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(54) **PROCESS FOR PREPARING A UREA GREASE**

VERFAHREN ZUR HERSTELLUNG VON HARNSTOFFSCHMIERMITTEL

PROCÉDÉ DE PRÉPARATION DE GRAISSE À BASE D'URÉE

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EP 2 954 035 B1

Description

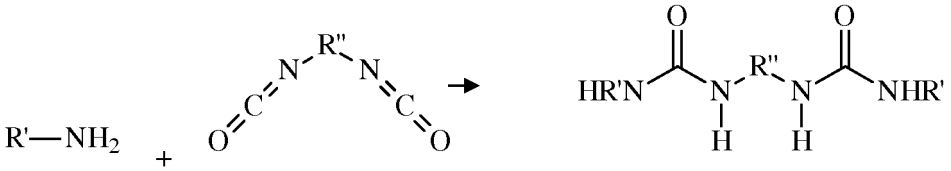
Field of the Invention

[0001] The invention relates to a process for preparing a urea grease.

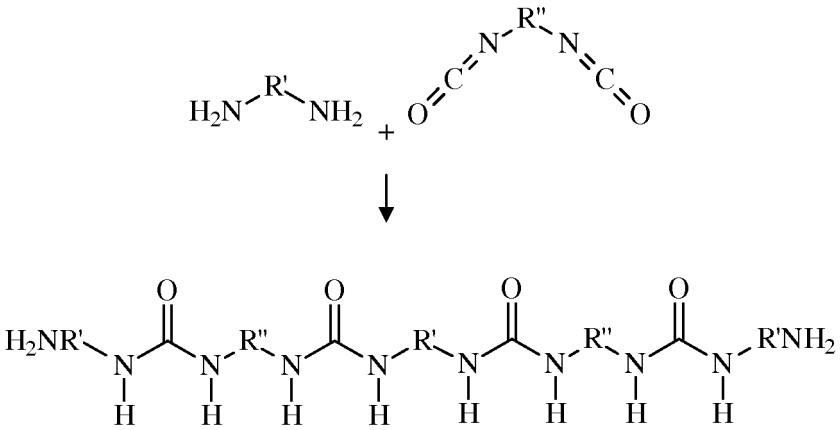
Background of the Invention

[0002] Urea greases are used in a variety of applications including bearings for constant-velocity joints, ball joints, wheel bearings, alternators, cooling fans, ball screws, linear guides of machine tools, sliding areas of construction equipment, and bearings and gears in steel equipment and various other industrial mechanical facilities. Urea greases typically have excellent heat and oxidation resistance, and can extend the lifetime of bearings.

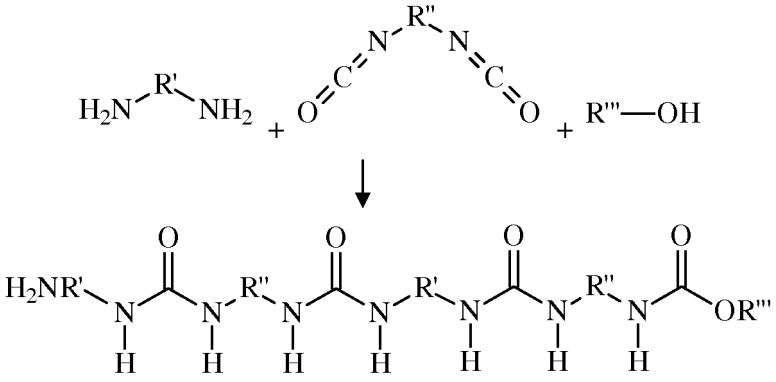
[0003] Urea greases contain low molecular weight organic compounds, sometimes referred to as polyureas, that are typically synthesized from isocyanates and amines. A diisocyanate and a monoamine can be used to form a diurea:



[0004] A diisocyanate and a diamine can be used to form a tetraurea:



[0005] A diisocyanate, an alcohol and a diamine can be used to form a triurea-urethane:



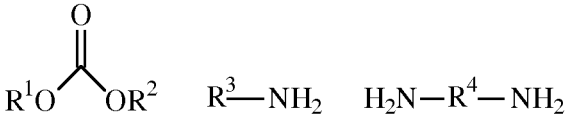
[0006] Urea greases are formed by carrying out these reactions in a base oil, thereby directly providing the grease product wherein the urea thickener is dispersed throughout the base oil.

[0007] The reaction of the diisocyanate and the amine does not require any heat and proceeds at a good rate at room

temperature. There are no reaction byproducts that must be removed. However, the diisocyanate reagents are highly toxic and volatile and require special treatment and handling equipment. It is desirable to find an alternative route for the manufacture of urea greases that avoids the use of diisocyanate reagents.

Summary of the Invention

[0008] Accordingly, the invention provides a process for preparing a urea grease comprising one or more steps in which a compound of formula (I), a compound of formula (II) and a compound of formula (III) are reacted:



(I) (II) (III) wherein R^1 and R^2 are chosen from hydrocarbyl having from 1 to 30 carbon atoms, or R^1 and R^2 are linked and form a hydrocarbylene group having from 1 to 30 carbon atoms, R^3 is chosen from hydrocarbyl comprising from 2 to 30 carbon atoms and R^4 is hydrocarbylene comprising from 2 to 30 carbon atoms;
wherein at least one of the reaction steps is carried out in the presence of a base oil.

[0009] The process of the invention provides a urea grease, but avoids the use of diisocyanate reagents. Isocyanate-free syntheses of ureas are described by Luc Ubaghs in the PhD thesis "Isocyanate-free synthesis of (functional) polyureas, polyurethanes and urethane-containing copolymers", but this document does not disclose the preparation of a urea grease. The present inventors have found that urea greases may be prepared by reacting compounds (I), (II) and (III) wherein at least one of the reaction steps takes place in the presence of a base oil.

Brief Description of the Drawings

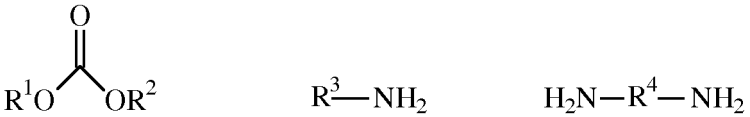
[0010]

Figure 1 is a reaction scheme showing the preparation of a urea grease according to the invention.
Figure 2 is a reaction scheme showing the preparation of a urea grease according to the invention.
Figure 3 is a reaction scheme showing the preparation of a urea grease according to the invention.
Figure 4 is a reaction scheme showing the preparation of a urea grease according to the invention.

Detailed Description of the Invention

[0011] The term "hydrocarbyl" as used in the present description refers to a monovalent organic radical comprising hydrogen and carbon and may be aliphatic, aromatic or alicyclic, for example, but not limited to, aralkyl, alkyl, aryl, cycloalkyl, alkylcycloalkyl, or a combination thereof, and may be saturated or olefinically unsaturated (one or more double-bonded carbons, conjugated or non-conjugated). The term "hydrocarbylene" as used in the present description refers to a divalent organic radical comprising hydrogen and carbon and may be aliphatic, aromatic or alicyclic, for example, but not limited to, aralkyl, alkyl, aryl, cycloalkyl or alkylcycloalkyl, and may be saturated or olefinically unsaturated (one or more double-bonded carbons, conjugated or non-conjugated).

[0012] The invention provides a process for the preparation of a urea grease. A compound of formula (I), a compound of formula (II) and a compound of formula (III) are reacted:



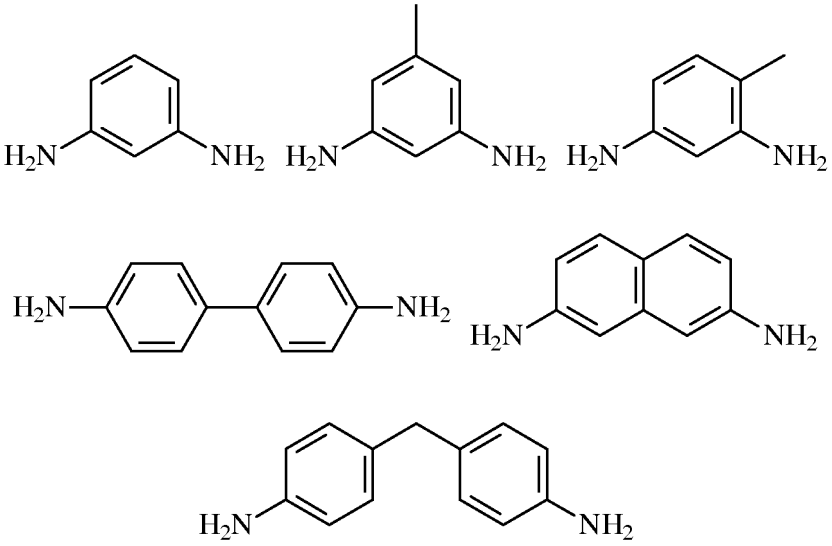
(I) (II) (III)

[0013] R^1 and R^2 are chosen from hydrocarbyl having from 1 to 30 carbon atoms, or R^1 and R^2 are linked and form a hydrocarbylene group having from 1 to 30 carbon atoms. R^1 and R^2 are preferably hydrocarbyl groups or a hydrocarbylene group comprising only hydrogen and carbon atoms, but it is possible that R^1 and R^2 may also comprise heteroatom substituents such as halo, nitro, hydroxyl or alkoxy substituents, particularly if one or more of R^1 or R^2 is an aryl group. Suitably R^1 and R^2 are chosen from aryl having from 6 to 12 carbon atoms and alkyl having from 1 to 12 carbon atoms, or R^1 and R^2 are linked and form an alkylene group having from 1 to 12 carbon atoms. Preferably R^1 and R^2 are chosen

from phenyl and substituted-phenyl groups having from 6 to 12 carbon atoms and alkyl groups having from 1 to 12 carbon atoms, or R^1 and R^2 are linked and form an alkylene group having from 1 to 6 carbon atoms. Substituted phenyl includes methyl-substituted or ethyl-substituted phenyl (preferably in the para or ortho positions) or ethoxy-substituted phenyl. Most preferably R^1 and R^2 are both phenyl or R^1 and R^2 are linked and form an ethylene group, i.e. the compound of formula (I) is diphenylene carbonate or ethylene carbonate. R^1 and R^2 are suitably chosen such that R^1-OH and R^2-OH (or HO-R^1-R^2-OH) are compounds that may be readily removed from the reaction mixture.

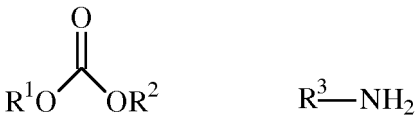
[0014] R^3 is chosen from hydrocarbyl comprising from 2 to 30 carbon atoms. R^3 preferably comprises only hydrogen and carbon atoms, but it is possible that R^3 may also comprise heteroatom substituents such as halo, nitro, hydroxyl or alkoxy substituents, particularly if R^3 is an aryl group. Preferably R^3 is aryl having from 6 to 12 carbon atoms or is alkyl comprising from 2 to 18 carbon atoms. Most preferably the compound of formula (II) is chosen from octylamine, dodecylamine (laurylamine), tetradecylamine (myristylamine), hexadecylamine, octadecylamine (tallow amine, also referred to as stearylamine), oleylamine, aniline, benzyl amine, p-toluidine, p-chloro-aniline or m-xylidine.

[0015] R^4 is hydrocarbylene comprising from 2 to 30 carbon atoms. R^4 preferably comprises only hydrogen and carbon atoms, but it is possible that R^4 may also comprise heteroatom substituents such as halo, nitro, hydroxyl or alkoxy substituents particularly if R^4 is an arylene group. Preferably R^4 is arylene comprising from 6 to 12 carbon atoms or alkylene comprising from 2 to 12 carbon atoms. Most preferably the compound of formula (III) is chosen from arylene comprising from 6 to 12 carbon atoms. Preferred compounds of formula (III) are shown below:



[0016] In one embodiment of the process of the invention a compound of formula (I), a compound of formula (II) and a compound of formula (III) are reacted in one step in the presence of a base oil. However, in more preferred embodiments, the reaction takes place in two steps and the second step takes place in the presence of a base oil. In a first preferred embodiment, the process for preparing a urea grease comprises steps of:

(a1) reacting a compound of formula (I) with a compound of formula (II):



(I) (II)

and

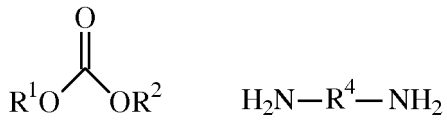
(b1) reacting the product of step (a1) with a compound of formula (III):

$$H_2N\text{-}R^4\text{-}NH_2 \qquad \text{(III)}$$

wherein step (b1) is carried out in the presence of a base oil. In a second preferred embodiment, the process

for preparing a urea grease comprises steps of:

(a2) reacting a compound of formula (I) with a compound of formula (III):



(I) (III)

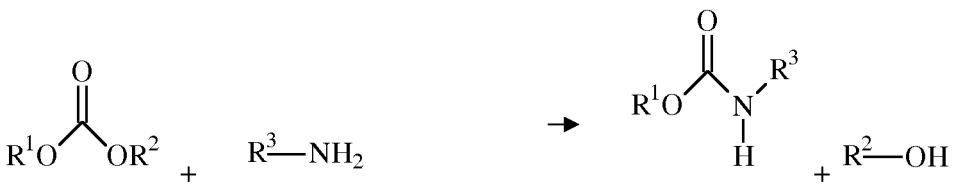
and

(b2) reacting the product of step (a2) with a compound of formula (II):

$$R^3\text{-}NH_2 \qquad \text{(II)}$$

wherein step (b2) is carried out in the presence of a base oil.

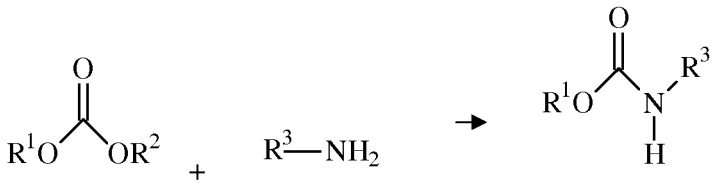
[0017] In the first preferred embodiment, in step (a1) the compound of formula (I) reacts with the compound of formula (II):



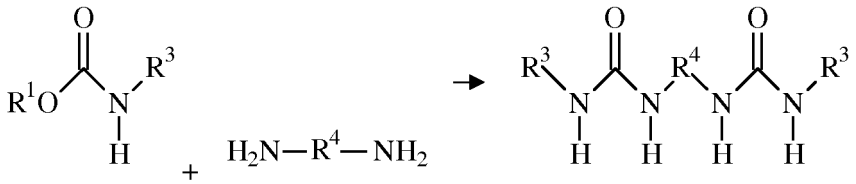
(I) (II)

[0018] If R^1 and R^2 are linked and form a hydrocarbylene group, then there will be just one product. If R^1 and R^2 are hydrocarbyl groups (and are not linked), then an alcohol byproduct will result in step (a1) and this byproduct is preferably removed before step (b1).

[0019] A diurea grease is suitably prepared by reacting compounds of formula (I) and (II) in step (a1) and subsequently reacting the product of step (a1) with a compound of formula (III) in step (b1):



(I) (II)

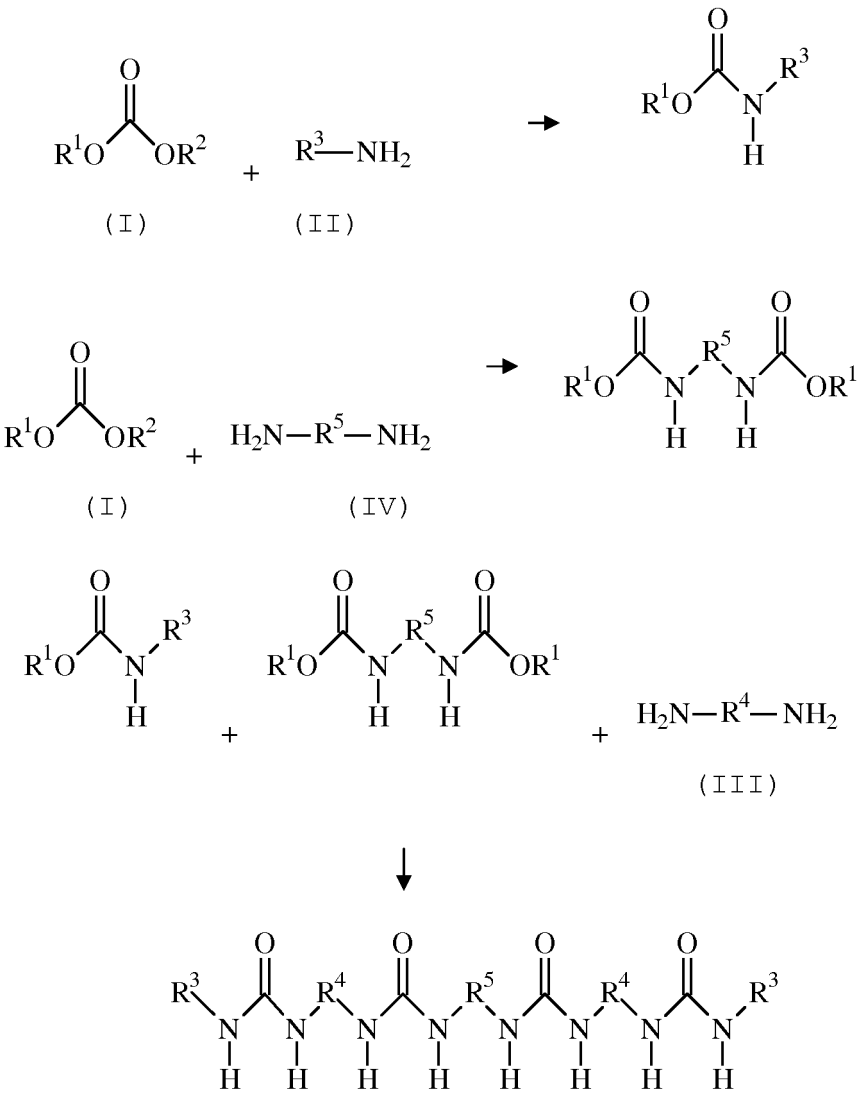


(III)

[0020] If a tetraurea grease is the desired product, then in step (a1) the compounds of formula (I) and (II) are additionally reacted with a compound of formula (IV):

$H_2N\text{-}R^5\text{-}NH_2$ (IV)

wherein R^5 is hydrocarbylene comprising from 2 to 30 carbon atoms. The product of step (a1) is then reacted with a compound of formula (III) in step (b1):



[0021] R^5 preferably comprises only hydrogen and carbon atoms, but it is possible that R^5 may also comprise heteroatom substituents such as halo, nitro, hydroxyl or alkoxy substituents. R^5 is preferably arylene comprising from 6 to 12 carbon atoms or alkylene comprising from 2 to 12 carbon atoms. Preferred compounds of formula (IV) include ethylenediamine, propylenediamine, butylenediamine, pentylenediamine and hexamethylenediamine.

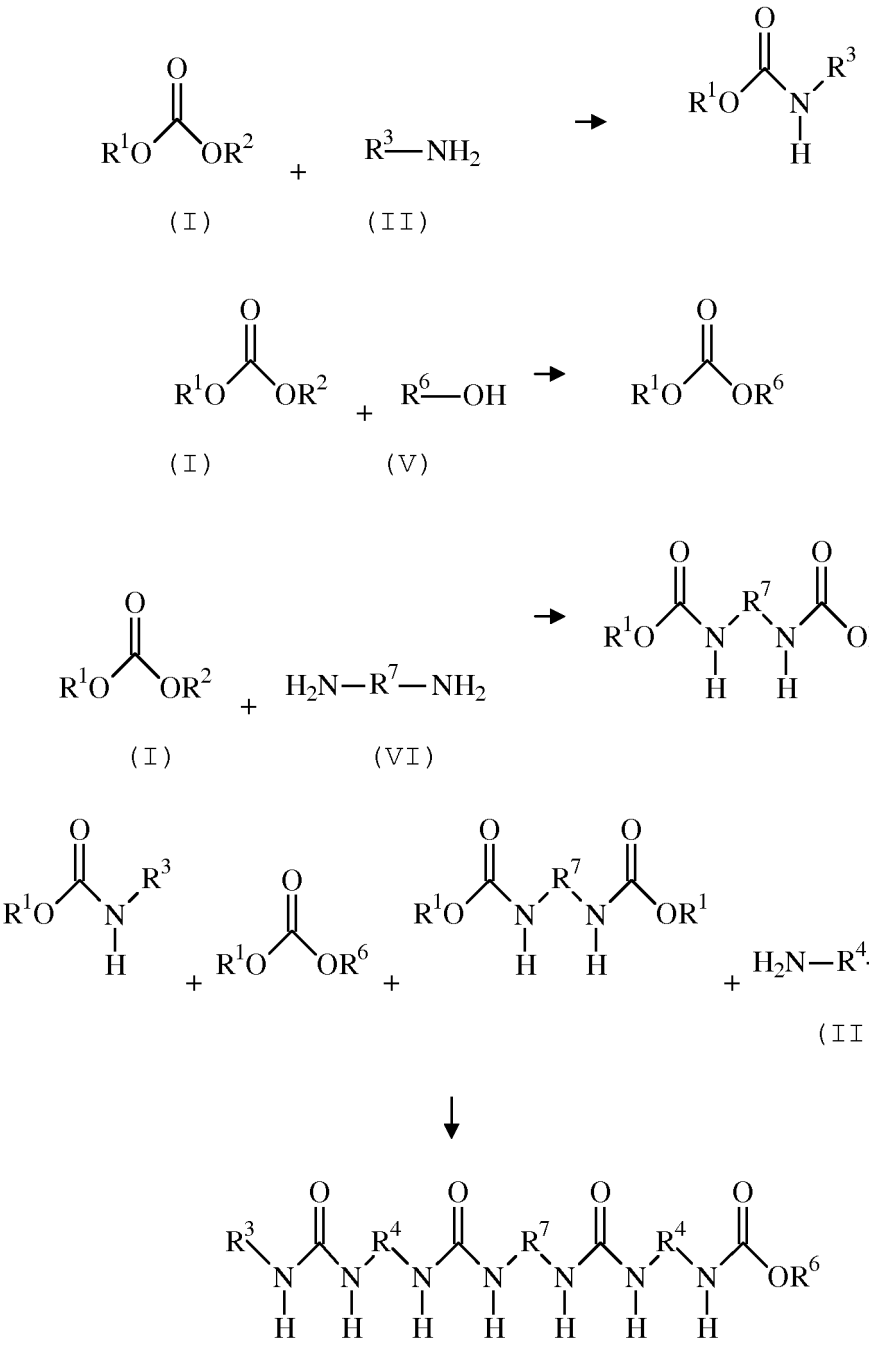
[0022] If a triurea-urethane grease is the desired product, then in step (a1) the compounds of formula (I) and (II) are additionally reacted with a compound of formula (V) and a compound of formula (VI):

R^6OH (V)

$H_2N\text{-}R^7\text{-}NH^2$ (VI)

wherein R^6 and R^7 are independently chosen from hydrocarbyl comprising from 2 to 30 carbon atoms.

[0023] The product of step (a1) is then reacted with a compound of formula (III) in step (b1):

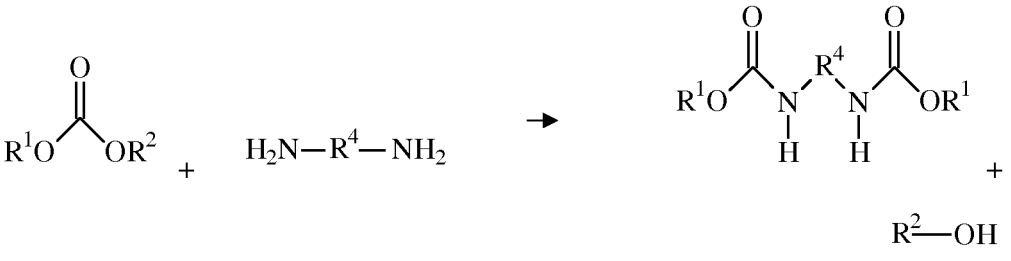


[0024] R^6 preferably comprises only hydrogen and carbon atoms, but it is possible that R^6 may also comprise heteroatom substituents such as halo, nitro, hydroxyl or alkoxy substituents. R^6 is preferably alkylene or alkenylene comprising from 2 to 24 carbon atoms. Preferred compounds of formula (V) include 1-dodecanol (lauryl alcohol), 1-tetradecanol (myristyl alcohol), 1-hexadecanol (cetyl (or palmityl) alcohol), 1-octadecanol (stearyl alcohol), cis-9-octadecen-1-ol (oleyl alcohol), 9-octadecadien-1-ol (unsaturated palmitoleyl alcohol), 12-octadecadien-1-ol (linoleyl alcohol).

[0025] R^7 preferably comprises only hydrogen and carbon atoms, but it is possible that R^7 may also comprise heteroatom substituents such as halo, nitro, hydroxyl or alkoxy substituents. R^7 preferably arylene comprising from 6 to 12 carbon atoms or alkylene comprising from 2 to 12 carbon atoms. Preferred compounds of formula (VI) include ethylenediamine, propylenediamine, butylenediamine, pentylenediamine and hexamethylenediamine.

[0026] Before the product of step (a1) is used in step (b1) it is preferable to remove any unreacted compounds of formula (I) and (II), any solvent that may have been used and any byproducts (especially R^1-OH and R^2-OH compounds). Removal is suitably achieved using vacuum.

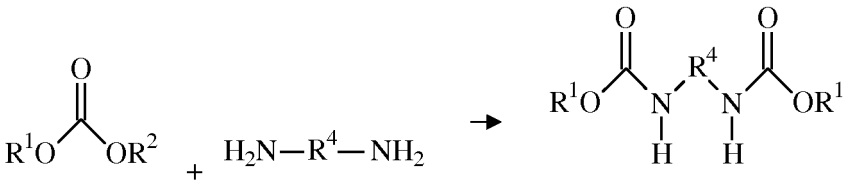
[0027] In the second preferred embodiment, in step (a2) the compound of formula (I) reacts with the compound of formula (III):



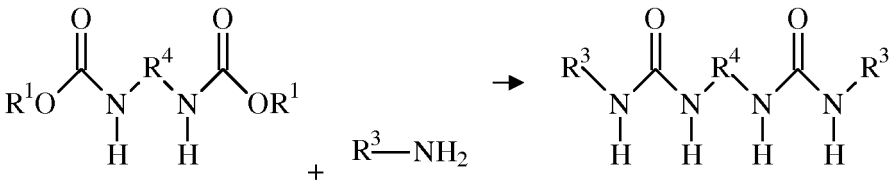
(I) (III)

[0028] If R^1 and R^2 are linked and form a hydrocarbylene group, then there will be just one product. If R^1 and R^2 are hydrocarbyl groups (and are not linked), then an alcohol byproduct will result in step (a2) and this byproduct is preferably removed before step (b2).

[0029] A diurea grease is suitably prepared by reacting compounds of formula (I) and (III) in step (a2) and subsequently reacting the product of step (a2) with a compound of formula (II) in step (b2) in the presence of a base oil:



(I) (III)

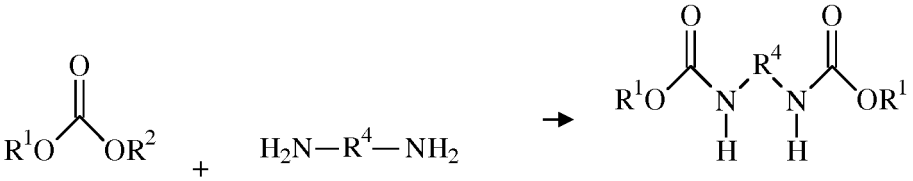


(II)

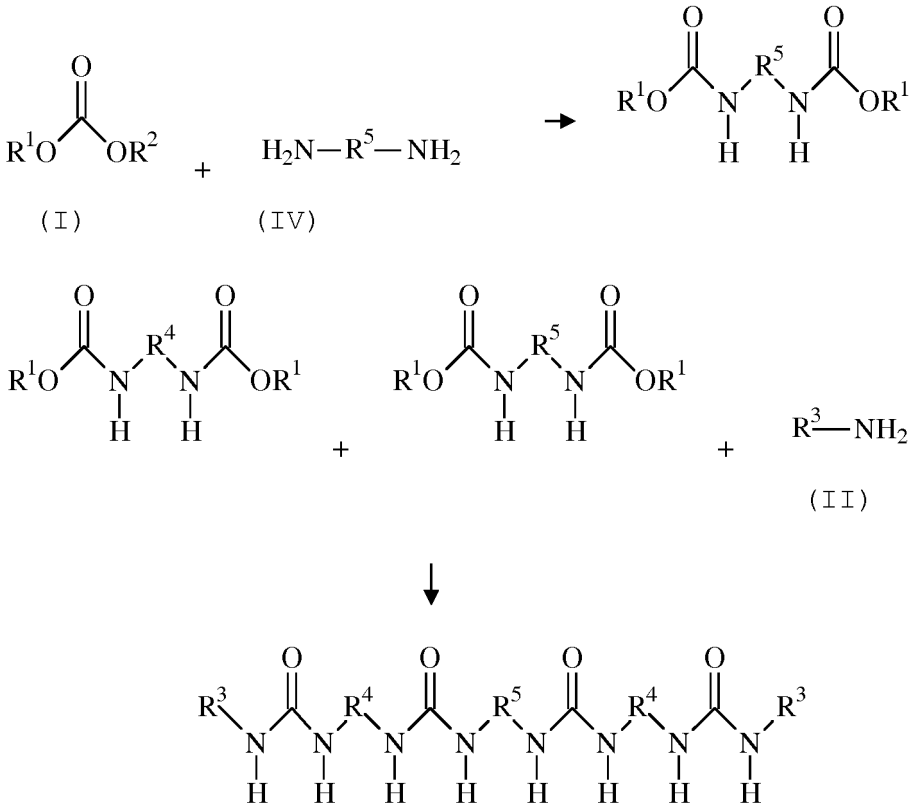
[0030] If a tetraurea grease is the desired product, then in step (a2) the compounds of formula (I) and (III) are additionally reacted with a compound of formula (IV):

H_2N-R^5- NH_2 (IV)

wherein R^5 is hydrocarbylene comprising from 2 to 30 carbon atoms. Preferred R^5 groups are as described for the first preferred embodiment of the invention. In step (a2) the compound of formula (I) will react with the compound of formula (III), and the compound of formula (I) will react with the compound of formula (IV). In step (b2) the reaction products of step (a2) are then reacted with a compound of formula (II):



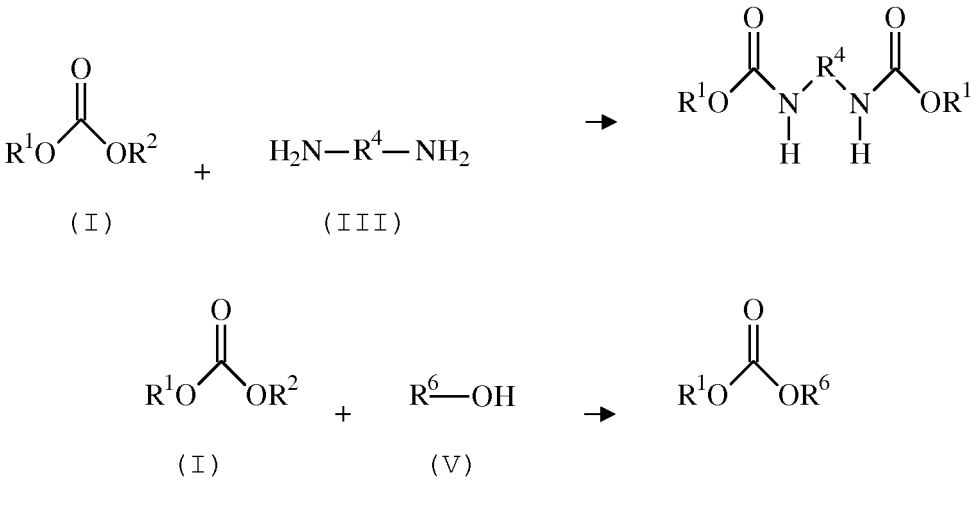
(I) (III)

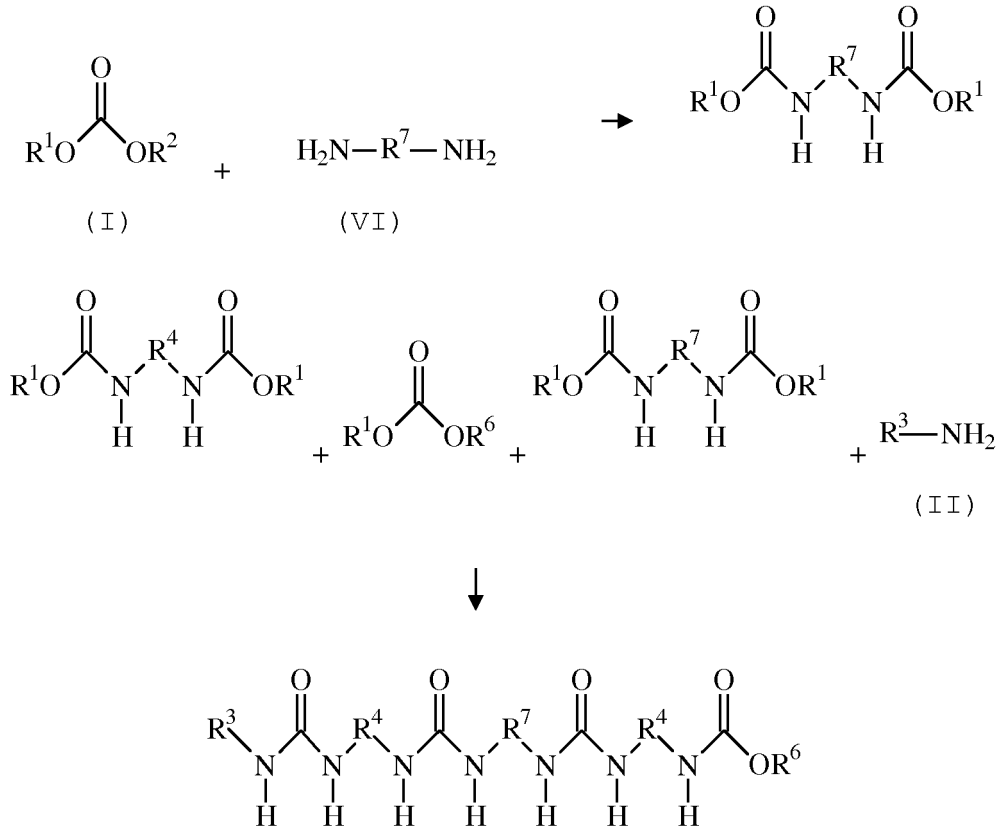


[0031] If a triurea-urethane grease is the desired product, then in step (a2) the compounds of formula (I) and (III) are additionally reacted with compounds of formula (V) and (VI):

R^6-OH H_2N-R^7- NH_2 (V) (VI)

wherein R^6 and R^7 are independently chosen from hydrocarbyl comprising from 2 to 30 carbon atoms. Preferred R^6 and R^7 groups are as described for the first embodiment of the invention. In step (a2) the compound of formula (I) will react with the compound of formula (III), the compound of formula (I) will react with the compound of formula (V) and the compound of formula (I) will react with the compound of formula (VI). In step (b2) the reaction products of step (a2) are then reacted with a compound of formula (II):

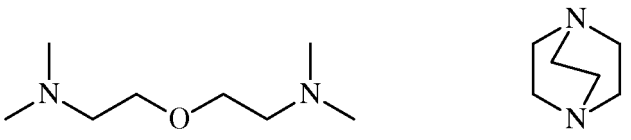




(I) (VI) (II)

[0032] Before the product(s) of step (a2) is/are used in step (b2) it is preferable to remove any unreacted compounds of formula (I) and (III), any solvent that may have been used and any byproducts (especially R^1-OH and R^2-OH compounds). Removal is suitably achieved using vacuum or adequate solvent washes.

[0033] The preferred reaction conditions in step (a1) and (a2) will be affected by the choice of the compound (I). If compound (I) is diphenyl carbonate, then step (a1) or (a2) preferably takes place without solvent or in the presence of a solvent such as toluene or dimethylformamide. The reaction preferably takes place in the presence of a catalyst such as diphenylphosphinic acid. Phenol will be produced as a byproduct of the reaction. The phenol byproduct should be removed, e.g. by use of a vacuum. If compound (I) is dimethyl carbonate, then it is desirable to use a catalyst such as dibutyl tin methoxide, dibutyl tin dilaurate or tin (II) octoate. Other catalysts that could be used include potassium t-butoxide, copper (II) acetylacetonate, DABCO BL11 and DABCO LV33.



DABCO BL11 DABCO LV33

[0034] The preferred reaction conditions in step (b1) and (b2) will be affected by the choice of the compound (I). If compound (I) is diphenyl carbonate then the reactants are preferably heated to at least 90°C and more preferably about 100°C. The reaction is preferably carried out in the absence of catalyst. If compound (I) is dimethyl carbonate then the reactants are preferably heated to at least 130°C and more preferably about 140°C. The reaction is preferably carried out in the presence of a catalyst such as dibutyl tin dilaurate. The inventors have found that additional heating is often necessary to transform the reaction product of step (b1) or (b2) into a grease. Preferably the reaction products of step (b1) or (b2) are heated to at least 170°C and then cooled.

[0035] The base oil that is present in at least one of the reaction steps may be of mineral origin, synthetic origin, or a combination thereof. Base oils of mineral origin may be mineral oils, for example, those produced by solvent refining or hydroprocessing. Base oils of synthetic origin may typically comprise mixtures of C_{10}-C_{50} hydrocarbon polymers, for example, polymers of alphaolefins, ester type synthetic oils, ether type synthetic oils, and combinations thereof. Base

oils may also include Fischer-Tropsch derived highly paraffinic products.

[0036] Suitable examples of mineral base oils include paraffinic base oils and naphthenic base oils. Paraffinic base oils typically have a proportion of carbons in aromatic structure (Ca) in a range of from 1 to 10%, in naphthenic structure (Cn) in a range of from 20 to 30% and in paraffinic structure (Cp) in a range of from 60 to 70%. Naphthenic base oils typically have a proportion of carbons in aromatic structure (Ca) in a range of from 1 to 20%, in naphthenic structure (Cn) in a range of from 30 to 50% and in paraffinic structure (Cp) in a range of from 40 to 60%.

[0037] Suitable examples of base oils include medium viscosity mineral oils, high viscosity mineral oils, and combinations thereof. Medium viscosity mineral oils have a viscosity generally in a range of from 5 mm^2/s centistokes (cSt) at 100 °C to 15 mm^2/s (cSt) at 100 °C, preferably in a range of from 6 mm^2/s (cSt) at 100 °C to 12 mm^2/s (cSt) at 100 °C, and more preferably in a range of from 7 mm^2/s (cSt) at 100 °C to 12 mm^2/s (cSt) at 100 °C. High viscosity mineral oils have a viscosity generally in a range of from 15 mm^2/s (cSt) at 100 °C to 40 mm^2/s (cSt) at 100 °C and preferably in a range of from 15 mm^2/s (cSt) at 100 °C to 30 mm^2/s (cSt) at 100 °C.

[0038] Suitable examples of mineral oils that may conveniently be used include those sold by member companies of the Shell Group under the designations "HVI", "MVIN", or "HMVIP". Polyalphaolefins and base oils of the type prepared by the hydroisomerisation of wax, for example, those sold by member companies of the Shell Group under the designation "XHVI" (trade mark), may also be used.

[0039] At least one of the reaction steps is carried out in the presence of a base oil and preferably the final reaction step is carried out in the presence of a base oil. The urea grease that is the product of the process of the invention comprises a urea thickener and a base oil. Preferably the urea grease comprises a weight percent of urea based on the total weight of urea grease in a range of from 2 weight percent to 25 weight percent, more preferably in a range of from 3 weight percent to 20 weight percent, and most preferably in a range of from 5 weight percent to 20 weight percent.

[0040] The product of the process of the invention is a urea grease. Preferably the base grease that results from step (b1) or step (b2) is subjected to further finishing procedures such as homogenisation, filtration and deaeration.

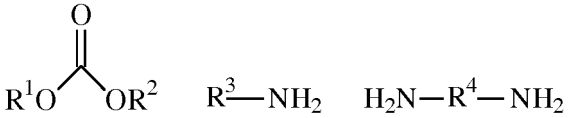
[0041] A urea grease prepared according to a process of the invention may comprise one or more additives, in amounts normally used in this field of application, to impart certain desirable characteristics to the urea grease including, for example, oxidation stability, tackiness, extreme pressure properties, corrosion inhibition, reduced friction and wear, and combinations thereof. The additives are preferably added to the base grease before the finishing procedures. Most preferably, the base grease is homogenised, then the additives are added, and then the grease is subjected to further homogenization.

[0042] Suitable additives include one or more extreme pressure/antiwear agents, for example zinc salts such as zinc dialkyl or diaryl dithiophosphates, borates, substituted thiadiazoles, polymeric nitrogen/phosphorus compounds made, for example, by reacting a dialkoxy amine with a substituted organic phosphate, amine phosphates, sulphurised sperm oils of natural or synthetic origin, sulphurised lard, sulphurised esters, sulphurised fatty acid esters, and similar sulphurised materials, organo-phosphates for example according to the formula $(OR)_3P=O$ where R is an alkyl, aryl or aralkyl group, and triphenyl phosphorothionate; one or more overbased metal-containing detergents, such as calcium or magnesium alkyl salicylates or alkylarylsulphonates; one or more ashless dispersant additives, such as reaction products of polyisobutenyl succinic anhydride and an amine or ester; one or more antioxidants, such as hindered phenols or amines, for example phenyl alpha naphthylamine, diphenylamine or alkylated diphenylamine; one or more antirust additives such as oxygenated hydrocarbons which have optionally been neutralised with calcium, calcium salts of alkylated benzene sulphonates and alkylated benzene petroleum sulphonates, and succinic acid derivatives, or friction-modifying additives; one or more viscosity-index improving agents; one or more pour point depressing additives; and one or more tackiness agents. Solid materials such as graphite, finely divided MoS_2, talc, metal powders, and various polymers such as polyethylene wax may also be added to impart special properties.

[0043] A urea grease prepared according to a process of the invention may comprise from 0.1 weight percent to 15 weight percent, preferably from 0.1 weight percent to 5 weight percent, more preferably from 0.1 weight percent to 2 weight percent, and even more preferably from 0.2 weight percent to 1 weight percent of one or more additives based on the total weight of urea grease.

[0044] The urea greases produced by the process of the invention are suitably used in typical applications for urea greases such as in constant-velocity joints, ball joints, wheel bearings, alternators, cooling fans, ball screws, linear guides of machine tools, sliding areas of construction equipment, and bearings and gears in steel equipment and various other industrial mechanical facilities.

[0045] In an alternative embodiment of the invention, a urea grease may be prepared by a process comprising one or more steps in which a compound of formula (I), a compound of formula (II) and a compound of formula (III) are reacted:



(I) (II) (III)

wherein R^1 and R^2 are chosen from hydrocarbyl having from 1 to 30 carbon atoms, or R^1 and R^2 are linked and form a hydrocarbylene group having from 1 to 30 carbon atoms, R^3 is chosen from hydrocarbyl comprising from 2 to 30 carbon atoms and R^4 is hydrocarbylene comprising from 2 to 30 carbon atoms;
and comprising a step wherein the resulting urea product is dispersed in a base oil. In this variant of the invention the urea is synthesised from compounds (I), (II) and (III) and then the urea powder is dispersed in a base oil to form a grease.

[0046] Reaction schemes showing proposed four proposed syntheses of urea greases are shown in Figures 1, 2,3 and 4.

[0047] Figure 1 shows a process wherein diphenyl-carbonate (2) is reacted with ethylenediamine (4) and octylamine (1) without solvent under nitrogen atmosphere. After the reaction is completed the excess phenol is removed in vacuum. The two intermediates (3,5) are then combined to the final tetraurea (7) by introducing the methylene diphenyl diamine (6) under the same conditions and in the presence of a base oil. The reaction product is heated to 170°C to form a tetraurea grease.

[0048] Figure 2 shows a process wherein octylamine (1) and ethylenediamine (4) are added to a ice-cooled solution of ethylenecarbonate (8) in water. The reaction is catalysed with $(Bu_2Sn(OMe)_2)$. After a short reaction time the solvent and excess amines are removed under vacuum and the products 9 and 10 are isolated. In a further linking reaction the products 9 and 10 and the methylene diphenyl diamine (6) are connected at 150°C catalysed by $(Bu_2Sn(OMe)_2)$ and the presence of a base oil. The resulting ethylene glycol is removed in vacuum. The reaction product is heated to 170°C to form a tetraurea grease.

[0049] Figure 3 shows a process wherein dimethylcarbonate (1) and 4,4'-methylenedianiline (2) are reacted at 80°C in the presence of potassium t-butoxide. Methanol will be removed as a byproduct. The diphenylcarbamate product (3) is reacted with octylamine (4) in the presence of a base oil and dibutyltin dilaureate at 100°C to provide a grease product which is a diurea in base oil. The reaction product is heated to 170°C to form a diurea grease.

[0050] Figure 4 shows a process wherein diphenylcarbonate (1) and 4,4'-methylenedianiline (2) are reacted at 100°C in the presence of diphenylphosphinic acid. Phenol will be removed as a byproduct. The diphenylcarbamate product (3) is reacted with octylamine (4) in the presence of a base oil at 100°C to provide a grease product which is a diurea in base oil. The reaction product is heated to 170°C to form a diurea grease.

Examples

[0051] The invention is further explained in detail below by means of examples and comparative examples, but the invention is in no way limited by these examples.

Example 1a: Step (a2) - Synthesis of Diphenylcarbamate

[0052] A mixture of diphenylcarbonate (2 equivalents), 4,4'-methylenedianiline, and diphenylphosphinic acid (5-10%) was reacted at 100°C overnight (the solids melted, and then solids were formed again).

[0053] The product was worked up by adding dimethyl ether, filtering and washing with dimethyl ether. A yield of 91-94% diphenylcarbamate was achieved.

Example 1b: Step (a2) - Synthesis of Diphenylcarbamate

[0054] A mixture of diphenylcarbonate (2 equivalents), 4,4'-methylenedianiline, and diphenylphosphinic acid (10%) was reacted at 100°C in toluene (1ml/g of diphenylcarbonate). The mixture was heated to reflux and after 14 hours, only 7% of starting material remained.

Example 1c: Step (b2) - Synthesis of Diurea in Base Oil

[0055] 5g of diphenylcarbamate in base oil (14.5g) was reacted with octylamine overnight at 110°C. The products were washed with 5 x 15ml of acetone. Additional base oil (14.5g) was added and the mixture was stirred for 10 minutes at 100°C and cooled to room temperature. No grease formed after cooling. The sample was heated to 100°C again and stirred at 1000rpm overnight. Still there was no formation of a grease. The material was then stirred at 170°C for 30

minutes and cooled, and a grease was formed. The properties of the grease were measured and are shown in Table 1.

Example 1d: Step (b2) - Synthesis of Diurea in Base Oil

[0056] 101g of diphenylcarbamate, prepared according to Example 1a, was heated in base oil (506g) and octylamine (60g) overnight at 96°C. The mixture was cooled and stirred with acetone (4x500ml), settled and decanted to remove phenol and by-products (according to NMR 95% pure). The material was dried using a rotary evaporator and heated to 170°C then cooled down to form a grease. The properties of the grease were measured and are shown in Table 1.

Example 2: One-Pot Two-Step Synthesis of Diurea in Base Oil

[0057] A mixture of diphenylcarbonate (150g), 4,4'-methylenedianiline (69g), and diphenylphosphinic acid (7.5g) was reacted at 90°C. The solids melted to a stirrable mixture. After a few hours it became solid again. The reaction was stirred at 90°C during the night (mechanical stirring).

[0058] The next morning the mixture had become solid. Base oil (198g) was added and the mixture was stirred for 1hr at 90°C. Additional base oil was added (303.3g). Then octylamine (90.5g) was added. The mixture started to become milky white/pink. The mixture was warmed up to 104°C for 6.30hrs. The mixture was suspended in acetone (11) and decanted. This was repeated several times until all the phenol was removed. The material was dried using a rotary evaporator, 130g of base oil was added and the mixture was heated to 170°C and cooled down to obtain a grease. The properties of the grease were measured and are shown in Table 1.

Example 3a: Step (a2) - Synthesis of Dimethylcarbamate

[0059] 4,4'-methylenedianiline was heated with potassium t-butoxide (4.4 eq) in dimethyl carbonate (neat) at 80°C for 0.5h to give dimethylcarbamate (89%) after filtration and washing with water.

Example 3b: Step (b2) - Synthesis of Diurea in Base Oil

[0060] Dimethylcarbamate (65g) prepared according to example 3a was reacted with octylamine and dibutyltin dilaureate (added over several days) in base oil at 140°C for 7 days to give the diurea product together with some monourea. 498g of a grease was isolated. The properties of the grease were measured and are shown in Table 1.

Example 3c: Step (b2) and Acetone Washing

[0061] A sample of grease from example 3b (40-50g) was washed with acetone and evaporated to give 31g with a purity of 97%. The properties of the grease were measured and are shown in Table 1.

Example 4: Synthesis of Diurea and Subsequent Dispersal in Base Oil

[0062] A mixture of diphenylcarbonate (10g), 4,4'-methylenedianiline (4.6g), and diphenylphosphinic acid (0.5g) was reacted at 100 °C overnight. The mixture was cooled to room temperature after which it solidified. The reaction was worked up by washing with diethyl ether (3 x 25ml). The white material was filtered off and dried. The dicarbamate was reacted with octylamine for 2 hrs at 105 °C. The product was washed with dichloromethane and was then purified by crystallization from dimethylformamide.

[0063] 5g of the urea product was suspended in base oil (20g). The mixture was heated to 170°C for 30 min and was then cooled to give a grease.

Grease Properties

[0064] The unworked penetration and worked penetration of the greases were measured according to ASTM D217. The Delta penetration (difference between unworked and worked penetration) was calculated. The dropping point was measured according to IP 396. The values are shown in Table 1:

Table 1

	Unworked Penetration	Worked Penetration	Delta Penetration	Dropping Point
Example 1c	260	264	4	295

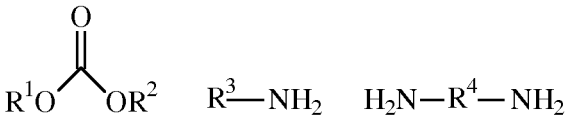
(continued)

	Unworked Penetration	Worked Penetration	Delta Penetration	Dropping Point
Example 1d (sample 1)	215	253	38	>300
Example 1d (sample 2)	207	249	42	>300
Example 2 (sample 1)	219	247	28	>300
Example 2 (sample 2)	227	254	27	>300
Example 3b (sample 1)	238	336	98	235
Example 3b (sample 2)	215	333	118	232
Example 3c	290	343	53	242
Example 4	332	339	7	>300

[0065] Desirably the delta penetration is as low as possible, and low values were achieved by some of the greases. The worked penetration values range from 247 to 340 which will give greases that would typically fall into the category of NLGI grade 1, 2 or 3. The dropping point is desirably as high as possible and several of the greases gave dropping points in excess of 300.

Claims

1. A process for preparing a urea grease comprising one or more steps in which a compound of formula (I), a compound of formula (II) and a compound of formula (III) are reacted:



(I) (II) (III)

wherein R^1 and R^2 are chosen from hydrocarbyl having from 1 to 30 carbon atoms, or R^1 and R^2 are linked and form a hydrocarbylene group having from 1 to 30 carbon atoms, R^3 is chosen from hydrocarbyl comprising from 2 to 30 carbon atoms and R^4 is hydrocarbylene comprising from 2 to 30 carbon atoms; wherein at least one of the reaction steps is carried out in the presence of a base oil.

2. A process for preparing a urea grease according to claim 1, comprising steps of:

(a1) reacting a compound of formula (I) with a compound of formula (II):



(I) (II)

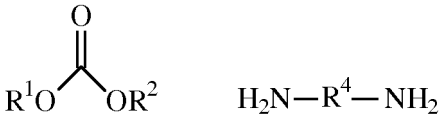
and
(b1) reacting the product of step (a1) with a compound of formula (III):

$$\mathbf{H_2N\text{-}R^4\text{-}\ NH_2} \qquad \text{(III)}$$

wherein step (b1) is carried out in the presence of a base oil.

3. A process for preparing a urea grease according to claim 1 comprising steps of:

(a2) reacting a compound of formula (I) with a compound of formula (III):



(I) (III)

and
(b2) reacting the product of step (a2) with a compound of formula (II):

$$R^3\text{-}NH_2 \qquad (II)$$

wherein step (b2) is carried out in the presence of a base oil.

4. A process according to claim 2 or claim 3, wherein a catalyst is present in step (a1), step (a2), step (b1) and/or step (b2).

5. A process according to claim 2, 3 or 4 wherein the reaction products of step (b1) or (b2) are heated to at least 170°C and then cooled.

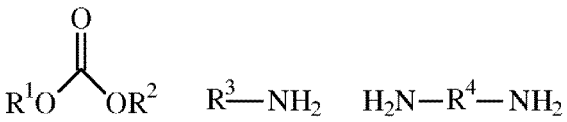
6. A process according to any preceding claim, wherein the urea grease comprises a weight percent of urea based on the total weight of urea grease in a range of from 2 weight percent to 25 weight percent.

7. A process according to any preceding claim, wherein the grease is subjected to one or more finishing procedures chosen from homogenisation, filtration and deaeration.

8. A process according to any preceding claim, wherein one or more additives are added to the grease.

Patentansprüche

1. Verfahren zur Herstellung eines Harnstoff-Schmierfetts mit einem oder mehreren Schritten, bei dem man eine Verbindung der Formel (I), eine Verbindung der Formel (II) und eine Verbindung der Formel (III) umsetzt:

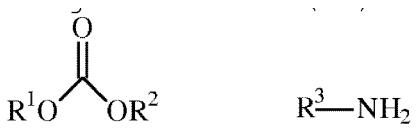


(I) (II) (III)

wobei R^1 und R^2 aus Hydrocarbyl mit 1 bis 30 Kohlenstoffatomen ausgewählt sind oder R^1 und R^2 miteinander verknüpft sind und eine Hydrocarbylengruppe mit 1 bis 30 Kohlenstoffatomen bilden, R^3 aus Hydrocarbyl mit 2 bis 30 Kohlenstoffatomen ausgewählt ist und R^4 für Hydrocarbylen mit 2 bis 30 Kohlenstoffatomen steht;
wobei mindestens einer der Reaktionsschritte in Gegenwart eines Grundöls durchgeführt wird.

2. Verfahren zur Herstellung eines Harnstoff-Schmierfetts nach Anspruch 1, das folgende Schritte umfasst:

(a1) Umsetzen einer Verbindung der Formel (I) mit einer Verbindung der Formel (II):



(I) (II)

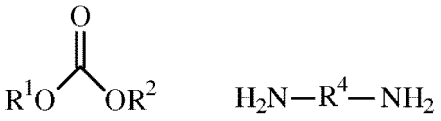
und
(b1) Umsetzen des Produkts aus Schritt (a1) mit einer Verbindung der Formel (III):

$$\mathbf{H_2N\text{-}R^4\text{-}NH_2} \qquad \text{(III)}$$

wobei Schritt (b1) in Gegenwart eines Grundöls durchgeführt wird.

3. Verfahren zur Herstellung eines Harnstoff-Schmierfetts nach Anspruch 1, das folgende Schritte umfasst:

(a2) Umsetzen einer Verbindung der Formel (I) mit einer Verbindung der Formel (III):



(I) (III)

und
(b2) Umsetzen des Produkts aus Schritt (a2) mit einer Verbindung der Formel (II):

$$\mathbf{R^3\text{-}NH_2} \qquad \text{(II)}$$

wobei Schritt (b2) in Gegenwart eines Grundöls durchgeführt wird.

4. Verfahren nach Anspruch 2 oder 3, bei dem in Schritt (a1), Schritt (a2), Schritt (b1) und/oder Schritt (b2) ein Katalysator vorliegt.

5. Verfahren nach Anspruch 2, 3 oder 4, bei dem die Reaktionsprodukte von Schritt (b1) bzw. (b2) auf mindestens 170°C erhitzt und dann abgekühlt werden.

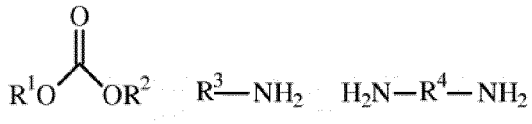
6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Harnstoff-Schmierfett einen Gewichtsprozentanteil an Harnstoff, bezogen auf das Gesamtgewicht an Harnstoff-Schmierfett, im Bereich von 2 Gewichtsprozent bis 25 Gewichtsprozent umfasst.

7. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Schmierfett einer oder mehreren Fertigbearbeitungsprozeduren, ausgewählt aus Homogenisierung, Filtration und Entlüftung, unterworfen wird.

8. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Schmierfett mit einem oder mehreren Additiven versetzt wird.

Revendications

1. Procédé de préparation d'une graisse à base d'urée comprenant une ou plusieurs étapes dans lesquelles on fait réagir un composé de formule (I), un composé de formule (II) et un composé de formule (III) :



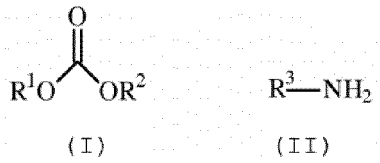
(I) (II) (III)

dans lesquelles R^1 et R^2 sont choisis parmi les groupes hydrocarbyle ayant de 1 à 30 atomes de carbone, ou bien R^1 et R^2 sont liés et forment un groupe hydrocarbylène ayant de 1 à 30 atomes de carbone, R^3 est choisi parmi les groupes hydrocarbyle comprenant de 2 à 30 atomes de carbone et R^4 est un groupe hydrocarbylène comprenant de 2 à 30 atomes de carbone ;

au moins une des étapes réactionnelles étant réalisée en présence d'une huile de base.

2. Procédé de préparation d'une graisse à base d'urée selon la revendication 1, comprenant les étapes consistant à :

(a1) faire réagir un composé de formule (I) avec un composé de formule (II)



(I) (II)

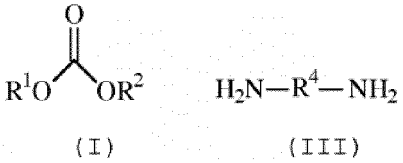
et
(b1) faire réagir le produit de l'étape (a1) avec un composé de formule (III) :

$$H_2N\text{-}R^4\text{-}NH_2 \qquad \text{(III)}$$

dans lequel l'étape (b1) est réalisée en présence d'une huile de base.

3. Procédé de préparation d'une graisse à base d'urée selon la revendication 1 comprenant les étapes consistant à :

(a2) faire réagir un composé de formule (I) avec un composé de formule (III)



(I) (III)

et
(b2) faire réagir le produit de l'étape (a2) avec un composé de formule (II) :

$$R^3\text{-}NH_2 \qquad \text{(II)}$$

dans lequel l'étape (b2) est réalisée en présence d'une huile de base.

4. Procédé selon la revendication 2 ou la revendication 3, dans lequel un catalyseur est présent à l'étape (a1), l'étape (a2), l'étape (b1) et/ou l'étape (b2).

5. Procédé selon la revendication 2, 3 ou 4 dans lequel les produits réactionnels de l'étape (b1) ou (b2) sont chauffés jusqu'à au moins 170 °C puis refroidis.

6. Procédé selon une quelconque revendication précédente, dans lequel la graisse à base d'urée comprend un pourcentage pondéral d'urée rapporté au poids total de la graisse à base d'urée dans une gamme de 2 pour cent en poids à 25 pour cent en poids.

7. Procédé selon une quelconque revendication précédente, dans lequel la graisse est soumise à une ou plusieurs procédures de finition choisies parmi l'homogénéisation, la filtration et la désaération.

8. Procédé selon une quelconque revendication précédente, dans lequel un ou plusieurs additifs sont ajoutés à la graisse.

Figure 1

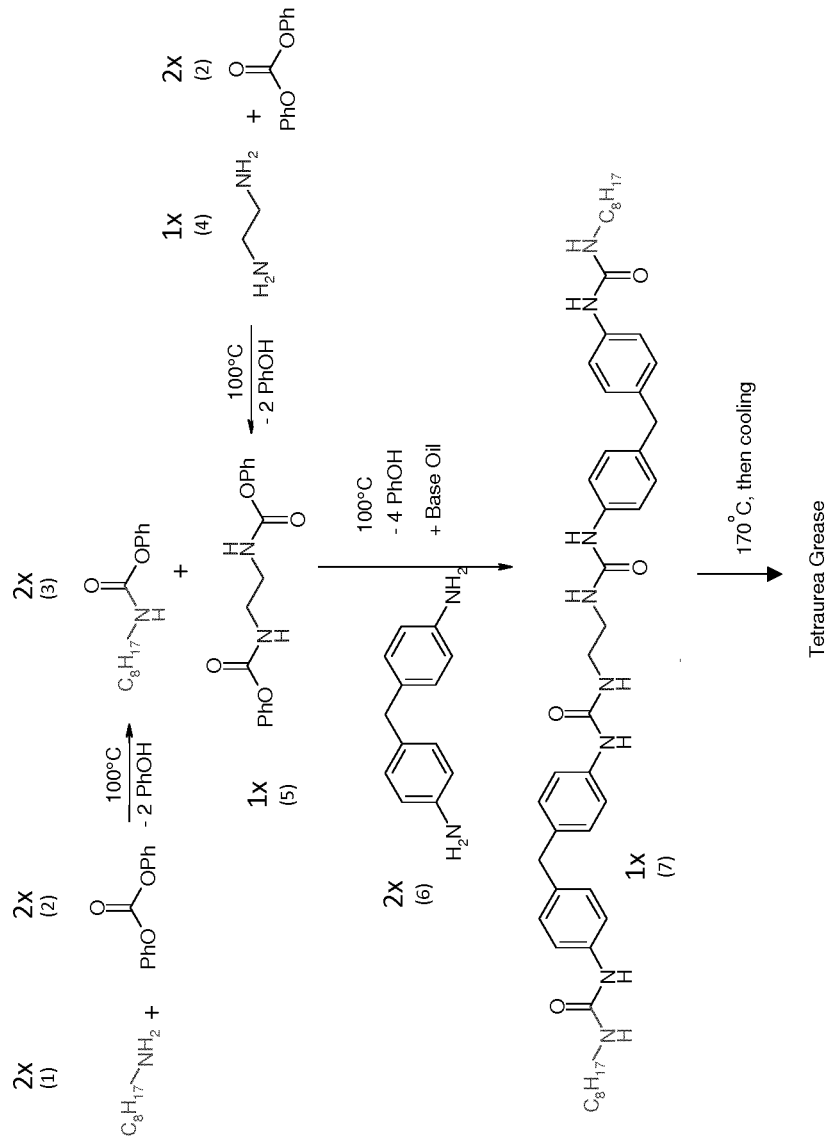

2x (1)
2x (2)
2x (3)
100°C
- 2 PhOH
1x (5)
1x (4)
2x (2)
100°C
- 2 PhOH
100°C
- 4 PhOH
+ Base Oil
2x (6)
1x (7)
170 °C, then cooling
Tetraurea Grease

Figure 2

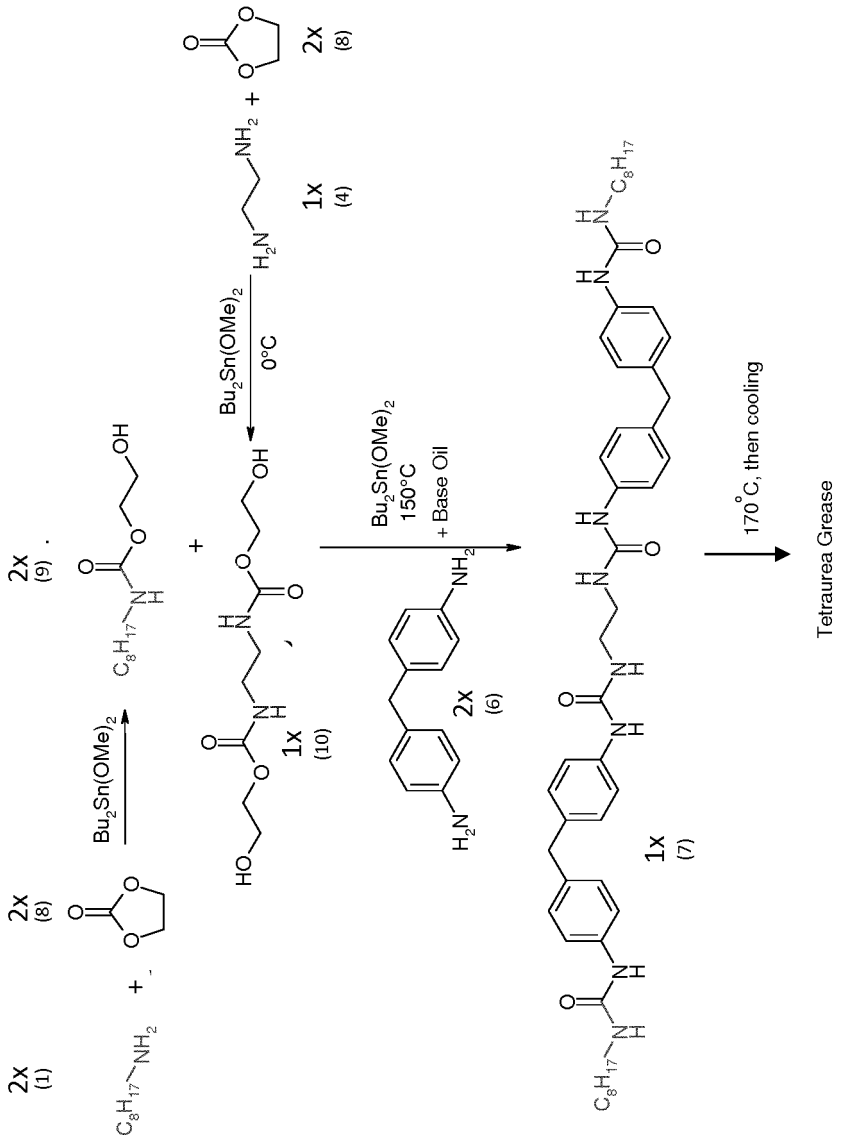

2x (1)
2x (8)
Bu2Sn(OMe)2
2x (9)
Bu2Sn(OMe)2
0°C
1x (4)
2x (8)
1x (10)
Bu2Sn(OMe)2
150°C
+ Base Oil
2x (6)
1x (7)
170°C, then cooling
Tetraurea Grease

Figure 3

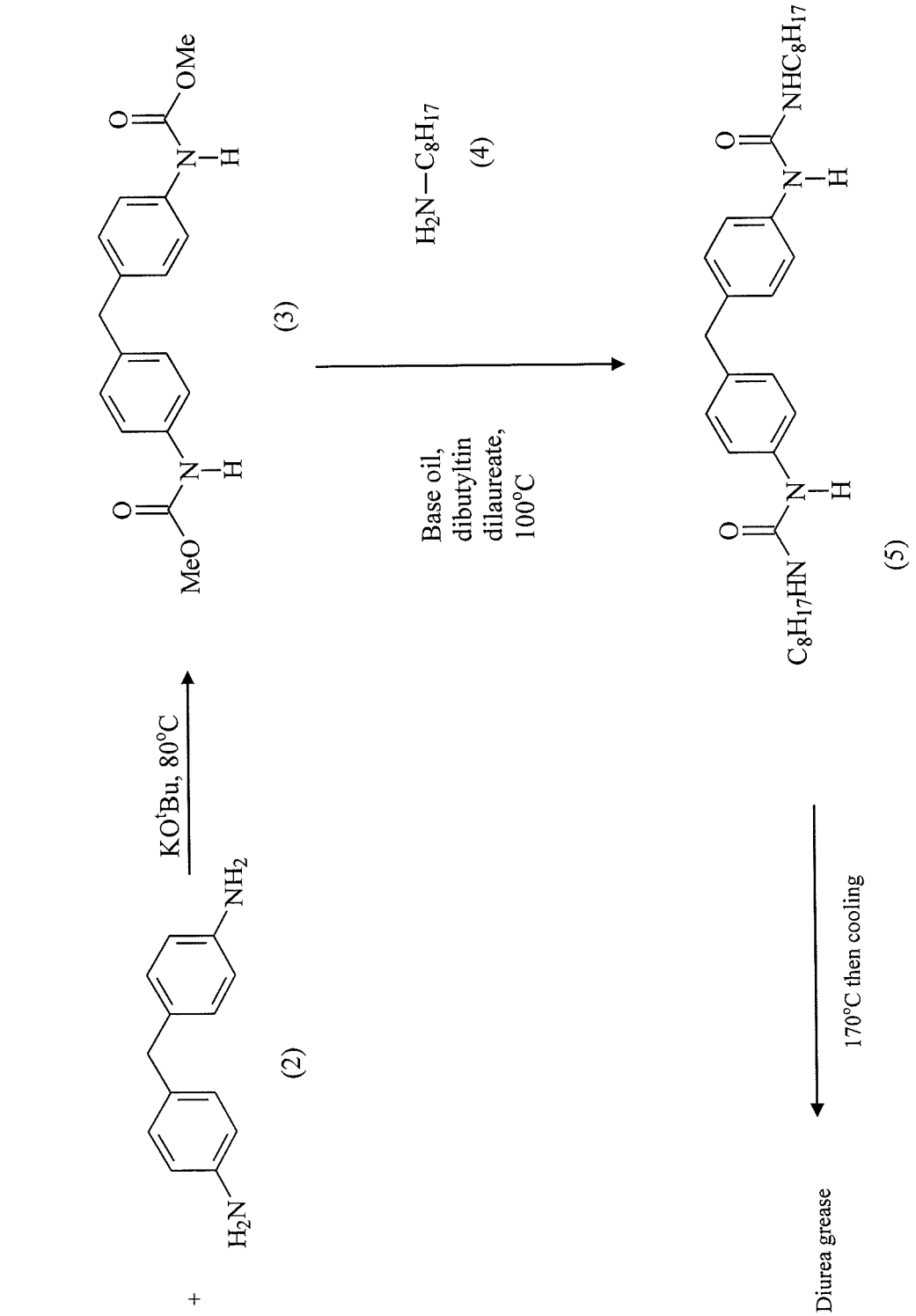
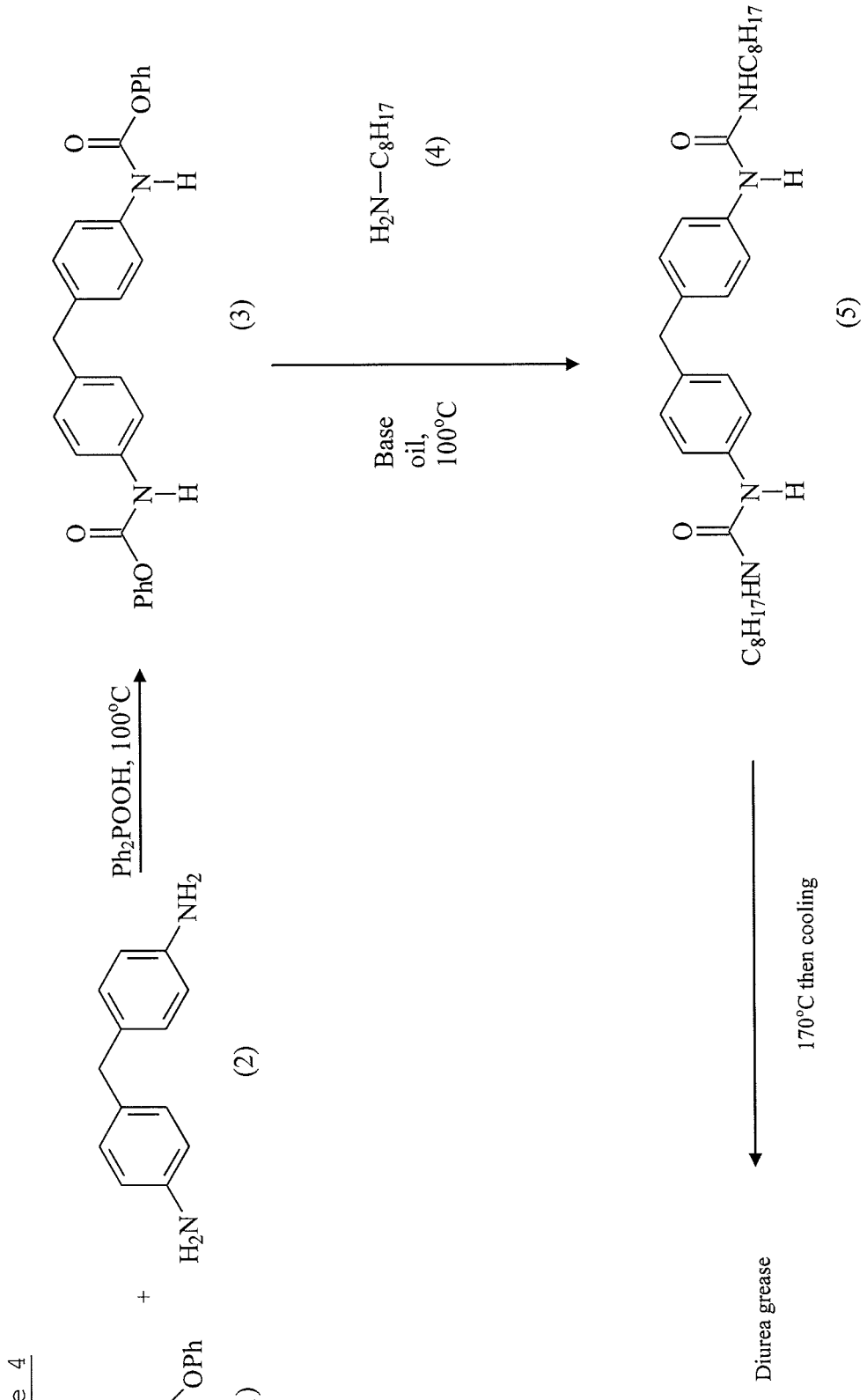

MeO
OMe
O
(1)
+
H_2N
NH_2
(2)
KO^tBu, 80°C
MeO
OMe
O
N
H
O
N
H
(3)
$H_2N-C_8H_{17}$
(4)
Base oil,
dibutyltin
dilaureate,
100°C
$C_8H_{17}HN$
NHC_8H_{17}
O
N
H
O
N
H
(5)
Diurea grease
170°C then cooling

Figure 4


Ph2POOH, 100°C
Base
oil,
100°C
H2N—C8H17
(4)
Diurea grease
170°C then cooling
(1)
(2)
(3)
(5)