properties compared to greases generally known in the prior art. Among the improved properties are those of shear stability, dropping point, oil separation over a wide range of temperatures, fretting wear, and thermal and oxidative stability.

Unlike the metal soap salt of fatty acid thickeners previously discussed, the improved thickener system of the present invention resists loss of thickening characteristics while maintaining its pumpability properties. Greases thickened with the thickener system of the present invention do not exhibit the lacquer deposition characteristics which are common when lithium and aluminum soap thickeners are used exclusively. Also, the high temperature hardening associated with calcium complex thickened greases is exhibited to a much lower extent, if at all, when using the improved thickener system of the present invention. Advantageously, skin/age hardening is also substantially reduced.

The improved properties of the urea-containing and lithium soap thickener system of the present invention are particularly surprising and unexpected since they significantly exceed levels mathematically expected from the individual properties, qualities, and characteristics of the individual urea-containing and lithium soap components. It has been found that the urea-containing and lithium soap thickeners do not function as a mixture of urea-containing and lithium soap thickeners but interact favorably and in a way that was not anticipated by the linear combination of components.

The improved thickener system of the present invention can be used in lubricating greases for a wide range of applications including, but not limited to, both extreme pressure and anti-wear conditions. Additives commonly used in soap and non-soap thickened greases can also be used in greases thickened by the improved thickener system of the present invention, thereby providing the grease formulator a high degree of flexibility by which improved products can be developed.

The lubricating grease of the present invention is described in further detail in connection with the following examples, it being understood that the same are for purposes of illustration and not limitation.

EXAMPLE 1

A lithium soap thickener composition comprising lithium soap and 40 weight mineral oil and formulated to meet an ASTM D-1403 worked penetration at 60 strokes of between 265 and 275 was prepared for use in preparing grease compositions in accordance with the present invention. About 6,810 grams of a solvent extracted, hydrotreated, paraffinic 40 weight mineral oil having a viscosity of about 850 SUS at 100°C was added to a laboratory grease kettle. The oil was heated and stirred until the temperature reached 170°F. The heated oil was combined with 2340.2 grams of methyl 12-hydroxystearate and the mixture was stirred until the methyl 12-hydroxystearate melted. About 318.4 grams of lithium hydroxide monohydrate and 50 grams of water was added to the mixture and the grease kettle was sealed and held without adding heat for a period of 30 minutes. The mixture was heated to 300°F and maintained at that temperature for a period of 35 minutes. The kettle was subsequently vented and opened. The batch was then heated to 400°F under a nitrogen blanket and held at 400°F for 15 minutes. Heat addition to the mixture was reduced such that the mixture temperature dropped to 250°F. Once the mixture reached 250°F, an additional 2,270 grams of 40 weight mineral oil was added and the mixture cooled to 150°F.

A 10 pound portion of the mixture was combined with 2.8 pounds of 40 weight mineral oil, stirred, and heated to 200°F. About 7.2 pounds of a solvent extracted, hydrotreated, paraffinic 10 weight mineral oil having a viscosity of about 160 SUS at 100°C was graded into the mixture over a period of 30 minutes and the mixture was cooled to a temperature of about 150°F. The mixture was milled in an Eppenbach mill and the grease product identified as Grease 1. The

unworked and worked penetration (ASTM D-1403) of Grease 1 at 60, 10,000, and 100,000 strokes and the worked dropping point (ASTM D-2265) at 10,000 and 100,000 strokes are set forth in Table 1. The worked dropping point at 10,000 strokes is plotted in Figure 1.

5

EXAMPLE 2

A urea-containing thickener composition comprising polyurea and a mixture of 10 weight and 40 weight mineral oils was prepared for use in preparing grease compositions in accordance with the present invention. About 14.94 pounds of 40 weight mineral oil was added to a laboratory grease kettle, stirred, and heated to a temperature of 175°F. Once the 40 weight mineral oil reached 175°F, 2.95 pounds of fatty amine, sold under the brand name of Armeen T by Akzo Chemicals, Inc., was added to the kettle where it was melted and mixed well with the 40 weight mineral oil. After mixing, about 3.3 pounds of water was added and the mixture mixed for a period of about 5 minutes. The mixture was allowed to cool to a temperature of 130°F. A 3.35 pound charge of Mondur M, 4,4'-diphenylmethane diisocyanate, sold by Mobay Chemical Corporation, was added to the mixture in 3 equal portions and an additional 2.07 pounds of 40 weight mineral oil added to the mixture. The kettle was closed and the mixture mixed without heating for a period of about 30 minutes. The mixture was heated to a temperature of about 310°F, the kettle vented and opened, and the mixture reheated to a temperature of about 310°F. About 10.08 pounds of 10 weight mineral oil was added to the mixture and the mixture heated to 400°F while the kettle remained open and blanketed with nitrogen. Once the mixture reached 400°F, the mixture was maintained at a temperature of between 390°F - 400°F for a period of 15 minutes. The mixture was cooled to 350°F whereafter 3.17 pounds of 40 weight mineral oil and 5.44 pounds of 10 weight mineral oil were graded in and the mixture cooled to 175°F. The grease mixture was milled through a Gaulin mill at 8000 psi and the grease product identified as Grease 2.

The unworked and worked penetration (ASTM D-1403) of Grease 2 at 60, 10,000, and 100,000 strokes and the worked dropping point (ASTM D-2265) at 10,000 and 100,000 strokes are set forth in Table 1. The worked dropping point at 10,000 strokes is plotted in Figure 1. The worked dropping point at 10,000 strokes was retested during comparison tests of a calcium soap grease and these results are set forth in Table 2 and plotted in Figure 2.

35

EXAMPLE 3

Greases 1 and 2 were blended in various proportions to demonstrate the synergistic benefits of combining lithium soap and urea-containing thickeners formulated in accordance with the present invention. Greases 1 and 2 were blended into 1200 gram roll-milled blends in composition ratios of 20, 40, 50, 60, and 80 weight percent of Grease 1 (lithium soap thickener) calculated as a percentage of the total weight of both Grease 1 and Grease 2 (urea-containing thickener). These greases were identified as Greases 3, 4, 5, 6, and 7 respectively. The unworked and worked penetration (ASTM D-1403) of Greases 3 - 7 at 60, 10,000, and 100,000 strokes and the worked dropping point (ASTM D-2265) at 10,000 and 100,000 strokes are all set forth in Table 1. The worked dropping points at 10,000 strokes are also plotted in Figure 1.

Figure 1 includes all of the ASTM D-2265 droppings points at 10,000 strokes for Greases 1 through 7. Figure 1 also includes a linear regression of the dropping points of Greases 1 through 7 as a function of the percentage of Grease 1 compared to the total of Greases 1 and 2 combined. Examples 1 - 3 and Figure 1 clearly illustrate that combining lithium soap and urea-containing thickeners in accordance with the present invention provides synergistic and surprising and unexpected advantages in dropping point compared to the expected dropping point of a linear combination of the thickeners. This dropping point synergy is particularly prevalent over the lithium soap thickener to total lithium soap plus urea-containing thickener percentage range of from about 30 percent to about 95 percent and is especially prevalent at a lithium soap thickener to total lithium soap plus urea-containing thickener percentage of about 80 percent.

TABLE 1

GREASE

	1	2	3	4	5	6	7
GREASE COMPOSITION, WT%							
Grease 1 (Lithium soap)	100	0	20	40	50	60	80
Grease 2 (Urea-containing)	0	100	80	60	50	40	20

TESTS

Penetration, Full (ASTM D-1403)

Unworked	261	207	258	257	263	268	270
Worked - 60 strokes	257	267	263	270	271	277	275
Worked - 10,000 strokes	262	341	327	309	309	303	291
Worked - 100,000 strokes	295	351	341	327	321	319	309

Dropping point, °F (ASTM D-2265)
(550°F Block)

Worked - 10,000 strokes	377	531	521	511	511	483	495
Worked - 100,000 strokes	429	512	509	512	515	512	488

EXAMPLE 4

A calcium soap thickener composition comprising calcium soap and 10 and 40 weight mineral oil and formulated to meet an ASTM D-1403 worked penetration at 60 strokes of between 265 and 275 was prepared for use in
5 preparing grease compositions for comparison with grease compositions in accordance with the present invention. Both the lithium soap thickener composition of Example 1 and the calcium soap thickener composition of this Example 4 were standardized to the same ASTM D-1403 worked penetration at
10 60 strokes to provide for a proper comparison basis. About 150 gallons of 40 weight mineral oil was added to a laboratory grease kettle followed by 320 pounds of hydrated lime and the oil and hydrated lime stirred until smooth. Once the mixture reached a smooth consistency, 870 gallons of 40 weight mineral oil, 300 gallons of 10 weight mineral oil, 2,600 pounds of animal fatty acid, 44 pounds of 50 weight percent sodium hydroxide in water, and 60 pounds of water were
15 added to the grease kettle. The kettle was sealed pressure tight, heated to 270°F, and maintained at 270°F for a period of 1 hour. The mixture was then cooled to 200°F. Once the kettle temperature reached 200°F and the kettle pressure reached 0 psig, a sample was removed and the acidity or alkalinity measured in milliequivalents (meq) of calcium hydroxide. Hydrated lime was added to
20 maintain acidity/alkalinity within a range of between about 0.3 acid and 0.3 alkaline and the reheating and cooling sequence repeated. After the proper acidity and alkalinity was reached, 30 pounds of water was added and the temperature of the mixture was allowed to fall to 180 - 185°F within the sealed kettle. The kettle was opened and 900 gallons of 10 weight mineral oil was
25 added and the batch allowed to cool to 140 - 150°F. The mixture was sampled for water content, acidity/alkalinity, and penetration. The mixture had an ASTM D-1403 worked penetration at 60 strokes of between 265 and 275, an alkalinity of between 0.1% to 0.28% acid, and a water content of about 1 weight percent. A vacuum was pulled on the kettle while the kettle was maintained at a temperature
30 ranging from 140 - 150°F for a period of 1 hour. The grease was immediately removed from the kettle. The composition was identified as Grease 8. The worked dropping point (ASTM D-2265) at 10,000 strokes of Grease 8 is set forth in Table 2 and plotted in Figure 2.

EXAMPLE 5

Greases 8 and 2 were blended in the same proportions as Greases 1 - 7 in order to directly compare combinations of calcium soap and urea-containing thickeners to the combinations of lithium soap and urea-containing thickeners in accordance with the present invention. Greases 8 and 2 were blended into 1200 gram roll-milled blends in ratios of 20, 40, 50, 60, and 80 weight percent of Grease 8 (calcium soap thickener) as a percentage of the total weight of both Grease 8 and Grease 2 (urea-containing thickener). These greases were identified as Greases 9, 10, 11, 12, and 13 respectively. The worked dropping points (ASTM D-2265) at 10,000 strokes of Greases 9 - 13 are all set forth in Table 2 and plotted in Figure 2.

Figure 2 includes all of the ASTM D-2265 dropping points at 10,000 strokes for Greases 2 and 8 through 13. Figure 2 also includes a linear regression of the dropping points for Greases 2 and 8 through 13 as a function of the percentage of Grease 8 compared to the total of Greases 8 and 2 combined. Examples 2, 4 and 5 and Figure 2 clearly illustrate that combining lithium soap and urea-containing thickeners in accordance with the present invention provides synergistical and surprising and unexpected advantages in dropping point compared to the expected dropping point of a linear combination of the thickeners. Figures 1 and 2 also illustrate that combining lithium soap and urea-containing thickeners provide superior performance and cost effectiveness compared to grease containing calcium soap and urea-containing thickeners. The beneficial combination performance range of the calcium soap/urea-containing grease of Figure 2 extends from a calcium soap to total calcium soap plus urea-containing grease percentage range of about 15 percent to about 55 percent whereas the beneficial combination performance range of the lithium soap/urea-containing grease of Figure 1 extends from about 30 percent to about 95 percent.

TABLE 2**GREASE**

GREASE COMPOSITION, WT%	GREASE									
	8	2	9	10	11	12	13			
Grease 8 (Calcium soap)	100	0	20	40	50	60	80			
Grease 2 (Urea-containing)	0	100	80	60	50	40	20			

TESTS

Dropping point, °F (ASTM D-2265)
(550°F Block)

Worked - 10,000 strokes	266	520	516	490	472	300	293
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EXAMPLE 6

A lithium soap thickener composition comprising lithium soap and HVI Bright Stock mineral oil was prepared for use in preparing grease compositions in accordance with the present invention and for identifying the effects of adding boric acid to a grease composition in accordance with the present invention. The lithium soap thickener portion was prepared by adding 6810 grams of HVI Bright Stock mineral oil having a viscosity of 2500 SUS at 100°F (Stauffer Chemical Company) into a grease kettle and heating the Bright Stock mineral oil to 170°F. The heated Bright Stock mineral oil was combined with 2340.2 grams of methyl 12-hydroxystearate and the mixture was stirred until the methyl 12-hydroxystearate melted. About 318.4 grams of lithium hydroxide monohydrate and 50 grams of water was added to the mixture and the grease kettle was sealed and held without adding heat for a period of 30 minutes. The mixture was heated to 300°F and maintained at a temperature of 300°F for a period of 35 minutes. The kettle was subsequently vented and opened. The batch was then heated to 400°F while blanketed with nitrogen and held at 400°F for 15 minutes. The heat added to the mixture was reduced such that the mixture temperature dropped to 250°F. Once the mixture reached 250°F, an additional 2270 grams of Bright Stock mineral oil was added and the mixture cooled to 150°F. The lithium soap grease composition was identified as Grease 14.

EXAMPLE 7

A urea-containing thickener base grease composition comprising polyurea and HVI Bright Stock mineral oil was also prepared for use in preparing grease compositions in accordance with the present invention and for identifying the effects of adding boric acid to a grease composition in accordance with the present invention. The urea-containing thickener composition was prepared by adding 4086 grams of Bright Stock mineral oil into a grease kettle and heating the Bright Stock mineral oil to 175°F. Once the Bright Stock mineral oil reached 175°F, 639 grams of Armeen T fatty amine was added to the kettle where it was melted and mixed well with the Bright Stock mineral oil. After mixing, about 950 grams of water was added and the mixture mixed for a period of about 5 minutes. The mixture was allowed to cool to a temperature of 130°F. A 723 gram charge of Mondur M, 4,4'-diphenylmethane diisocyanate was added to the mixture in 3 equal portions, the kettle closed, and the mixture mixed without heating for a

period of about 30 minutes. The mixture was heated to a temperature of about 300°F, the kettle vented and opened, and the mixture reheated to a temperature of about 310°F. About 3064 grams of Bright Stock mineral oil was added to the mixture and the mixture heated to 400°F while the kettle remained open and
5 blanketed with nitrogen. Once the mixture reached 400°F, the mixture was maintained at a temperature of between about 390°F - 400°F for a period of about 15 minutes. The mixture was cooled to 350°F whereafter 2838 grams of Bright Stock mineral oil were graded in and the mixture cooled to 175°F. The grease mixture was milled through a Gaulin mill at 8000 psi. The urea-containing
10 composition was identified as Grease 15.

EXAMPLE 8

Lithium soap and urea-containing thickener compositions further comprising HVI Bright Stock mineral oil and various amounts of boric acid were
15 prepared in order to identify the effects of adding boric acid to a grease composition in accordance with the present invention. The first grease composition was prepared by mixing with a spatula 60.0 grams of Grease 15 (urea-containing), 84.0 grams of Grease 14 (lithium soap), 55.8 grams of Bright Stock mineral oil, and 0.2 grams of solid 100 percent boric acid. The mixture was
20 roll milled four times and placed in an oven at 250°F for 5 hours. The grease comprised 0.1 weight percent boric acid and was identified as Grease 16. The undisturbed, unworked, and worked penetration (ASTM D-1403) of Grease 16 at 60 strokes and the worked dropping point (ASTM D-2265) at 10,000 strokes are set forth in Table 3. The worked dropping point at 10,000 strokes is plotted in
25 Figure 3.

Greases 17, 18, 19, and 20 were prepared in a manner similar to that described above except that the addition rate of boric acid was increased so as to provide greases comprising 0.2, 0.5, 1.0, and 2.0 weight percent boric acid respectively. The undisturbed, unworked, and worked penetration (ASTM D-
30 1403) of Grease 17 through 20 at 60 strokes and the worked dropping point (ASTM D-2265) at 10,000 strokes are set forth in Table 3. The worked dropping point at 10,000 strokes is plotted in Figure 3.

Table 3 and Figure 3 clearly illustrate that a lithium soap/urea-containing base grease in accordance with the present invention and containing a critically
35 targeted amount of boric acid provides surprising and unexpected dropping point

property advantages compared to greases in accordance with the present invention that do not have boric acid in the amounts illustrated. The identified critical range of boric acid occurs between about 0.1 and 2.0 weight percent and preferably between about 0.2 and 1.2 weight percent for best results.

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TABLE 3

GREASE

16 17 18 19 20

GREASE COMPOSITION, g

Grease 14 (Lithium soap)	84.0	84.0	252.0	84.0	84.0
Grease 15 (Urea-containing)	60.0	60.0	180.0	60.0	60.0
Bright Stock mineral oil	55.8	55.6	165.0	54.0	52.0
Boric acid	0.2	0.4	3.0	2.0	4.0

THICKENER COMPOSITION, WT%

Polyurea	3.6	3.6	3.6	3.6	3.6
Lithium Soap	8.4	8.4	8.4	8.4	8.4
Boric Acid	0.1	0.2	0.5	1.0	2.0
TOTAL	12.1	12.2	12.5	13.0	15.0

TESTS

Penetration, 1/2 scale					
Undisturbed	187	201	214	245	295
Unworked	236	242	271	305	359
Worked - 60 Strokes	265	275	297	343	385
Dropping point, °F (D-2265) (550°F Block)					
Worked - 10,000 strokes	446	461	476	465	442

EXAMPLE 9

A lithium soap and urea-containing base grease composition in accordance with the present invention and containing boric acid similar to that described for Grease 18 was prepared using the preparation method set forth in Example 8. Grease 18 was selected as the base grease for identifying the effects of oven temperature on greases blended in accordance with the present invention and further comprising boric acid. The oven temperatures for heating the grease composition were 70°F, 130°F, 210°F, 250°F, 300°F, and 350°F and the grease produced thereby identified as Greases 21, 22, 23, 24, 25, and 26 respectively. The undisturbed, unworked, and worked penetration (ASTM D-1403) at 60 strokes of Greases 21 through 26 and the worked dropping point (ASTM D-2265) at 10,000 strokes are set forth in Table 4. The worked dropping point at 10,000 strokes is plotted in Figure 4.

Table 4 and Figure 4 clearly illustrate that lithium soap and urea-containing greases comprising boric acid experience a substantial increase in rate of dropping point improvement at oven temperatures in excess of 200°F and preferably at oven temperatures in excess of 250°F for best results.

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TABLE 4**GREASE**

21 22 23 24 25 26

THICKENER COMPOSITION, WT%

Polyurea

3.6 3.6 3.6 3.6 3.6 3.6

Lithium soap

8.4 8.4 8.4 8.4 8.4 8.4

Boric acid

0.5 0.5 0.5 0.5 0.5 0.5

TOTAL

12.5 12.5 12.5 12.5 12.5 12.5

TEMPERATURE OF OVEN, °F

70 130 210 250 300 350

TESTS

Penetration, 1/2 scale

Undisturbed

283 218 192 197 199 199

Unworked

253 250 237 266 288 289

Worked - 60 strokes

258 266 265 292 315 325

Dropping point, °F (D-2265)
(550°F Block)

Worked - 10,000 strokes

453 460 464 479 488 503

EXAMPLE 10

A lithium soap and polyurea base grease product comprising boric acid was prepared in accordance with the present invention. The grease composition and its various properties are set forth in Table 5.

TABLE 5

<u>Grease Composition, components</u>		<u>Weight percent</u>
10	Methyl 12-Hydroxystearate	7.22
	Lithium Hydroxide Monohydrate	1.07
	Mondur M Flakes	1.60
	Armeen TM98	1.40
	Sulfonate Corrosion Inhibitor	1.00
15	Alkylated Diphenyl Amine Antioxidant	0.75
	Alkylated Triaryl Phosphate Ester Antiwear Additive	0.90
	Borated Amine Corrosion Inhibitor	2.50
	Alkyl Zinc dithiophosphate Antiwear Agent	3.00
	Sulfurized Hydrocarbon Antiwear Agent	0.75
20	Boric Acid	0.50
	Blue Dye	0.02
	40 Weight Mineral Oil	64.38
	10 Weight Mineral Oil	16.10
<u>Laboratory Analysis, ASTM, Units</u>		<u>Results</u>
25	Timken, D-2509, lbs	50/60
	Penetration, D-217 (Worked 60/100,000)	278/311
	Automotive Grease Spec., D-4950-89 (pass/fail)	GC-LB (pass)
	Worked Penetration, D217, mm/10	278
	Dropping Point, D-2265, °C, (°F)	258/497
30	Dropping Point, D-566, °C, (°F)	260+ (500+)
	Low Temperature Perf, D-4693, -40°C, Nm	7.3
	Water Resistance, D-1264, 80°C, percent	7
	Oil Separation, D-1742, Mass percent	2.4
	Rust Protection Rating, D-1743 (pass/fail)	pass
35	Wear Protection Scar Diameter, D-2266, mm	0.44
	High Temperature Life, D-3527, hours	140
	Elastomer Compatibility, D-4289	
	Volume Change, percent	5
	Hardness Change, Durometer A Points	-2
40	Leakage Tendencies, D-4290, gm	7.8
	4-Ball EP Performance, D-2596	
	Load Wear Index, kgf	51
	Weld Point, kgf	250
	Fretting Protection, D-4170, mg loss	4.3

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That which is claimed is:

1. A lubricating grease, comprising:
a base oil;
an additive package; and
5 a blended thickener system comprising a urea-containing thickener and a lithium soap thickener wherein said lithium soap thickener comprises from about 30 percent to about 95 percent of said blended thickener system, calculated by weight.
- 10 2. The lubricating grease of Claim 1 wherein said urea-containing thickener comprises at least one member selected from the group consisting of monourea, diurea, and polyurea.
- 15 3. The lubricating grease of Claim 1 wherein said lithium soap thickener comprises a reaction product of a lithium base material and a monocarboxylic acid and said lithium base material comprises at least one member selected from the group consisting of lithium oxide, lithium carbonate, lithium bicarbonate, and lithium hydroxide.
- 20 4. The lubricating grease of Claim 3 wherein said monocarboxylic acid comprises at least one member selected from the group consisting of 12-hydroxystearic acid, 14-hydroxystearic acid, 16-hydroxystearic acid, 6-hydroxystearic acid, and 9,10-dihydroxystearic acid.
- 25 5. The lubricating grease of Claim 1 wherein said lithium soap thickener comprises lithium 12-hydroxystearate and said urea-containing thickener comprises polyurea.
- 30 6. A lubricating grease, comprising:
a base oil;
an additive package;
a blended thickener system comprising a urea-containing thickener and a lithium soap thickener wherein said lithium soap thickener comprises from about 60 percent to about 90 percent of said blended thickener system, calculated by weight; and
boric acid in an amount ranging from about 0.1 weight percent to about 2.0 weight percent calculated as a percentage of said lubricating grease.
- 35 7. The lubricating grease of Claim 6 wherein said lithium soap thickener comprises a reaction product of a lithium base material and a monocarboxylic acid and said lithium base material comprises at least one

member selected from the group consisting of lithium oxide, lithium carbonate, lithium bicarbonate, and lithium hydroxide and said monocarboxylic acid comprises at least one member selected from the group consisting of 12-hydroxystearic acid, 14-hydroxystearic acid, 16-hydroxystearic acid, 6-hydroxystearic acid, and 9,10-dihydroxystearic acid.

8. The lubricating grease of Claim 6 wherein said lithium soap thickener comprises lithium 12-hydroxystearate and said urea-containing thickener comprises polyurea.

9. The lubricating grease of Claim 8 wherein said boric acid comprises from about 0.2 weight percent to about 1.2 weight percent of said lubricating grease.

10. The lubricating grease of Claim 9 wherein said lubricating grease is heated to temperatures in excess of 200°F during grease preparation.

FIG. 2

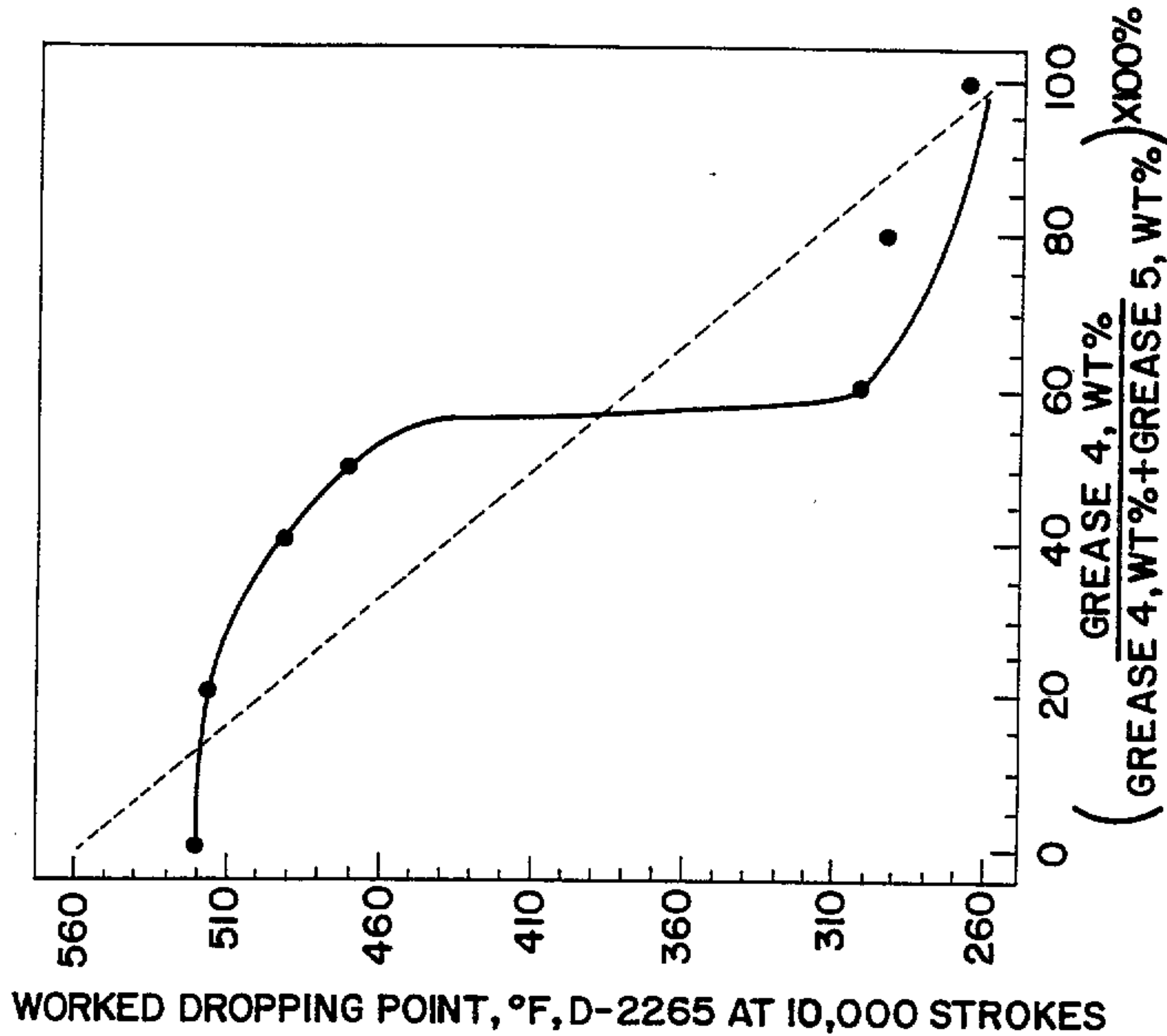


FIG. 1

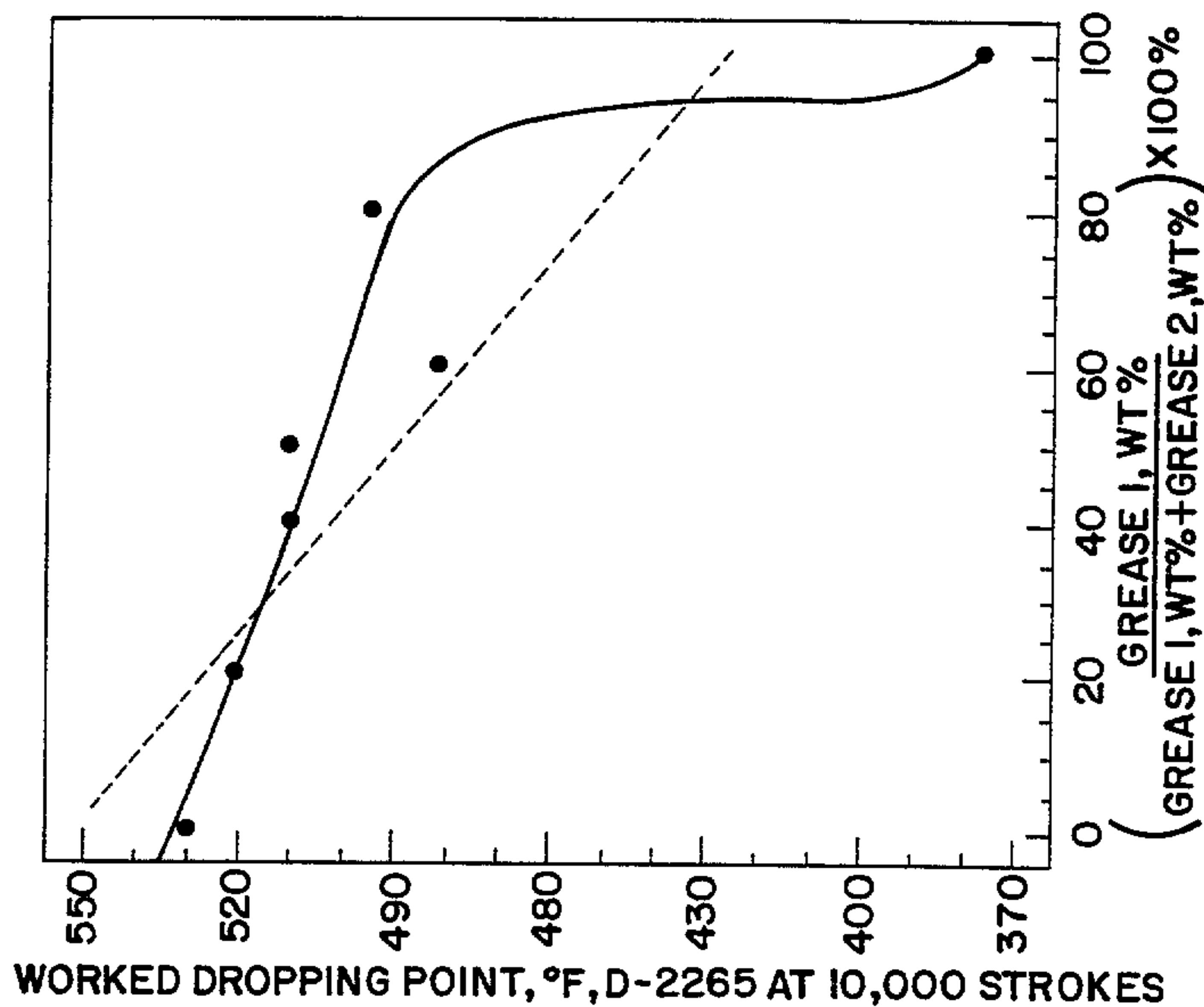


FIG. 4

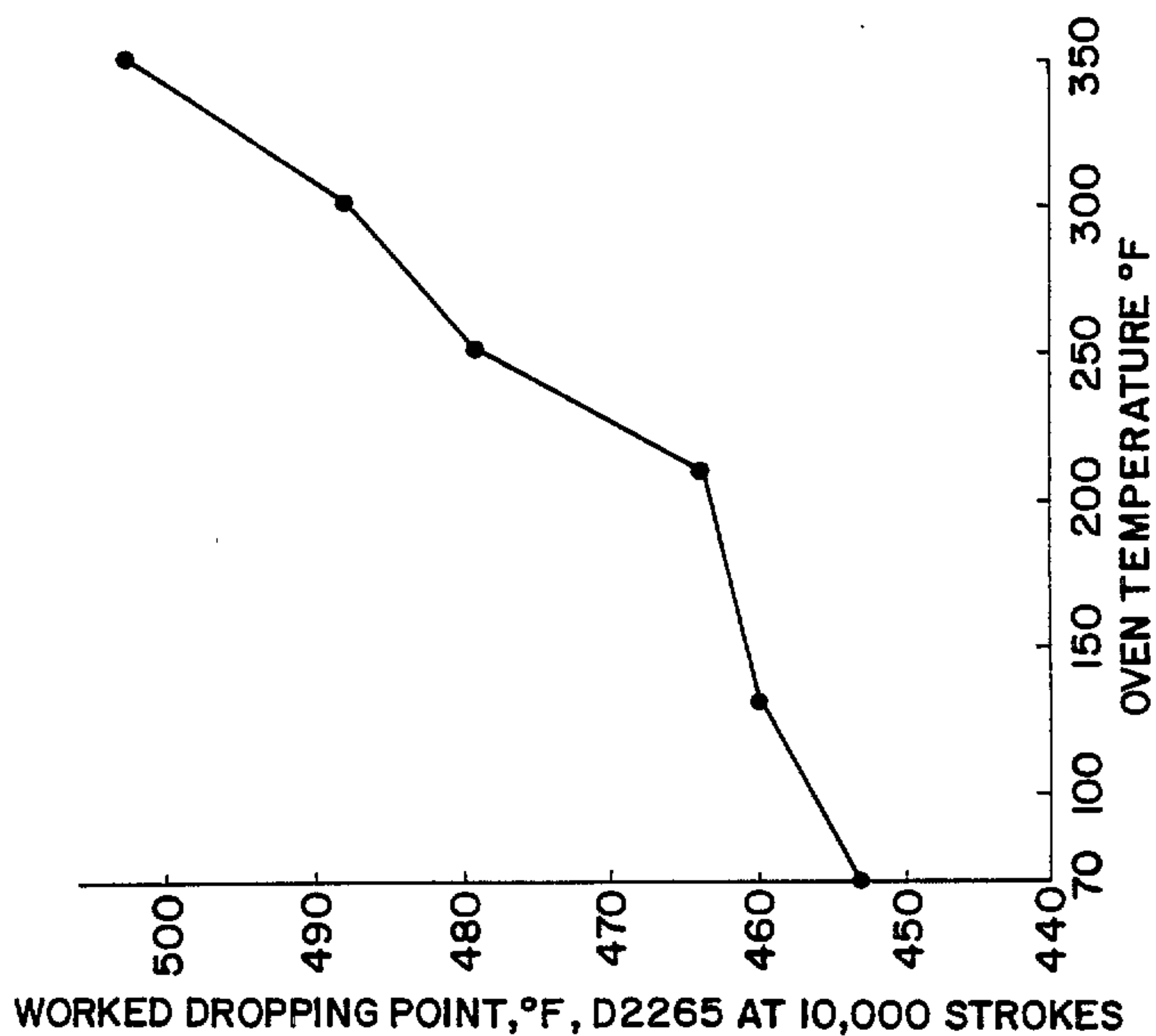


FIG. 3

