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(11) **EP 1 080 171 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
12.01.2005 Bulletin 2005/02

(51) Int Cl.7: **C11D 1/62**, C11D 3/32,
C11D 3/20

(21) Application number: **99924984.0**

(86) International application number:
PCT/EP1999/003366

(22) Date of filing: **12.05.1999**

(87) International publication number:
WO 1999/060081 (25.11.1999 Gazette 1999/47)

(54) **STABILISED QUATERNARY AMMONIUM COMPOSITIONS**

STABILISIERTE QUATERNÄRE AMMONIUMZUSAMMENSETZUNGEN

COMPOSITIONS STABLES D'AMMONIUM

(84) Designated Contracting States:
BE DE ES FR GB IT

(30) Priority: **18.05.1998 GB 9810655**

(43) Date of publication of application:
07.03.2001 Bulletin 2001/10

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EP 1 080 171 B1

DescriptionTechnical Field

[0001] The present invention relates to the stability of quaternary ammonium materials, in particular it relates to maintaining stable quaternary ammonium materials containing at least one ester group in the raw material form or as a solution in a suitable solvent.

Background and Prior Art

[0002] Quaternary ammonium materials both solid or liquid are used extensively in fabric softener compositions. Typically such compositions contain a water insoluble quaternary ammonium fabric softening agent dispersed in water at a level of quaternary ammonium softening agent up to 8% by weight in which case the compositions are considered dilute or at levels from 8 to 50% in which case the compositions are considered concentrates.

[0003] A problem associated with quaternary ammonium materials containing at least one ester group is their instability on storage.

[0004] The problem is particularly noticeable in the storage of these materials at variable temperatures over time.

[0005] The instability of both such solid and liquid quaternary ammonium material manifests itself by the discolouration of such material during storage at various temperatures. The amount of discolouration is generally an indication of the level of decomposition occurring over time. This decomposition is of greatest concern when quaternary ammonium material is stored at temperatures above their melting points.

[0006] In the past, stability of quaternary ammonium compounds has been improved by the storage of compounds at low temperatures, i.e. temperatures well below the melting points of the compounds being stored. Also, the addition of anti-oxidants have been used to counteract decomposition.

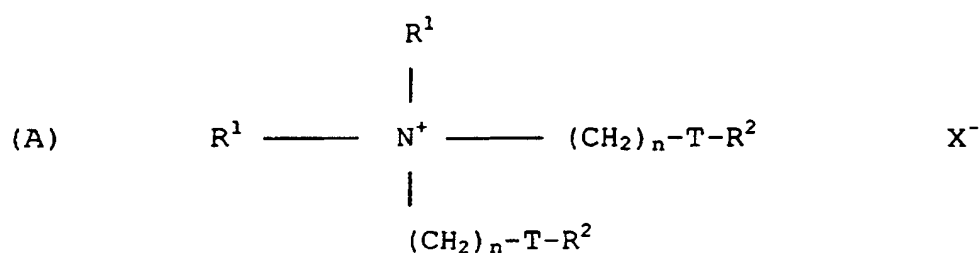
[0007] EP 299 176 (Kao) discloses soft-finishing agents comprising a di-long chained quaternary ammonium salt containing a single ester group and a decyldimethyl amine.

[0008] US 4 937 008 (Kao) discloses concentrated fabric softening agents comprising one or more quaternary ammonium salts and a di or tri-valent polyol with 2 to 3 carbon atoms.

[0009] Surprisingly, we have found that low and high temperature stability of solid or liquid quaternary ammonium compounds containing at least one ester group may be improved by the addition of one or more of a select group of stabilising agents which act to prevent the extent of decomposition of the quaternary ammonium material.

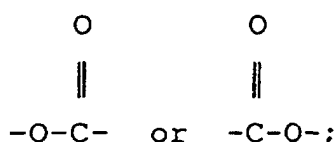
Definition of the Invention

[0010] Thus according to one aspect of the invention there are provided stabilised compositions comprising quaternary ammonium material represented by the formula:



wherein each R^1 group is independently selected from C_{1-4} alkyl, hydroxyalkyl or C_{2-4} alkenyl groups; and wherein each R^2 group is independently selected from C_{8-28} alkyl or alkenyl groups; X^- is any suitable counter-ion.

T is



and

n is an integer from 1-5 or is 0
 characterised in that they further comprise one or more
 stabilising agent(s) wherein the one or more
 stabilising agents are chosen from one or more of the group comprising:

- a) urea,
- b) urea derivative
- c) primary or secondary amides, and/or
- d) polyhydric alcohols.

and are present at levels of 0.05 to 10% of the weight of the quaternary ammonium material, preferably 0.5 to 6.0%, even more preferably 0.5 to 4%, with the proviso that the composition is in a liquid, molten, semi-solid or solid form containing less than 10% by weight water.

[0011] In a second aspect of the present invention there is provided the step of adding at least one stabilising agent during the manufacture of the quaternary ammonium material, preferably following the quaternisation step in the synthesis of the quaternary ammonium material.

[0012] In a third aspect of the present invention, the composition as defined is incorporated into a solid and/or liquid rinse conditioner.

[0013] Also provided is the use of a stabilising agent to reduce the level of discoloration of quaternary ammonium material containing at least one ester group.

[0014] As used herein the term 'ester group' in the quaternary ammonium material includes an ester group which is a linking group in the molecule. References herein to quaternary ammonium material are to those having at least one ester group in their structure.

[0015] It has surprisingly been found that compounds which readily donate hydrogen bonds to the aforementioned quaternary ammonium material assist in maintaining a high level of quaternary ammonium material and avoiding high levels of the decomposition products.

Detailed Description of the Invention

[0016] The stabilising agent(s) are chosen from one or more of the following group comprising,

- a) urea
- b) urea derivative
- c) primary or secondary amides, and/or
- d) polyhydric alcohols.

[0017] Such compositions show improved stability at varying temperatures.

[0018] The quaternary ammonium compounds containing at least one ester group are referred to herein as ester-linked quaternary ammonium compounds.

[0019] The quaternary ammonium compounds contain two or more ester groups. In the diester quaternary ammonium compounds of the invention the ester group(s) is a linking group between the nitrogen atom and an alkyl group. The ester groups(s) are attached to the nitrogen atom via another hydrocarbyl group.

[0020] The invention is most useful for quaternary ammonium compounds containing two ester groups, wherein at least one higher molecular weight group containing at least one ester group and two or three lower molecular weight groups are linked to a common nitrogen atom to produce a cation and wherein the electrically balancing anion is a halide, acetate or lower alkylsulphate ion, such as chloride or methosulphate. The higher molecular weight substituent on the nitrogen is preferably a higher alkyl group, containing 12 to 28, preferably 12 to 22, eg 12 to 20 carbon atoms, such as coco-alkyl, tallowalkyl, hydrogenated tallowalkyl or substituted higher alkyl, and the lower molecular weight substituents are preferably lower alkyl of 1 to 4 carbon atoms, such as methyl or ethyl, or substituted lower alkyl. One

or more of the said lower molecular weight substituents may include an aryl moiety or may be replaced by an aryl, such as benzyl, phenyl or other suitable substituents.

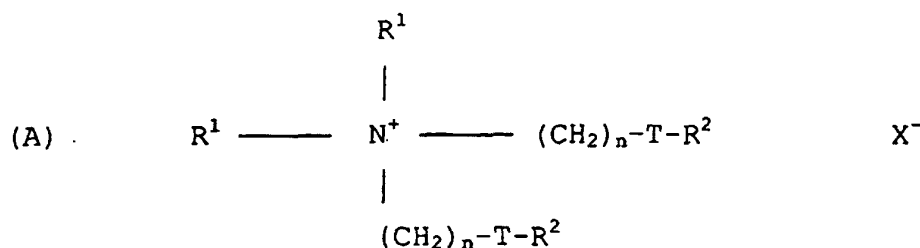
[0021] Preferably the quaternary ammonium material used in the invention is a compound having two C₁₂-C₂₂ alkyl or alkenyl groups connected to a quaternary ammonium head group via two ester links.

[0022] More preferably the invention is useful for quaternary ammonium material comprising a compound having two long chain alkyl or alkenyl chains with an average chain length equal to or greater than C₁₄. Even more preferably each chain has an average chain length equal to or greater than C₁₆. Most preferably at least 50% of each long chain alkyl or alkenyl group has a chain length of C₁₈. It is preferred if the long chain alkyl or alkenyl groups are predominantly linear.

[0023] The problems referred to above have found to be particularly associated with quaternary ammonium compounds having an ester link and wherein the compound has two or three electron withdrawing groups connected to the quaternary nitrogen atom by one or two carbon atoms on different substituents, and, a methyl group also attached to said nitrogen atom. This arrangement is shown in the following formula (A). Such compounds having a chloride counterion have been found to particularly benefit from the present invention in terms of stability.

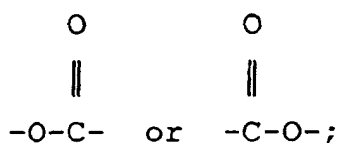
[0024] Without wishing to be bound by theory the applicant believes that the problems of discolouration/instability are most common in quaternary ammonium compounds containing an ester linking group and having a methyl group attached to the nitrogen and a chloride counter-ion and two or three electron withdrawing groups separately attached to the quaternary nitrogen atom, and are especially prevalent in the compounds of the type (A) below.

[0025] Thus the ester-linked quaternary ammonium material for use in the invention is represented by the formula:



wherein each R¹ group is independently selected from C₁₋₄ alkyl, hydroxyalkyl or C₂₋₄ alkenyl groups; and wherein each R² group is independently selected from C₈₋₂₈ alkyl or alkenyl groups; X⁻ is any suitable counterion, i.e. a halide, acetate or lower alkylsulphate ion, such as chloride or methosulphate.

T is



and

n is an integer from 1-5 or is 0

[0026] It is especially preferred that each R¹ group is methyl and each n is 2 as such compounds are found to be particularly susceptible to the stability problems referred to above.

[0027] Di (tallowyloxyethyl) dimethyl ammonium chloride, available from Hoechst, is especially preferred, also Di (hardened tallowyloxyethyl) dimethyl ammonium chloride, ex Hoechst.

[0028] It is advantageous for environmental reasons if the quaternary ammonium material is biologically degradable.

[0029] It is especially preferred that such compounds falling within general formula A have two methyl substituents on the nitrogen and in the remaining radicals n is 1 or 2 and R² is C₁₂-C₂₂, especially C₁₆-C₂₂ e.g. tallow.

[0030] The quaternary ammonium compound used in the present invention is substantially anhydrous, meaning containing less than 10% water in the context of the present invention.

[0031] The quaternary ammonium material may contain optional additional components, as known in the art, in

particular, low molecular weight solvents, for instance isopropanol and/or ethanol, and co-actives such as nonionic softeners, for example fatty acid or sorbitan esters.

[0032] The stabilising agent may be urea or a derivative thereof, a primary or secondary amide or a polyhydric alcohol, or mixtures thereof. Two or more stabilising agents may be used.

[0033] The stabilising agent is added to the composition of the present invention at levels of 0.05 to 10% by weight of the weight of the quaternary ammonium material. However, lower amounts than this are preferred, more preferably 0.1 to 7.5% is added based on the weight of the quaternary ammonium material, especially 0.5 to 6.0% and even more preferably 0.5 to 4%.

[0034] The stabilising agent may be introduced to the quaternary ammonium material at any stage during the manufacture of the quaternary ammonium material or after manufacture i.e. on storage. The stabilising agent may be added in any form, as a powder direct to the molten quaternary ammonium material or as a solution in a suitable solvent, for instance iso propanol.

[0035] The addition step can take place during the synthesis of the quaternary ammonium material, preferably following the quaternisation step. The addition may take alternatively, or additionally, place during storage of the quaternary ammonium material.

[0036] The stabilising agent is most effectively introduced at any stage following the quaternisation step of the synthesis of the quaternary ammonium material.

[0037] An example of amide to be used in the present invention is acetamide. Polyhydric alcohols such as glycerol may be used as stabilising agents. Another preferred stabilising agent is urea. A combination of glycerol and a quaternary ammonium compound of general formula (A) is particularly preferred, especially wherein both R^1 are CH_3 , n is 2 and R^2 is tallow.

[0038] The stabilised composition is in a liquid, molten or semi-solid form containing less than 10% by weight water.

[0039] Also provided according to the invention is a solid rinse conditioner comprising a stabilised composition as defined above, preferably a composition in a granular or powdered form. Another type of rinse conditioner provided by the invention is a liquid rinse conditioner comprising a stabilised composition as defined above.

[0040] The invention will now be illustrated by the following example. Further examples within the scope of the invention will be apparent to the person skilled in the art.

Example

[0041] Urea was added to the quaternary ammonium material as a powder and heated to 82°C. The combined material was stored for three days.

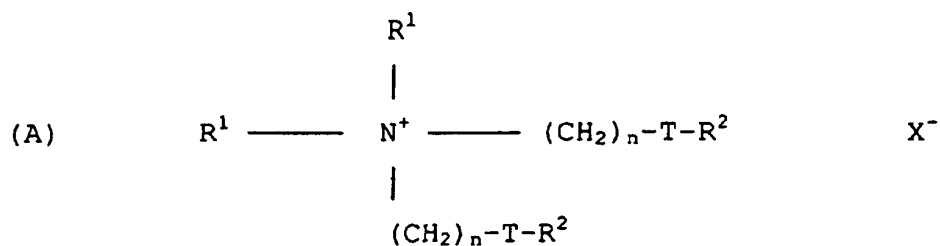
[0042] The reflectance was measured on a datacolor international Spectraflash SF600 plus reflectometer after 3 days storage at 82°C.

	R540 after 3 days at 82°C
DEQ (control)	19.8
DEQ + 3.6% urea	25.1
DEQ + 7.3% urea	27.4
DEQ is di(2-[hardened tallow]oxyl oxyethyl) dimethyl ammonium chloride ex Hoechst. It includes approximately 10% mono ester and minor amounts of unquaternised amine/amine salt as well as approximately 2% fatty acid and 14% isopropanol.	

[0043] These results show that addition of urea to compositions comprising a quaternary ammonium compound counteracts decomposition at high temperature. This is indicated by the greatly increased R540 reflectance values found for samples of quaternary ammonium compound stored in admixture with urea.

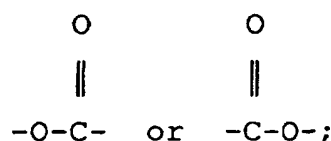
Claims

1. Stabilised compositions comprising quaternary ammonium material represented by the formula:



wherein each R¹ group is independently selected from C₁₋₄ alkyl, hydroxyalkyl or C₂₋₄ alkenyl groups; and wherein each R² group is independently selected from C₈₋₂₈ alkyl or alkenyl groups; X⁻ is any suitable counter-ion.

T is



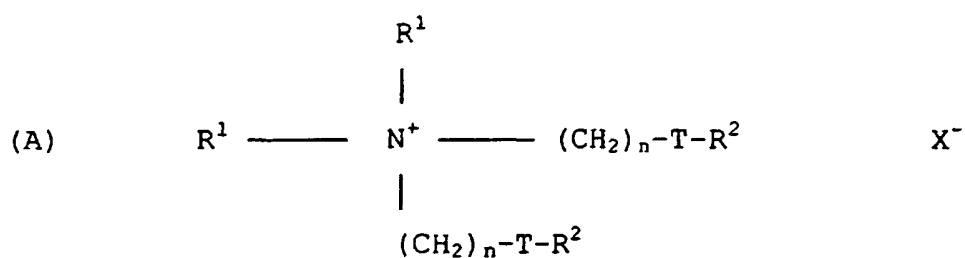
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n is an integer from 1-5 or is 0

characterised in that they further comprise one or more stabilising agent(s) wherein the one or more stabilising agents are chosen from one or more of the group comprising:

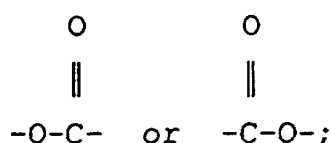
- a) urea,
- b) urea derivative
- c) primary or secondary amides, and/or
- d) polyhydric alcohols. and are present at levels of 0.05 to 10% of the weight of the quaternary ammonium material, preferably 0.5 to 6.0%, even more preferably 0.5 to 4%, with the proviso that the composition is in a liquid, molten, semi-solid or solid form containing less than 10% by weight water.

2. Process of stabilising quaternary ammonium material represented by the formula:



wherein each R¹ group is independently selected from C₁₋₄ alkyl, hydroxyalkyl or C₂₋₄ alkenyl groups; and wherein each R² group is independently selected from C₈₋₂₈ alkyl or alkenyl groups; X⁻ is any suitable counter-ion.

T is



and

n is an integer from 1-5 or is 0

via the steps of adding at least one stabilising agent to the quaternary ammonium material, wherein the stabilising agent is chosen from one or more of the group comprising:

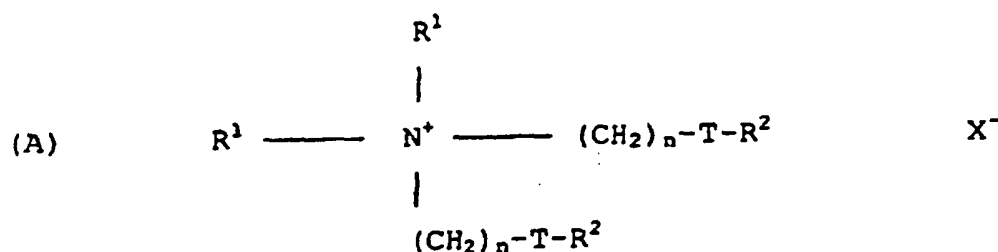
- a) urea,
- b) urea derivative
- c) primary or secondary amides, and/or
- d) polyhydric alcohols.

and is present at levels of 0.05 to 10% of the weight of the quaternary ammonium material, preferably 0.5 to 6.0%, even more preferably 0.5 to 4%, with the proviso that the composition is in a liquid, molten or semi-solid form containing less than 10% by weight water.

3. Process according to claim 2 wherein the step of adding at least one stabilising agent occurs during the manufacture of the quaternary ammonium material, preferably following the quaternisation step in the synthesis of the quaternary ammonium material.
4. Process according to claim 2 wherein the step of adding at least one stabilising agent occurs after manufacture of the quaternary ammonium material, preferably during storage of the quaternary ammonium material.
5. Use of a stabilising agent as defined in claim 1 to reduce the level of discoloration of quaternary ammonium material containing at least one ester group.
6. A solid or liquid rinse conditioner comprising a stabilised composition as defined in claim 1.

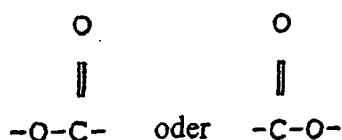
Patentansprüche

1. Stabilisierte Zusammensetzungen, umfassend quartäres Ammoniummaterial, dargestellt durch die Formel:



worin jede Gruppe R^1 unabhängig voneinander aus C_1 - C_4 -Alkyl-, Hydroxyalkyl- oder C_2 - C_4 -Alkenylgruppen ausgewählt ist, und worin jede Gruppe R^2 unabhängig aus C_8 - C_{28} -Alkyloder Alkenylgruppen ausgewählt ist; X^- irgendein geeignetes Gegenion ist;

T



ist und

n eine ganze Zahl von 1 bis 5 oder 0 ist;

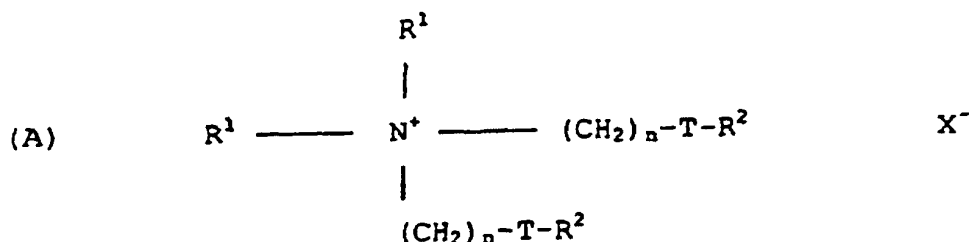
dadurch gekennzeichnet, daß sie ferner ein oder mehrere Stabilisierungsmittel umfassen, worin das eine oder die mehreren Stabilisierungsmittel aus einer oder mehreren der Gruppe, umfassend

- a) Harnstoff,
- b) Harnstoffderivat
- c) primäre oder sekundäre Amide und/oder
- d) mehrwertige Alkohole,

ausgewählt ist,

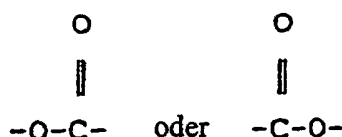
und in Niveaus von 0,05 bis 10 Gew.-% des quartären Ammoniummaterials, bevorzugt 0,5 bis 6,0 Gew.-%, noch stärker bevorzugt 0,5 bis 4 Gew.-%, vorhanden sind, mit dem Vorbehalt, daß die Zusammensetzung in flüssiger, geschmolzener, halbfester oder fester Form vorliegt, und weniger als 10 Gew.-% Wasser enthält.

2. Verfahren zur Stabilisierung von quartärem Ammoniummaterial, dargestellt durch die Formel:



worin

jede Gruppe R^1 unabhängig voneinander aus C_1 - C_4 -Alkyl-, Hydroxyalkyl- oder C_2 - C_4 -Alkenylgruppen ausgewählt ist, und worin jede Gruppe R^2 unabhängig aus C_8 - C_{28} -Alkyloder Alkenylgruppen ausgewählt ist; X^- irgendein geeignetes Gegenion ist; T



ist und

n eine ganze Zahl von 1 bis 5 oder 0 ist;

mittels des Schrittes der Zugabe zumindest eines Stabilisierungsmittels zu dem quartären Ammoniummaterial, worin das Stabilisierungsmittel aus einer oder mehreren der Gruppe, umfassend

- a) Harnstoff,
- b) Harnstoffderivat
- c) primäre oder sekundäre Amide und/oder
- d) mehrwertige Alkohole, ausgewählt ist,

und in Niveaus von 0,05 bis 10 Gew.-% des quartären Ammoniummaterials, bevorzugt 0,5 bis 6,0 Gew.-%, noch stärker bevorzugt 0,5 bis 4 Gew.-%, vorhanden ist, mit dem Vorbehalt, daß die Zusammensetzung in flüssiger, geschmolzener, halbfester oder fester Form vorliegt, und weniger als 10 Gew.-% Wasser enthält.

3. Verfahren nach Anspruch 2, wobei der Schritt der Zugabe zumindest eines Stabilisierungsmittels während der Herstellung des quartären Ammoniummaterials, bevorzugt nach dem Quaternisierungsschritt in der Synthese des quartären Ammoniummaterials stattfindet.

4. Verfahren nach Anspruch 2, wobei der Schritt der Zugabe des zumindest einen Stabilisierungsmittels nach der Herstellung des quartären Ammoniummaterials, bevorzugt während der Lagerung des quartären Ammoniummaterials, stattfindet.

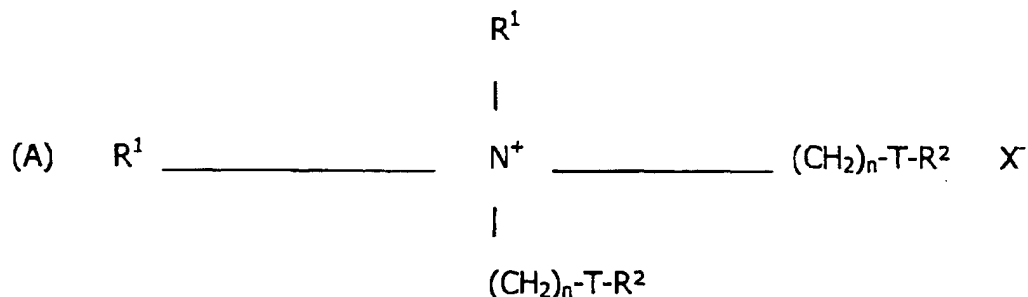
5. Verwendung eines Stabilisierungsmittels wie nach Anspruch 1 definiert, zur Verringerung des Niveaus der Verfärbung von quartärem Ammoniummaterial, das zumindest eine Estergruppe enthält.

6. Fester oder flüssiger Spülkonditionierer, umfassend eine stabilisierte Zusammensetzung wie in Anspruch 1 defi-

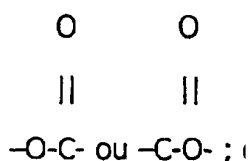
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Revendications

1. Compositions stabilisées comprenant un ammonium quaternaire représenté par la formule :



dans laquelle chaque groupe R^1 est choisi indépendamment parmi les groupes alkyle en C1-4, hydroxyalkyle ou alcényle en C2-4 et dans laquelle chaque groupe R^2 est choisi indépendamment parmi les groupes alkyle ou alcényle en C8-28 ; X^- est tout contre-ion approprié,
Test



et

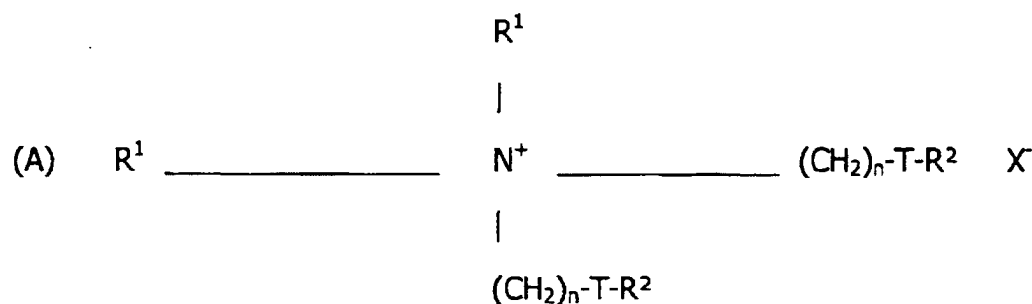
n est un nombre entier de 1 à 5 ou est 0,

caractérisées en ce qu'elles comprennent de plus un ou plusieurs agent(s) de stabilisation où ces agents de stabilisation sont choisis parmi un ou plusieurs composés dans le groupe comprenant :

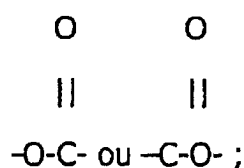
- (a) l'urée,
- (b) un dérivé d'urée
- (c) des amides primaires ou secondaires et/ou
- (d) des polyols,

et sont présents en des quantités de 0,05 à 10% du poids de l'ammonium quaternaire, de préférence 0,5 à 6,0%, mieux de préférence 0,5 à 4%, à la condition que la composition soit sous une forme liquide, fondue, semi solide ou solide contenant moins de 10% en poids d'eau.

2. Procédé de stabilisation d'ammonium quaternaire représenté par la formule :



dans laquelle chaque groupe R^1 est choisi indépendamment parmi les groupes alkyle en C1-4, hydroxyalkyle ou alcényle en C2-4 et dans laquelle chaque groupe R^2 est choisi indépendamment parmi les groupes alkyle ou alcényle en C8-28 ; X^- est tout contre-ion approprié, T est



; et

n est un nombre entier de 1 à 5 ou est 0,

via les étapes d'addition d'au moins un agent de stabilisation à l'ammonium quaternaire, où l'agent de stabilisation est choisi parmi un ou plusieurs composés dans le groupe comprenant :

- (a) l'urée,
- (b) un dérivé d'urée
- (c) des amides primaires ou secondaires, et/ou
- (d) des polyols,

et est présent en des quantités de 0,05 à 10% du poids de l'ammonium quaternaire, de préférence 0,5 à 6,0%, mieux de préférence 0,5 à 4%, à la condition que la composition soit sous une forme liquide, fondue ou semi solide contenant moins de 10% en poids d'eau.

3. Procédé selon la revendication 2, dans lequel l'étape d'addition d'au moins un agent de stabilisation a lieu pendant la fabrication de l'ammonium quaternaire, de préférence à la suite de l'étape de quaternisation dans la synthèse de l'ammonium quaternaire.
4. Procédé selon la revendication 2, dans lequel l'étape d'addition d'au moins un agent de stabilisation a lieu après la fabrication de l'ammonium quaternaire, de préférence pendant le stockage de l'ammonium quaternaire.
5. Utilisation d'un agent de stabilisation comme défini dans la revendication 1 pour réduire le taux de décoloration de l'ammonium quaternaire contenant au moins un groupe ester.
6. Conditionneur de rinçage solide ou liquide comprenant une composition stabilisée comme défini dans la revendication 1.