Feb. 16, 1960 T. TRAISE ET AL 2,925,387

METHOD OF PREPARING UREIDO GREASE-THICKENER CONCENTRATE AND LUBRICATING GREASES CONTAINING SAME

Filed July 21, 1958 2 Sheets-Sheet 1

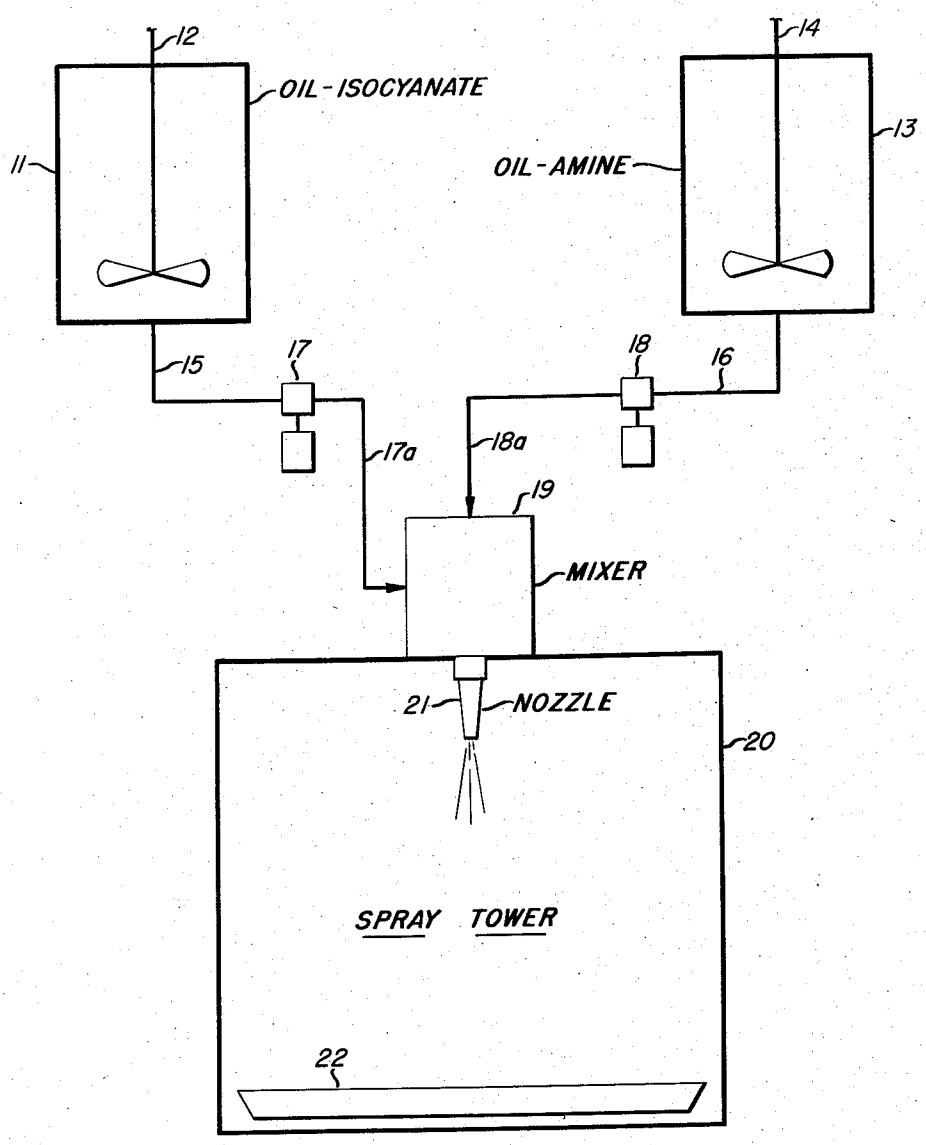


Fig. 1

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BY

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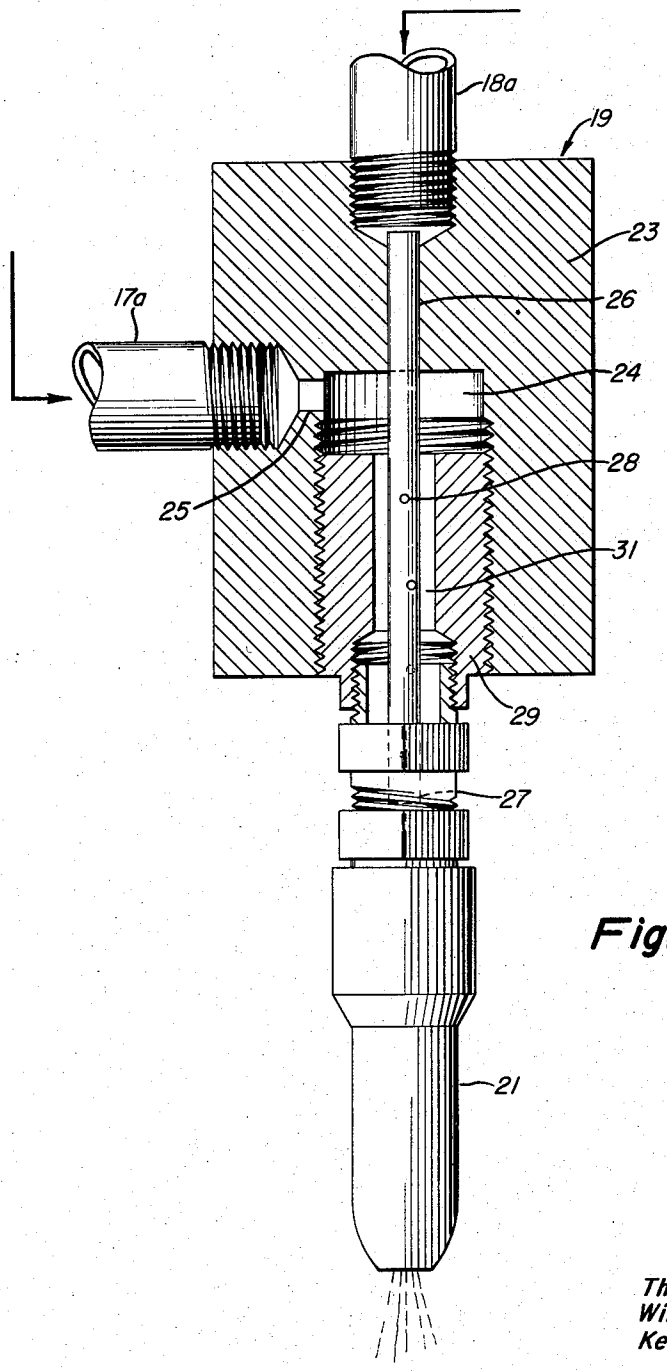


Fig. 2

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United States Patent Office 2,925,387 Patented Feb. 16, 1960

2,925,387

METHOD OF PREPARING UREIDO GREASE-THICKENER CONCENTRATE AND LUBRICATING GREASES CONTAINING SAME

Thornton Traise, Chicago Heights, Ill., and Wilbur L. Hayne, Jr., Hammond, and Kemp R. Bunting, East Chicago, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application July 21, 1958, Serial No. 750,015

11 Claims. (Cl. 252—51.5)

This invention relates to an improvement in the preparation of a grease-thickener concentrate, and more particularly pertains to an improved method of preparing a preformed oil-concentrate of the reaction product of a hydroabietyl amine and an organic polyisocyanate.

The co-pending application Serial No. 750,050, filed July 21, 1958, by R. J. Rosscup and Hubert J. Liehe, describes and claims as a new composition of matter the reaction product of a hydroabietyl amine, e.g. dehydroabietyl amine with an organic polyisocyanate, e.g. bitolylene diisocyanate, and lubricant compositions, such as lubricating oil and lubricating grease compositions, containing such reaction products. In respect to lubricating compositions, the reaction product of the hydroabietyl amine and the organic polyisocyanate can be formed in situ in the lubricating oil vehicle, e.g. the hydrocarbon oil, or the reaction product can be preformed and then incorporated in the lubricating oil vehicle in the desired amounts to obtain the lubricating oil composition or the lubricating grease composition. The preformed product is suitably prepared in a 25% to 60% concentration in a lubricating oil.

It is an object of the present invention to provide an improved method of preparing a preformed lubricating oil concentrate of the reaction product of a hydroabietyl amine and an organic polyisocyanate. Another object of the invention is to provide a method of preparing a preformed concentrate of a lubricating oil and the reaction product of a hydroabietyl amine and an organic polyisocyanate. Still another object of the present invention is to provide an improved method for the preparation of a preformed concentrated grease thickener capable of being incorporated in a lubricating oil to form a lubricating grease composition. A further object of the invention herein described is to provide an improved method of preparing a preformed concentrate of the reaction product of a hydroabietyl amine and bitolylene diisocyanate in a mineral lubricating oil which concentrate can be incorporated in additional mineral lubricating oil to form a lubricating grease composition. Other objects and advantages of the invention will become apparent from the following description thereof, read in conjunction with the accompanying drawings in which

Figure 1 is a flow diagram of a preferred method of carrying out the invention, and

Figure 2 is a cross-section drawing of a variable volume mixing chamber and discharge nozzle used in the herein described process.

As disclosed in the Rosscup and Liehe application, supra, their new composition of matter, employed in the lubricant compositions disclosed therein, are ureido compounds having the general formula

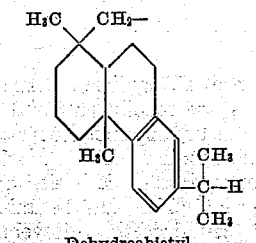


(I)

where R and R'' are the same or different hydroabietyl

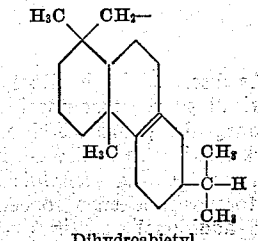
radicals selected from the group consisting of a dehydroabietyl radical, a dihydroabietyl radical, and tetrahydroabietyl radical and mixtures thereof and R' is an alkylene radical or substituted alkylene radical of from 1 to about 30 carbon atoms or an arylene radical or a substituted arylene radical. The radicals R, R' and R'' can contain substituents such as, for example, alkyl, alkoxy, cyano, aryl, hydroxy, carboxy, halogen, nitro and other substituent group. The alkylene radical can be straight and/or branched chain, and the arylene radicals can be mononuclear or polynuclear such as phenylene, biphenylene, naphthylene, anthrylene and phenanthrylene radicals. The terms "alkylene and arylene radicals" as used therein includes substituted alkylene radicals and substituted arylene radicals.

The general structural formula of the hydroabietyl radicals are:



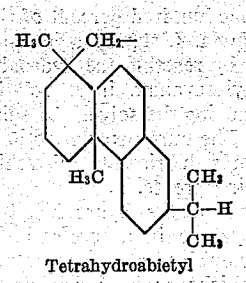
Dehydroabietyl

II



Dihydroabietyl

III



Tetrahydroabietyl

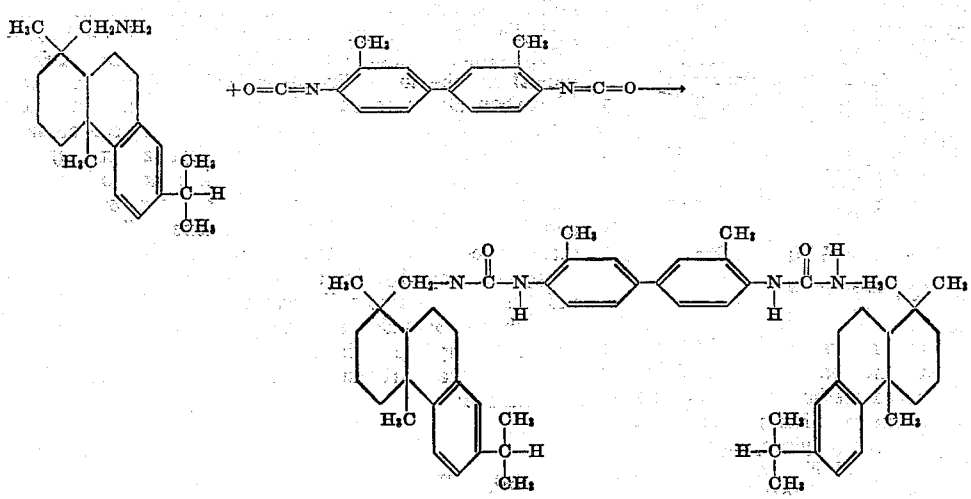
IV

Examples of hydroabietyl amines, i.e. aliphatic amines attached to an alicyclic structure, which can be used in the preparation of the above described ureido compounds are dehydroabietyl amine, dihydroabietyl amine and tetrahydroabietyl amine or mixtures of such amines. Particularly well suited amines are products marketed by Hercules Powder Company as "Rosin Amine D." Distilled and undistilled grades are available as Amine 750 and Amine 751. These products are prepared by the catalytic hydrogenation of "Rosin Nitrile D" prepared by the action at elevated temperatures of ammonia on hydrogenated rosin. The "Rosin Amine D" or the "Amine 750" is a mixture of hydroabietyl amines in the following approximate proportions:

	Percent
Dehydroabietyl amine	60
Dihydroabietyl amine	30
Tetrahydroabietyl amine	10

The organic polyisocyanate can be an alkyl or an aryl polyisocyanate, for example, tolylene diisocyanate; p,p'-diisocyanate biphenyl; 1,4-diisocyanate-benzene; p,p'-diisocyanate-diphenylmethane; 1,6-diisocyanate-hexane; 1,12-diisocyanate-dodecane; 1,3,5-benzene-triisocyanate; naphthylene diisocyanate; bitolylene diisocyanate; tris-p-isocyanate-phenylmethane; etc.

The following is illustrative of the apparent reaction which takes place:



As disclosed in the Rosscup et al. application, supra, lubricating grease compositions are readily prepared by forming the hydroabietyl amine-organic polyisocyanate thickener in situ in the lubricating oil vehicle. In addition to preparing such thickeners in situ, it is desirable to form a thickener concentrate which can be mixed with additional quantities of the lubricating oil vehicle to produce lubricating grease compositions of the desired consistency.

Substantially one hundred percent of the subject ureido compound (Formula, I, supra) a hard, white powder is readily prepared by reacting the hydroabietyl amine and the organic polyisocyanate in a volatile solvent, and subsequently removing the solvent by suitable means, e.g. under vacuum. The pure product so attained is difficult to incorporate in a lubricating oil vehicle to form an effective lubricating grease.

When solutions of the hydroabietyl amine and the organic polyisocyanate in a lubricating oil, e.g. a petroleum oil, are combined at a temperature of about 200° F., an effective thickener for lubricating greases can be obtained. However, the amine-polyisocyanate reaction is very rapid, and, in general, the rate of formation of the ureido compound is greater than the rate of precipitation at the beginning of the reaction. As a result, as the percentage of the reaction product increases in the reaction mixture, it becomes progressively more difficult to stoichiometrically combine the two reactants without resorting to intensive mixing, which has a tendency to reduce the average length of the crystalline fiber.

We have discovered, in accordance with the present invention, that the disabilities of the above methods are overcome by rapidly and intimately combining oil solutions of stoichiometric amounts of the two reactants and substantially instantaneously removing the reaction solution to an area where it can remain quiescent during precipitation and crystallization, a pale yellow granular concentrated thickener can be obtained which is readily incorporated in oil to form an excellent, stable, lubricating grease composition. Grease thickener concentrates containing from about 25% to about 60% of the ureido compound herein described can be so prepared.

The process of the present invention, comprises maintaining a 70–80% solution of the hydroabietyl amine in a lubricating oil at a temperature of from about 70° F. to about 100° F., preferably about 90° F., and a 20–30% solution of the organic polyisocyanate in a lubricating oil at a temperature of from about 150° F. to about 250° F., preferably about 200° F., separately introducing the two solutions into suitable variable mixing chambers, provided with a suitable spray nozzle attached to the bottom thereof, and discharging the mixture through said spray nozzle in the form of droplets into a spray tower of suitable height before precipitation of the reaction product occurs. As the droplets of the reaction mixture fall through the spray tower precipitation of the product occurs, followed by the crystallization thereof. When the reaction product reaches the bottom of the spray tower in the form of a relatively hard granular solid, it is caught or collected in pans of suitable size. The collected granular solid thickener received in the collecting pan at a temperature of from about 150° F. to about 250° F., is removed from the spray tower and allowed to cool to ambient room temperature.

The lubricating oil employed in the preparation of the herein described thickener is preferably a petroleum lubricating oil of the desired viscosity; suitable oils are solvent extracted or otherwise refined SAE 10 and 20 base petroleum oils. However, depending upon the intended use of the finished lubricating grease, other oils in the lubricating oil viscosity range can be used, such as, for example silicone polymer oils, synthetic hydrocarbon lubricating oils, and other synthetic lubricating oils such as polyalkylene glycols and their derivatives, high molecular weight esters of dicarboxylic acids, polyfluoro derivatives of organic compounds such as the trifluorovinyl chloride polymers known as "Fluorolube" (made by Hooker Chemical Company) and the trifluorochloroethylene polymers, known as "Kel–F–40" (made by The M. W. Kellogg Company), etc.

The present invention will be clearly understood from the following specific examples which is given by way of illustration only and is not to be construed as a limitation of the invention.

Referring to Figure 1, a solution of about 25% bitolylene diisocyanate in a solvent extracted SAE 10 base mineral oil is prepared in tank **11**, provided with a stirrer **12**, by heating the mixture oil and isocyanate at a temperature of 200° F. with continuous stirring, and a solution of about 75% of "Rosin Amine D," supra, in a solvent extracted SAE 10 base mineral oil is prepared in tank **13** provided with a stirrer **14** at about 70–80° F. with continuous stirring. The oil-isocyanate solution from tank **11** and the oil-amine solution from tank **13** are pumped through lines **15** and **16**, pumps **17** and **18**, lines **17***a* and **18***a* respectively to the variable volume mixer **19** (hereinafter described in detail) located at the top of a spray tower **20**. Pumps **17** and **18**, which are suitable gear pumps, are geared to operate at the same rate and therefore deliver the same volumes of the solutions from tanks **11** and **13** to the mixer **19**. The volume of the variable mixer **19** is adjusted to the point where

the entering reactants are adequately mixed and discharged from the mixer before precipitation of the reaction product occurs.

The oil-isocyanate solution entering the mixer **19**, at a temperature of 160–190° F. and the oil-amine solution entering the mixer **19** at a temperature of 70–100° F. are contacted with each other therein and reaction initiated immediately. The reacting mixture moves rapidly through the mixer **19** and is sprayed into spray tower **20** through spray nozzle **21** located in the bottom of the mixing chamber **19** and projecting into the top of spray tower **20**. As the admixed solution is discharged from the spray nozzle **21** in the form of droplets, precipitation of the reaction product as relatively hard granular solids occurs as it falls through the spray tower **20**. The reaction product is collected in suitable containers **22**, e.g. relatively shallow steel pans at the bottom of the spray tower **20**, which are removed from the spray tower as they become filled. The temperature at the interior of a batch of the thickener concentrate immediately after removal from the spray tower is in the range of from about 150° F.–250° F. The product after cooling to ambient room temperature is in the form of loose agglomerates which are readily crumbled to give a pale yellow granular solid having the appearance of light yellow sugar.

The details of the mixer **19**, fabricated of a suitable metal, preferably of brass or bronze, are shown in Figure 2. Referring to Figure 2, mixer **19** consists of a body portion **23** and a chamber **24** in communication with line **17***a* through inlet **25**, and in communication with line **18***a* by means of pipe or tube **26** having a sealed end **27** and a plurality of holes **28** spirally spaced in the portion thereof extending from within the chamber **24**. The tube **26** extends through mixing chamber **24** and is concentric with the nozzle mount **29**, hereinafter described. The open end of chamber **24** is threaded to receive threaded nozzle mount **29** which is of sufficient length to be threaded, when necessary, into the mixing chamber **24** to a position put below the inlet **25**. Attached to the nozzle mount **29** is an adjustable spray nozzle **21**; a suitable nozzle is one marketed by the Spraying System Company as No. 5780–AX60. The area in which the two entering solutions are admixed is varied and controlled by the distance to which the threaded nozzle mount **29** is threaded into the chamber **24**. As the nozzle mount **29** is threaded farther into the chamber **24** less mixing of the solutions occur in chamber **24** and more mixing takes place in the annular space **31** between the tube **26** and the nozzle mount **29**. The distance in which the nozzle mount **29** extends into chamber **24** can be so adjusted that the two oil solutions are admixed and expelled through the nozzle **21** into the spray tower **20** before any substantial precipitation of the reaction product occurs.

Using a 20% to 30% solution of bitolylene diisocyanate in a mineral oil and a 70% to 80% solution of a hydroabietyl amine such as "Rosin Amine D" in a mineral oil, will yield a thickener concentrate having a typical analysis of about 44–47% thickener, 1 to 5% free amine and 0.25–1.5% undetermined.

By varying the quantities of the hydroabietyl amine and of the organic polyisocyanate concentrates containing 25–60% of the thickener (Formula I, supra) can be prepared by the above described spray technic.

Although in the foregoing, specific examples, illustrative of our invention, we have used bitolylene diisocyanate, other aryl or alkyl polyisocyanates such as above disclosed, can be used.

Lubricating grease compositions of any desired consistency, i.e. thickener concentration, can be obtained by incorporating, by a variety of methods, the desired amount of the thickener concentrate in a suitable lubricating oil. A suitable method comprises combining in a grease kettle 16–20 parts of the thickener concentrate

(approximately 50% thickener) and 10–18 parts of a solvent extracted SAE 10 base mineral oil and mixing to form a heavy base. The heavy base is then heated to about 200° F. and graded with 65–70 parts of a solvent extracted SAE 40 base mineral oil to give a fluid grease composition containing about 10% of the thickener (Formula I, supra). The resultant fluid mixture is heated to about 390–400° F., held at said temperature for about 35–40 minutes and then cooled to about 200° F., and passed through a colloid mill.

Greases prepared by forming the thickener in situ and prepared from preformed thickener concentrates, obtained by the method of the present invention are comparable, as shown by the data in Table I. The thickener used was the reaction product of bitolylene diisocyanate and "Rosin Amine D," supra.

Table I

	Preformed	Formed In Situ
Percent Thickener	8	7
Mechanical Stability, Percent Change	5	5
Leakage Assistance, Percent Loss	2.5	2.0
Water Resistance	Excellent	Excellent
Drop Point, ° F	480	480

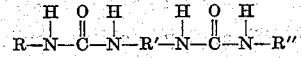
The feature of the above greases include mechanical stability, leakage, water resistance, and a high drop point.

Percentages and parts given herein and in the appended claims are by weight, unless otherwise stated.

Although the present invention has been described with reference to specific embodiments thereof, the invention is not limited thereto, but includes within its scope such modifications and variations as come within the scope and spirit of the appended claims.

We claim:

1. The method of preparing a concentrate of a lubricating oil containing at least 25% of a ureido compound having the general formula



wherein R and R'' are hydroabietyl radicals selected from the group consisting of a dehydroabietyl radical, a dihydroabietyl radical, a tetrahydroabietyl radical and mixtures thereof, and R' is an organic radical selected from the group consisting of an alkylene radical of from 1 to about 30 carbon atoms, and an arylene radical, comprising the steps (1) forming separate solutions of stoichiometric proportions of a hydroabietyl amine in a lubricating oil and of an organic polyisocyanate in a lubricating oil, (2) rapidly mixing together equal proportions of said oil solutions for a time sufficient to initiate reaction between said amine and said polyisocyanate, but insufficient to cause precipitation of any reaction product, (3) spraying, in the form of droplets, said admixed oil solutions of said reactants into the top of a spray tower before precipitation of the reaction product occurs, (4) permitting said droplets to descend in the spray tower for a time sufficient for said droplets to form a solid granular precipitate, and (5) collecting said solid granular precipitate.

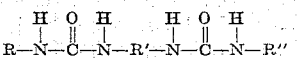
2. The method of claim 1 in which the organic polyisocyanate is an aryl polyisocyanate.

3. The method of claim 1 in which the organic polyisocyanate is bitolylene diisocyanate.

4. The method of claim 1 in which the organic polyisocyanate is an alkyl polyisocyanate.

5. The method of claim 1 in which the lubricating oil is a petroleum lubricating oil.

6. The method of preparing a concentrate of a lubricating oil containing from about 25% to about 60% of at least one ureido compound having the general formula



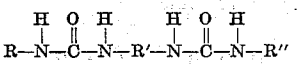
wherein R′ and R″ are hydroabietyl radicals selected from the group consisting of a dehydroabietyl radical, a dihydroabietyl radical, a tetrahydroabietyl radical and mixtures thereof, and R′ an arylene radical, comprising the steps (1) forming separate solutions of about 70% to about 80% of a hydroabietyl amine in a lubricating oil and of about 20% to about 30% of an aryl polyisocyanate in a lubricating oil, (2) rapidly mixing together equal proportions of said oil solution of said aryl polyisocyanate at a temperature of from about 150° F. to about 250° F., and said oil solution of said amine at a temperature of from about 70° F. to about 100° F. for a time sufficient to initiate reaction between said amine and said polyisocyanate, but insufficient to cause precipitation of any reaction product, (3) spraying, in the form of droplets, said admixed oil solutions of said reactants at a temperature of from about 150° F. to about 250° F., into the top of a spray tower before precipitation of the reaction product occurs, (4) permitting said droplets to descend in the spray tower for a time sufficient for said droplets to form a solid granular precipitate, (5) collecting said solid granular precipitate, and cooling to embient room temperature.

7. The method of claim 6 in which the hydroabietyl amine is a mixture consisting essentially of about 60% dehydroabietyl amine, about 30% dihydroabietyl amine and about 10% tetrahydroabietyl amine.

8. The method of claim 6 in which the aryl polyisocyanate is bitolylene diisocyanate.

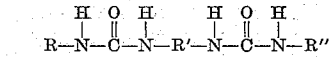
9. The method of claim 6 in which the lubricating oil is a hydrocarbon lubricating oil.

10. The method of preparing a lubricating grease comprising a lubricating oil thickened with a thickener concentrate comprising a lubricating oil containing at least 25% of a ureido compound having the general formula



wherein R and R″ are hydroabietyl radicals selected from the group consisting of a dehydroabietyl radical, a dihydroabietyl radical, a tetrahydroabietyl radical and mixtures thereof, and R′ is an organic radical selected from the group consisting of an alkylene radical of from 1 to about 30 carbon atoms, and an arylene radical, and prepared by the method of claim 1, comprising mixing said thickener concentrate with a small amount of a lubricating oil, heating said mixture to a temperature of 200° F. while stirring, adding additional lubricating oil in an amount sufficient to obtain the desired lubricating grease consistency, raising the temperature of the mixture to about 390–400° F., and maintain the said temperature for about 30–40 minutes, cooling the mixture to a temperature of about 200° F., and passing the mixture through a colloid mill.

11. The method of preparing a lubricating grease comprising a lubricating oil thickened with a thickener concentrate comprising a lubricating oil containing about 45–50% of a ureido compound having the general formula



in which R and R″ are hydroabietyl radicals selected from the group consisting of a dehydroabietyl radical, a dihydroabietyl radical, a tetrahydroabietyl radical and mixtures thereof, and R′ is a bitolylene radical, and prepared by the method of claim 1, comprising mixing said thickener concentrate with a small amount of a lubricating oil, heating said mixture to a temperature of 200° F. while stirring, adding additional lubricating oil in an amount sufficient to obtain the desired lubricating grease consistency, raising the temperature of the mixture to about 390–400° F., and maintain the said temperature for about 30–40 minutes, cooling the mixture to a temperature of about 200° F., and passing the mixture through a colloid mill.

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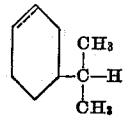
Certificate of Correction

Patent No. 2,925,387 February 16, 1960

Thornton P. Traise et al.

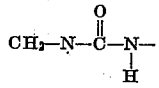
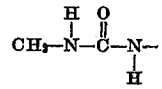
It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the grant, line 1, and in the heading to the printed specification, line 5, name of first inventor, for "Thornton Traise", each occurrence, read —Thornton P. Traise—; in the heading to the drawings, sheets 1 and 2, line 1, for "T. Traise et al." read —T. P. Traise et al.—; column 2, lines 25 to 30, Formula III, the lower right-hand portion should appear as shown below instead of as in the patent:



Dihydroabietyl

columns 3 and 4, for that portion of the formula reading

 read 

column 7, line 7, for "wherein R′" read —wherein R—.

Signed and sealed this 2nd day of August 1960.

[SEAL]

Attest:

KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.