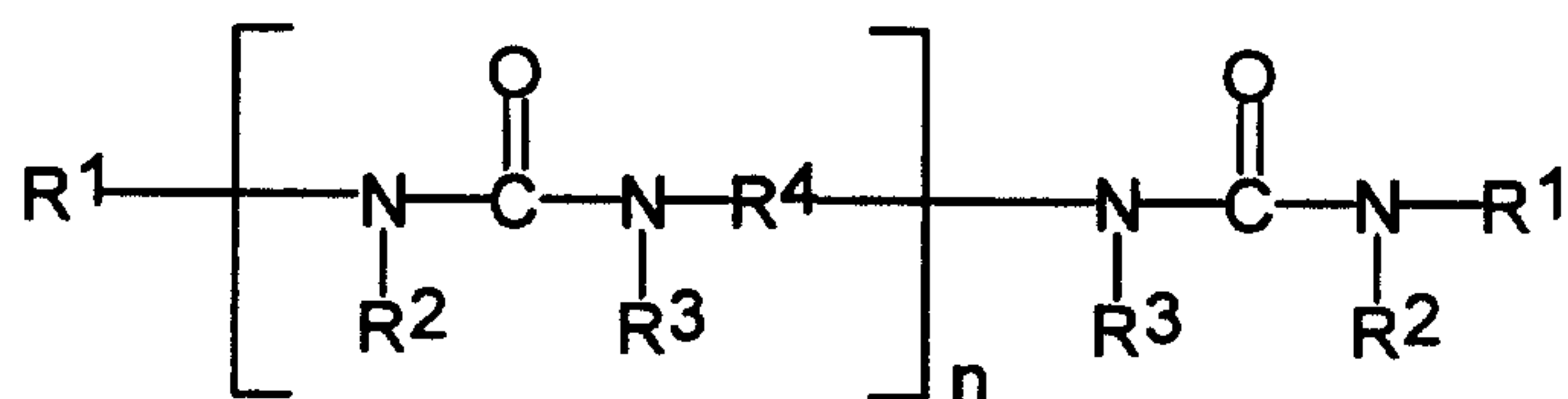




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(51) Int.Cl.⁷ B01D 19/04
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(54) **ADDITIFS ANTIMOUSSE POUR MILIEUX AQUEUX**
(54) **DEFOAMERS FOR AQUEOUS MEDIA**



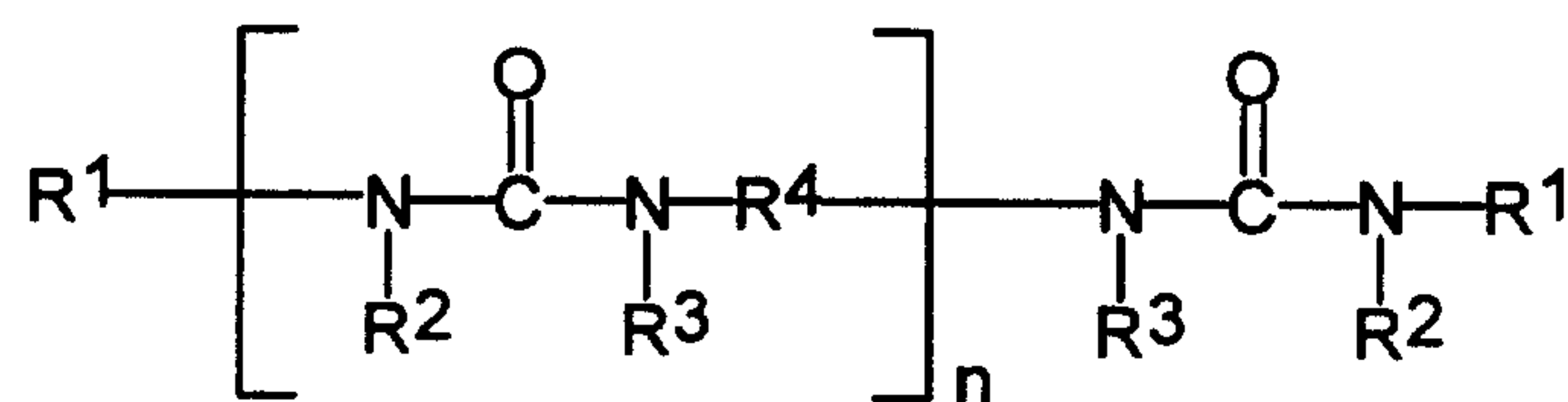
Formula I

(57) The invention relates to compositions for defoaming aqueous media, comprising as defoamers urea derivatives of the formula I (see formula I) where R¹ - is a hydrocarbon radical having 4 to 30 carbon atoms or a hydrocarbon radical having 4 to 24 carbon atoms and one nitrogen atom or a hydrocarbon radical having 4 to 30 carbon atoms and one carbonyl group, R² - is a hydrogen atom or a hydrocarbon radical having 1 to 24 carbon atoms, R³ - is a hydrogen atom or a hydrocarbon radical having 1 to 24 carbon atoms, R⁴ - is an organic radical having 2 to 30 carbon atoms and n - is from 0 to 5, in the form of solid particles, which are obtained by crystallization from a clear homogeneous melt dispersed in a carrier medium.



Abstract:

The invention relates to compositions for defoaming aqueous media, comprising as defoamers urea derivatives of the formula I



Formula I

where

R^1 - is a hydrocarbon radical having 4 to 30 carbon atoms or a hydrocarbon radical having 4 to 24 carbon atoms and one nitrogen atom or a hydrocarbon radical having 4 to 30 carbon atoms and one carbonyl group,

R^2 - is a hydrogen atom or a hydrocarbon radical having 1 to 24 carbon atoms,

R^3 - is a hydrogen atom or a hydrocarbon radical having 1 to 24 carbon atoms,

R^4 - is an organic radical having 2 to 30 carbon atoms and

n - is from 0 to 5,

in the form of solid particles, which are obtained by crystallization from a clear homogeneous melt dispersed in a carrier medium.

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G o l d s c h m i d t AG, Essen

Defoamers for aqueous media

The invention relates to defoamers for aqueous media, comprising as hydrophobic solids critically influencing the defoaming certain urea derivatives which acquire
5 the properties requisite for their particular activity as defoamers by crystallization from a clear melt dispersed homogeneously in the carrier medium.

In many industrial processes, and especially when
10 working in aqueous media, it is necessary to suppress, or prevent entirely, the unwanted formation of foam during the preparation or processing operations. This can be achieved by adding what are known as antifoams or defoamers, which even when used at very low
15 concentrations upward of about 0.001% by weight are able to prevent or destroy unwanted foams. Examples of such prior art defoamers are silicone oils, mineral oils, hydrophobic polyoxyalkylenes, long-chain alcohols, and also mixtures of these products with one
20 another and emulsions thereof. To reinforce the activity, it is common to add hydrophobic solids in amounts of from 0.1 to 10% by weight, which specifically promote dewetting processes on foam lamellae and therefore very actively assist in foam
25 collapse. Suitable hydrophobic solids are appropriate silicas, metal stearates, polyolefins, and waxes.

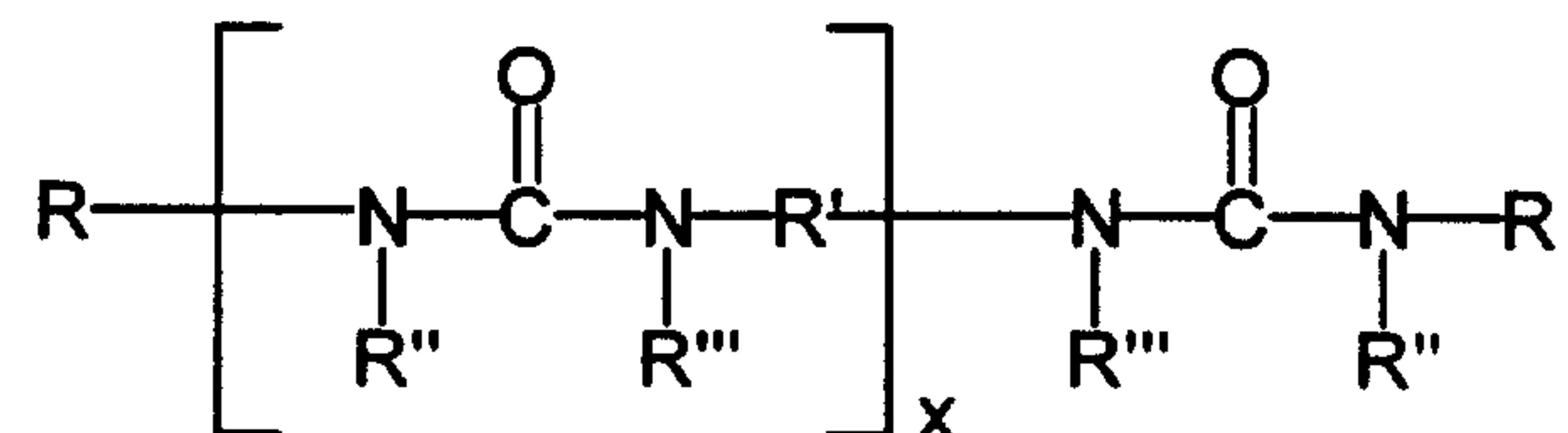
The use of urea and urea derivatives as additives to defoamer formulations is also known per se.

30 EP-A-0 115 585 describes ureas which are prepared in situ in an organic carrier medium at relatively low temperatures and which have defoaming properties for aqueous media. They are obtained by combining
35 preferably equivalent amounts of isocyanates and amines

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in the organic carrier medium in question at temperatures below the melting point of the reaction product.

5 This gives urea derivatives of the general formula



- R = alkyl C₄-C₃₀
 10 R' = single chemical bond; alkylene C₂-C₁₂, mono-
 to dinuclear aryl radicals which have
 additional alkyl groups C₁-C₉ on the aryl
 radical; cycloalkylene
 R'' = H, alkyl C₁-C₂₄
 15 R''' = H, -CH₃
 x = 0-5.

It is expressly emphasized that when heated beyond
 their melting point, or when prepared at above their
 20 melting point, the ureas possess only an insignificant
 defoaming action. This is correlated with the formation
 of monodisperse or micellar structures during the in
 situ formation of the urea derivatives.

25 A disadvantage here is that, as a result of the in situ
 formation of the urea derivatives in accordance with
 the procedure described in EP-A-0 115 585, it is
 necessary to resort to carrier media which cannot react
 with amines and in particular not with isocyanates
 30 either. For example, the hydroxy-functional
 polyoxypropylenes well-known to the skilled worker as
 carrier media for defoamers, and hydroxy-functional
 polyoxyalkylene-polysiloxanes as well, are rejected on
 account of their hydroxyl functionality. It is true
 35 that, in principle, the reaction of an amine with an
 isocyanate is clearly preferred over the reaction of a

- 3 -

hydroxy compound with an isocyanate, in respect of the reaction rate; however, and especially in the presence of the amines, which are known to be catalysts for the nucleophilic addition of hydroxy compounds onto isocyanates, hydroxy compounds react as well to uncontrollable extents and so result in urea derivatives which it is difficult, if possible at all, to crystallize. This would of course directly affect the activity of the resulting urea derivatives and would result at least in results that were difficult if not impossible to reproduce in the context of their use as defoamers.

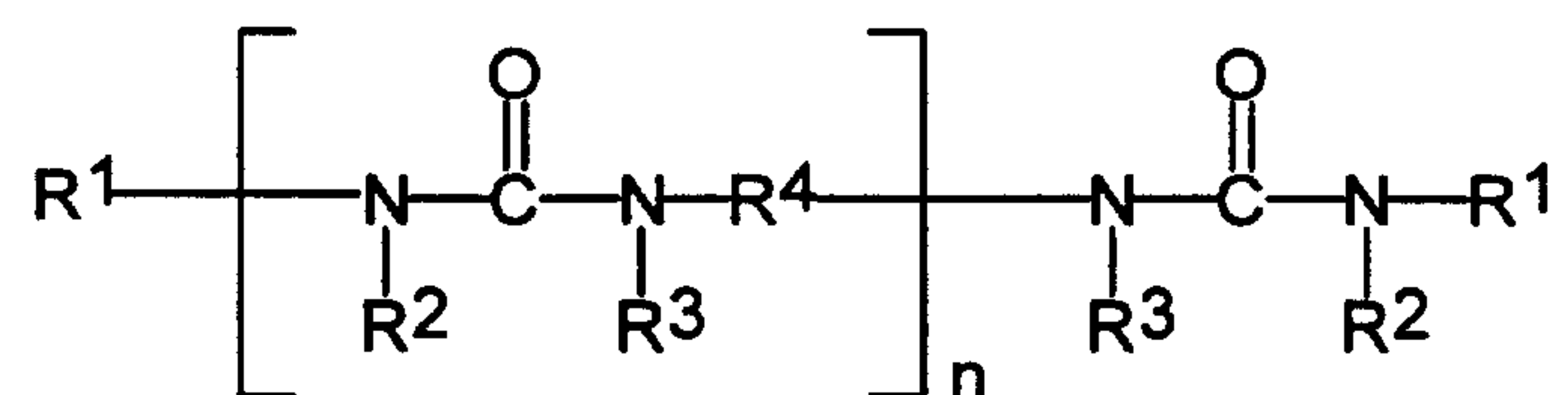
It has surprisingly now been found that, for the preparation of defoamer formulations containing urea derivatives as hydrophobic solids, the above-described in situ preparation of such urea derivatives below their melting point is neither necessary nor advantageous and that, instead, by means of controlled melting and recrystallization processes, it is possible to prepare defoamer formulations having improved properties and which, indeed, through the methodical variation of melting and recrystallization conditions, permit custom-tailored property profiles. By preparing the urea derivatives separately it is also possible, if required, to use exclusively carrier media which on account of their potential reactivity with respect to amines and/or isocyanates, because of the side reactions described above, are not amenable to precipitative crystallization in the manner described in EP-A-0 115 585. These include, for example, hydrophobic polyoxyalkylenes and organomodified siloxanes, which may also contain hydroxy functions.

This procedure is specifically successful even with urea derivatives which are explicitly described in EP-A-0 115 585 and which therefore, in accordance with the prior art, in the case of the process described in this patent, should no longer show any extraordinary

- 4 -

activity in defoamer formulations. Such urea derivatives are easy to prepare from the corresponding isocyanates and amines.

- 5 The invention therefore provides compositions for defoaming aqueous media, comprising as defoamers urea derivatives of the formula I



Formula I

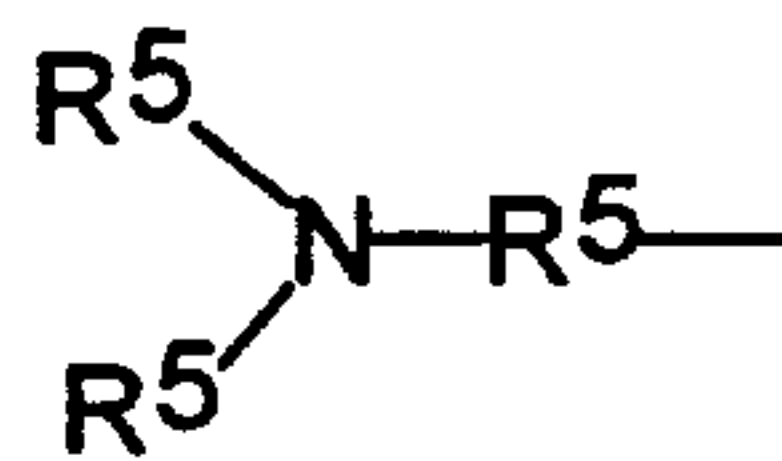
where

- 15 R^1 - is a hydrocarbon radical having 4 to 30 carbon atoms or a hydrocarbon radical having 4 to 24 carbon atoms and one nitrogen atom or a hydrocarbon radical having 4 to 30 carbon atoms and one carbonyl group,
 R^2 - is a hydrogen atom or a hydrocarbon radical having 1 to 24 carbon atoms,
 R^3 - is a hydrogen atom or a hydrocarbon radical
 20 having 1 to 24 carbon atoms,
 R^4 - is an organic radical having 2 to 30 carbon atoms, and
 n - is from 0 to 5, in the form of solid particles, which are obtained by crystallization from a clear
 25 homogeneous melt dispersed in a carrier medium.

Preferred compositions are those in which R^1 is a hydrocarbon radical having 4 to 24 carbon atoms, R^2 is a hydrogen atom, R^3 is a hydrogen atom, and R^4 is a
 30 hydrocarbon radical having 2 to 24 carbon atoms.

Preference is further given to those compositions of the invention in which R^1 is the organic radical

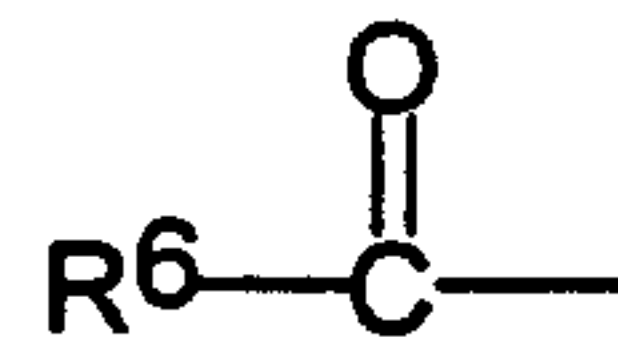
- 5 -



Formula II

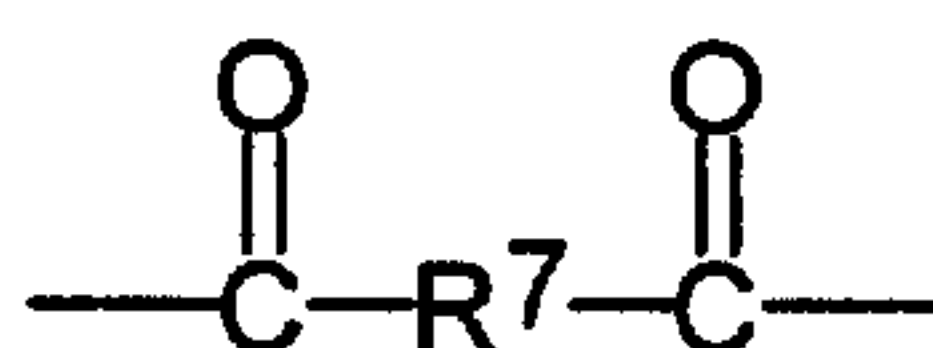
where R^5 is a hydrocarbon radical having 1 to 18 carbon atoms, R^2 and R^3 are a hydrogen atom, and R^4 is a hydrocarbon radical having 2 to 24 carbon atoms.

In addition, those compositions of the invention comprising as defoamers urea derivatives in which R^1 is the organic radical



Formula III

where R^6 is an organic radical having 2 to 30 carbon atoms, R^2 and R^3 are a hydrogen atom, and R^4 is a hydrocarbon radical having 2 to 24 carbon atoms, and compositions comprising as defoamers urea derivatives in which R^1 is a hydrocarbon radical having 2 to 24 carbon atoms, R^2 and R^3 are a hydrogen atom, and R^4 is the organic radical



Formula IV

where R^7 is a hydrocarbon radical having 2 to 20 carbon atoms, are preferred compositions according to the present invention.

For the present invention, therefore, it is completely irrelevant whether the urea derivatives of the invention are prepared separately and introduced as solids or are generated in the form of a precipitative crystallization in a liquid phase. What are critical at

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this point, in contrast, are the melting and recrystallization processes, which for the easy-to-prepare urea derivatives described herein result in surprising properties as hydrophobic solids in defoamers.

To this end, the recrystallization of the melted urea derivatives must take place from a clear melt dispersed homogeneously in the carrier medium, in order to reach optimum activity. This is easily possible by varying the main parameters, such as the chemical nature of the carrier oil, the urea derivative, and the temperature.

If the urea derivatives are merely melted in the carrier medium to form a nonhomogenous mixture - that is, not a clear mixture - the process of the invention cannot be used to prepare defoamers having sufficient activity.

The practical implementation of the above-described melting and recrystallization processes can be carried out by various methods. For example, the crystallization of the urea derivative melted in a carrier medium A can be influenced within a wide range, depending on the choice of the temperature gradients and the nature and extent of the shear energy employed, by addition of or addition to a carrier medium B of defined temperature. In this context, carrier media A and B can be identical or different.

Likewise, the melts of the urea derivatives can also be induced to crystallize in a particular way by measures ranging from simply leaving them to stand at room temperature through to the supply of external cooling by means of coolants. Here again, the chosen circumstances define the crystallization form of the urea derivatives and thus the activity of the resultant defoamer formulations. For instance, the recrystallization of the melted urea derivatives can

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also be carried out with advantage in the presence of additional solids, which can serve as crystallization nuclei, in order to obtain particular desired crystal morphologies.

5

In order to obtain urea derivatives which are as effective as possible in terms of the present invention, it is important to form particularly small, spherical urea crystals. This can be specifically
10 influenced by varying, for example, the concentration of the urea derivatives in the melt. The smaller the chosen concentration of the urea derivatives in the melt, the smaller the crystals that can be produced. Furthermore, the formation of small urea derivative
15 crystals is favored by a large, rapidly traversed temperature gradient, when, for example, a hot melt is shock-cooled by pouring it into a much colder carrier medium. High stirring outputs with stirrers which ensure effective, thorough mixing prevent the
20 development at this point of undesirably large, persistent concentration gradients, which in turn lead to relatively large crystals and/or agglomerates thereof. It is, however, also possible with advantage initially to establish, at least partially, conditions
25 which ought to promote the formation of relatively small crystals and then to follow these by conditions which promote large crystals. For example, a melt can be cooled rapidly at first and then slowly thereafter. In this way it is ensured that there are numerous
30 crystallization nuclei, formed suddenly, on which, subsequently and more slowly, regularly formed crystals grow.

Suitable carrier media include not only organic or
35 mineral oils but also siloxanes or organomodified siloxanes.

Defoamers of this kind can also be converted into aqueous emulsions by adding emulsifiers.

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The defoamers of the invention can be used, for example, to defoam cooling lubricants, polymer dispersions, coating materials, and printing inks.

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Preparation Examples:

Example 1

5 475 g of a naphthene-base mineral oil (40 mPas/25°C)
are charged at room temperature to a vessel having a
stirrer apparatus, 14.36 g of benzylamine are added,
and the mixture is stirred for 5 minutes. Following the
10 addition of 10.64 g of hexamethylene diisocyanate with
stirring, the sudden formation of a colorless
precipitate is observed. The subsequent reaction period
is 60 minutes.

Example 2

15 475 g of a polyethersiloxane (400 mPas/25°C; refractive
index $n = 1.440/25^\circ\text{C}$; insoluble in water) are charged
at room temperature to a vessel having a stirrer
apparatus, 14.36 g of benzylamine are added, and the
20 mixture is stirred for 5 minutes. Following the
addition of 10.64 g of hexamethylene diisocyanate with
stirring, the sudden formation of a colorless
precipitate is observed. The subsequent reaction period
is 60 minutes.

25

Example 3

475 g of a naphthene-base mineral oil (40 mPas/25°C)
are charged at room temperature to a vessel having a
30 stirrer apparatus, 2.78 g of diaminopropane are added,
and the mixture is stirred for 5 minutes. Following the
addition of 22.22 g of octadecyl isocyanate with
stirring, the sudden formation of a colorless
precipitate is observed. The subsequent reaction period
35 is 60 minutes.

- 10 -

Example 4

475 g of a polyethersiloxane (400 mPas/25°C; refractive index $n = 1.440/25^\circ\text{C}$; insoluble in water) are charged at room temperature to a vessel having a stirrer apparatus, 2.78 g of diaminopropane are added, and the mixture is stirred for 5 minutes. Following the addition of 22.22 g of octadecyl isocyanate with stirring, the sudden formation of a colorless precipitate is observed. The subsequent reaction period is 60 minutes.

Example 5 (inventive)

250 g of the mixture prepared in Example 1 are heated to 170°C, forming a clear, homogeneous mixture. This hot mixture is then introduced into 250 g of cold, naphthene-base mineral oil (40 mPas/25°C) and stirred up with it. Instantaneously, the formation of a finely dispersed, colorless precipitate and a sudden increase in the viscosity are observed.

Example 6 (inventive)

250 g of the mixture prepared in Example 2 are heated to 170°C, forming a clear, homogeneous mixture. This hot mixture is then introduced into 250 g of cold polyethersiloxane (400 mPas/25°C; refractive index $n = 1.440/25^\circ\text{C}$; insoluble in water) and stirred up with it. Instantaneously, the formation of a finely dispersed, colorless precipitate and a sudden increase in the viscosity are observed.

Example 7 (inventive)

250 g of the mixture prepared in Example 3 are heated to 170°C, forming a clear, homogeneous mixture. This hot mixture is then introduced into 250 g of cold, naphthene-base mineral oil (40 mPas/25°C) and stirred

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up with it. Instantaneously, the formation of a finely dispersed, colorless precipitate and a sudden increase in the viscosity are observed.

5 Example 8 (inventive)

250 g of the mixture prepared in Example 4 are heated to 170°C, forming a clear, homogeneous mixture. This hot mixture is then introduced into 250 g of cold polyethersiloxane (400 mPas/25°C; refractive index $n = 1.440/25^\circ\text{C}$; insoluble in water) and stirred up with it. Instantaneously, the formation of a finely dispersed, colorless precipitate and a sudden increase in the viscosity are observed.

15

Example 9 (inventive)

225 g of naphthene-base mineral oil (40 mPas/25°C) are mixed with 25 g of N',N''-propane-1,3-diylbis(N'-octadecylurea) and the mixture is heated to 170°C, forming a clear, homogeneous mixture. This hot mixture is then introduced into 250 g of cold, naphthene-base mineral oil (40 mPas/25°C) and stirred up with it. Instantaneously, the formation of a finely dispersed, colorless precipitate and a sudden increase in the viscosity are observed.

25

Example 10 (inventive)

250 g of the mixture prepared in Example 1 are heated to 170°C, forming a clear, homogeneous mixture. This hot mixture is then introduced into a mixture of 225 g of cold, naphthene-base mineral oil (40 mPas/25°C) and 25 g of sorbitan trioleate-20 EO and stirred up with it. Instantaneously, the formation of a finely dispersed, colorless precipitate and a sudden increase in the viscosity are observed.

30
35

- 12 -

Example 11 (inventive)

250 g of the mixture prepared in Example 2 are heated to 170°C, forming a clear, homogeneous mixture. This hot mixture is then introduced into a mixture of 225 g of cold polyethersiloxane (400 mPas/25°C; refractive index $n = 1.440/25^{\circ}\text{C}$; insoluble in water) and 25 g of sorbitan trioleate-20 EO and stirred up with it. Instantaneously, the formation of a finely dispersed, colorless precipitate and a sudden increase in the viscosity are observed.

Example 12 (not inventive)

250 g of the mixture prepared in Example 1 are stirred up with 250 g of naphthene-base mineral oil (40 mPas/25°C).

Example 13 (not inventive)

250 g of the mixture prepared in Example 2 are stirred up with 250 g of polyethersiloxane (400 mPas/25°C; refractive index $n = 1.440/25^{\circ}\text{C}$; insoluble in water).

Example 14 (not inventive)

250 g of the mixture prepared in Example 3 are stirred up with 250 g of naphthene-base mineral oil (40 mPas/25°C).

Example 15 (not inventive)

250 g of the mixture prepared in Example 4 are stirred up with 250 g of polyethersiloxane (400 mPas/25°C; refractive index $n = 1.440/25^{\circ}\text{C}$; insoluble in water).

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Example 16 (not inventive)

250 g of the mixture prepared in Example 1 are stirred up with a mixture of 225 g of naphthene-base mineral oil (40 mPas/25°C) and 25 g of sorbitan trioleate-20 EO.

Example 17 (not inventive)

250 g of the mixture prepared in Example 2 are stirred up with 225 g of polyethersiloxane (400 mPas/25°C; refractive index $n = 1.440/25^{\circ}\text{C}$; insoluble in water) and 25 g of sorbitan trioleate-20 EO.

Example 18 (not inventive)

In a stirred vessel, 130 g of a naphthene-base mineral oil (40 mPas/25°C) are heated to 170°C, 1.82 g of octylamine are added, and the mixture is stirred until the amine has completely dissolved. Following the addition of 1.18 g of 1,6-hexamethylene diisocyanate and a subsequent reaction period of 30 minutes, the unclear, nonhomogeneous reaction mixture is introduced dropwise into 143 g of naphthene-base mineral oil (40 mPas/25°C), cooled to 20°C, in a second stirred vessel, with thorough stirring and cooling. Instantaneously, the formation of a lumpy, flocculated, colorless precipitate is observed.

Example 19 (not inventive)

In a stirred vessel, 130 g of a naphthene-base mineral oil (40 mPas/25°C) are heated to 190°C, 1.82 g of octylamine are added, and the mixture is stirred until the amine has completely dissolved. Following the addition of 1.18 g of 1,6-hexamethylene diisocyanate and a subsequent reaction period of 30 minutes, the unclear, nonhomogeneous reaction mixture is introduced dropwise into 143 g of naphthene-base mineral oil

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(40 mPas/25°C), cooled to 20°C, in a second stirred vessel, with thorough stirring and cooling. Instantaneously, the formation of a lumpy, flocculated, colorless precipitate is observed.

5

Use Examples

The testing of the performance properties took place in a commercial cooling lubricant concentrate containing mineral oil, and two commercially available polymer dispersions.

10

Testing of the defoaming action in a commercially available cooling lubricant concentrate

15

99.6 g of a commercial cooling lubricant concentrate containing mineral oil were admixed with 0.4 g of the defoamers prepared in accordance with Examples 5 to 9 and Examples 12 to 15, 18 and 19. 15 g of these mixtures are placed in a graduated 1000 ml measuring cylinder and made up to 300 ml with deionized water. This solution is then gassed using a D1 frit with an air speed of 1.8 l/minute. A measurement is made of the time, in seconds, required for the formation of 700 ml of foam.

20

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- 15 -

Table 1: Results of performance testing in a cooling lubricant concentrate

Added defoamer	Time to form 700 ml of foam
None	22 seconds
Example 5 (inventive)	2100 seconds
Example 6 (inventive)	5220 seconds
Example 7 (inventive)	1560 seconds
Example 8 (inventive)	3840 seconds
Example 9 (inventive)	1980 seconds
Example 12 (not inventive)	480 seconds
Example 13 (not inventive)	780 seconds
Example 14 (not inventive)	180 seconds
Example 15 (not inventive)	360 seconds
Example 18 (not inventive)	110 seconds
Example 19 (not inventive)	90 seconds

5 As is evident from the examples shown, the inventive examples (Examples 5 to 9) are markedly superior to the noninventive examples (Examples 12 to 15, 18 and 19) in terms of their defoaming action. It is clear in particular that in order to obtain optimum activity
 10 from the defoamer formulations it is necessary for recrystallization of melted urea derivatives to take place from a clear melt dispersed homogeneously in the carrier medium.

15 Testing of the defoaming action in commercially available polymer dispersions

Testing was carried out in the styrene-acrylate dispersion Acronal® 290 D from BASF and in the all-
 20 acrylate dispersion Acronal® A603 from BASF.

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The inventive and noninventive defoamers were each incorporated into the dispersions for one minute at 1000 rpm.

- 5 Air was introduced into the polymer dispersions containing defoamer additive using a turbine stirrer (diameter 4 cm) at 2500 rpm for 1 minute. Straight after switching off the stirrer, the aerated dispersion was placed in a measuring cylinder up to the 50 ml
10 mark, and weighed. The weight is influenced by the amount of air introduced with stirring and is a measure of the activity of the defoamer.

15 Table 2: Results of performance testing in the polymer dispersion Acronal® 290 D

Defoamer	Amount of defoamer in % by weight	Sample density in g/50 ml
None	—	39.3
Example 10 (inventive)	0.2	49.6
Example 11 (inventive)	0.05	50.0
Example 16 (not inventive)	0.2	43.6
Example 17 (not inventive)	0.05	44.1

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Table 3: Results of performance testing in the polymer dispersion Acronal® A603

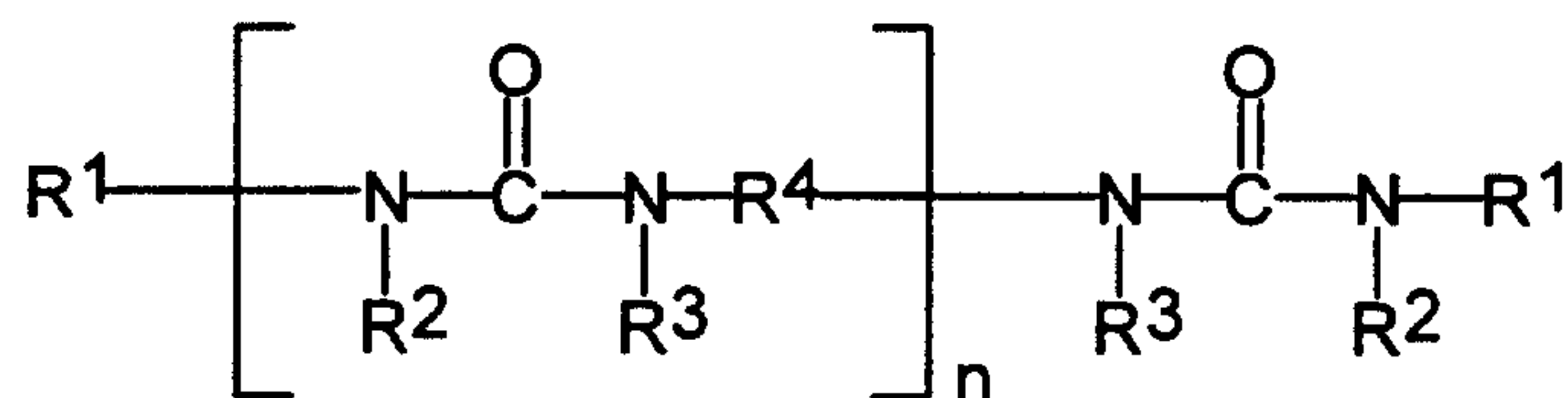
Defoamer	Amount of defoamer in % by weight	Sample density in g/50 ml
None	—	38.1
Example 10 (inventive)	0.2	48.8
Example 11 (inventive)	0.05	49.2
Example 16 (not inventive)	0.2	42.5
Example 17 (not inventive)	0.05	43.9

- 5 As is evident from the examples shown, the inventive examples (Examples 10 and 11) are markedly superior to the noninventive examples (Examples 16 and 17) in terms of their defoaming action.

_ 18 _

What is claimed is:

1. A composition for defoaming aqueous media,
comprising as defoamers urea derivatives of the
5 formula I



Formula I

10 where

R^1 - is a hydrocarbon radical having 4 to 30
carbon atoms or a hydrocarbon radical having 4 to
24 carbon atoms and one nitrogen atom or a
hydrocarbon radical having 4 to 30 carbon atoms and
15 one carbonyl group,

R^2 - is a hydrogen atom or a hydrocarbon radical
having 1 to 24 carbon atoms,

R^3 - is a hydrogen atom or a hydrocarbon radical
having 1 to 24 carbon atoms,

20 R^4 - is an organic radical having 2 to 30 carbon
atoms, and

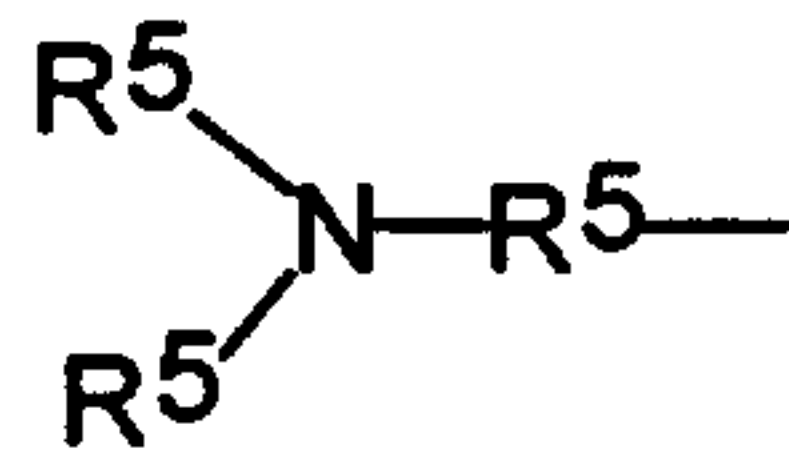
n - is from 0 to 5,

in the form of solid particles, which are obtained
by crystallization from a clear homogeneous melt
25 dispersed in a carrier medium.

2. The composition as claimed in claim 1, wherein R^1 is
a hydrocarbon radical having 4 to 24 carbon atoms,
 R^2 is a hydrogen atom, R^3 is a hydrogen atom, and R^4
30 is a hydrocarbon radical having 2 to 24 carbon
atoms.

3. The composition as claimed in claim 1, wherein R^1 is
the organic radical

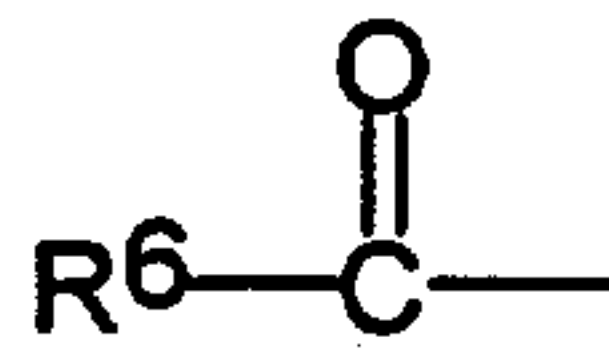
- 19 -



Formula II

5 where R^5 is a hydrocarbon radical having 1 to 18 carbon atoms, R^2 and R^3 are a hydrogen atom, and R^4 is a hydrocarbon radical having 2 to 24 carbon atoms.

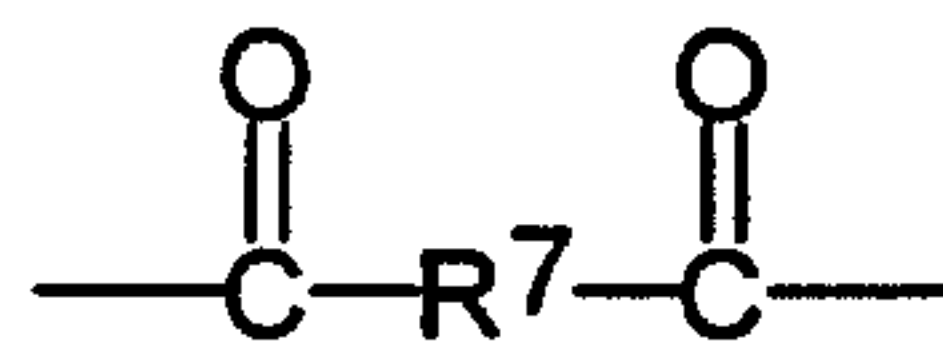
10 4. The composition as claimed in claim 1, wherein R^1 is the organic radical



Formula III

15 where R^6 is an organic radical having 2 to 30 carbon atoms,
 R^2 and R^3 are a hydrogen atom, and R^4 is a hydrocarbon radical having 2 to 24 carbon atoms.

20 5. The composition as claimed in claim 1, wherein R^1 is a hydrocarbon radical having 2 to 24 carbon atoms, R^2 and R^3 are a hydrogen atom, and R^4 is the organic radical



Formula IV

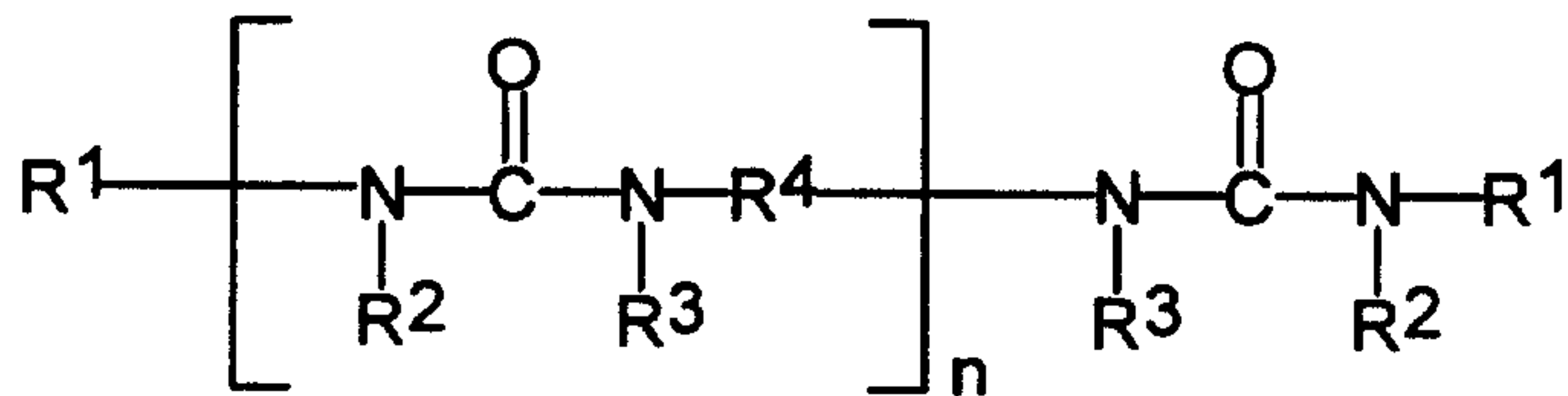
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where R^7 is a hydrocarbon radical having 2 to 20 carbon atoms.

30 6. The composition as claimed in any of claims 1 to 5, wherein organic or mineral oils are used as carrier media.

- 20 -

7. The composition as claimed in any of claims 1 to 6, wherein siloxanes or organomodified siloxanes are used as carrier media.
- 5 8. The use of a defoamer as set forth in any of claims 1 to 7 to defoam cooling lubricants.
9. The use of a defoamer as set forth in any of claims 1 to 7 to defoam polymer dispersions.
- 10 10. The use of a defoamer as set forth in any of claims 1 to 7 to defoam coating materials and printing inks.



Formula I