

Description

The present invention relates to a softener composition which confers excellent water absorbency on clothing treated with it.

Most of the presently commercially available softener compositions for ordinary household use are compositions comprising as a main ingredient, Di-(hydrogenated beef tallow alkyl) dimethyl ammonium chloride.

This quaternary ammonium salt confers good softening and antistatic effects on various fibers, even when used in small amounts.

It is believed that a softener molecule needs to impart a lipophilic property in order to confer excellent softening effects, since the softening effect results from a lowering of friction at the fabric surface which is caused by the lubricating effect of the lipophilic parts of the softener molecule absorbed onto the fabric surface.

However, this lipophilic property is disadvantageous when making the treated clothing water-repellant and reduces the water-absorbency of the treated clothing, causing a substantial reduction in water-absorbency when the concentration of the softening agent is high.

Consequently, many investigations on the softener compound have been conducted in order to improve the water-absorbency.

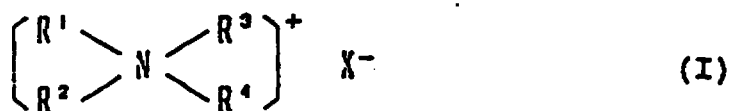
It is known that dioleyl dimethyl quaternary ammonium salt is a softener compound which confers excellent water-absorbency (JAOCS, Vol. 60, No. 6, 1166-1169).

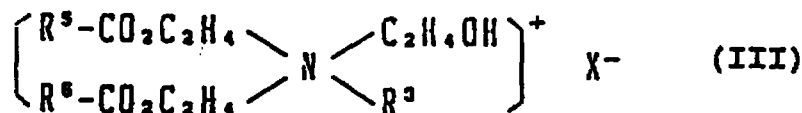
However, the softener compound comprising the above compound confers greater water-absorbency than Di-(hydrogenated beef tallow alkyl) dimethyl quaternary ammonium salt, but reduces the softening properties in comparison with the others.

On the other hand, even though the above compound is used with other softening agents, for example, Di-(hydrogenated beef tallow alkyl) dimethyl quaternary ammonium salt in order to improve the softening property, a reduction in water-absorbency occurs.

Consequently, the present inventors have conducted research and studies in order to find the quaternary ammonium salt which confers greater water-absorbency and a greater softening property than the usual dioleyl type quaternary ammonium salt. As a result the inventors have found that unsaturated quaternary ammonium salt having specific stereoisomeric structure confers good softening effects as well as a substantially increased water-absorbency.

The present invention provides a softener composition comprising at least one quaternary ammonium salt having the following formula (I)-(III):



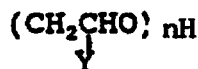


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wherein R^1 and R^2 each represent a hydrocarbon radical having 12-22 carbon atoms, preferably 16-22 carbon atoms and one unsaturated bond. Moreover, the stereoisomeric structure of the above salts having the formula (I) include both the cis-isomer and trans-isomer, with the cis-isomer/trans-isomer ratio being in the range of from 25/75 - 90/10;

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R^3 and R^4 each represent a methyl, ethyl or



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group in which n is an integer from 1 to 5, and Y represents H or methyl; R^5 and R^6 each represent a hydrocarbon radical having 11-21 carbon atoms, preferably 15-21 carbon atoms and one unsaturated bond. Moreover, the stereoisomeric structure of the above salts having the formula (II)-(III) include both the cis-isomer and trans-isomer with the cis-isomer/trans-isomer ratio being in the range of from 25/75-90/10; and X represents a halogen, CH_3SO_4 or $C_2H_5SO_4$.

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The invention will now be further described with reference to the following illustrative examples.

With regard to the properties of the softener composition of the present invention, the stereoisomeric ratio of R^1 and R^2 in formula (I) and R^5 and R^6 in formulas (II) and (III) is particularly important in order to satisfy the requirements of both the softening property and water-absorbency.

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Namely, it is necessary that the stereoisomeric structure of the quaternary ammonium salt having the formula (I) -(III) includes both the cis-isomer and trans-isomer, and moreover, it is necessary that the cis-isomer/trans-isomer ratio is in the range of from 25/75 - 90/10, preferably from 50/50 - 80/20.

The ratio of the cis-isomer to the trans-isomer in the present invention means, for example, with respect to the compound salt of formula(I), the total ratio of both R^1 and R^2 .

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As an example, with respect to the compound salt of formula (I), R^1 can be the cis-isomer, and R^2 can be the trans-isomer.

The present ratio can also be obtained by mixing a salt wherein both R^1 and R^2 are the cis-isomer with a salt wherein both R^1 and R^2 are the trans-isomer, such that the total ratio of the cis-isomer to the trans-isomer is within the required range as described above.

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Similarly, the ratio with regard to R^5 and R^6 in the compound salt of formulas (II) and (III) can also be obtained.

There are several methods to preferably adjust the ratio of the cis-isomer to the trans-isomer to arrive at the distinctive feature of the present invention.

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One method to adjust the cis- and trans-isomer ratio is by mixing the cis-isomeric and the trans-isomeric quaternary ammonium salt after producing them separately.

Another method is to produce the quaternary ammonium salt from a mixture of the cis-isomeric and the trans-isomeric fatty acid or ester thereof after mixing them according to the desired ratio.

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Another method is to produce the quaternary ammonium salt from the mixture after adjusting the ratio thereof by isomerizing a portion of the cis-isomeric fatty acid or ester thereof into the trans-isomer in the presence of, e.g., a metallic catalyst, etc.

Still a further method utilized to adjust the ratio is by isomerizing between the cis-isomer and the trans-isomer during the process for producing the quaternary ammonium salt using the fatty acid or ester thereof as a precursor.

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Examples of fatty acids used as precursors of the compound salt having the above formula (I)-(III) are cis-6-octadecenoic acid, cis-9-octadecenoic acid (oleic acid), cis-13-docosenoic acid, trans-6-octadecenoic acid, trans-7-octadecenoic acid, trans-13-docosenoic acid.

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When manufacturing the softener composition of the present invention, the unsaturated quaternary ammonium salt, having the formula (I)-(III) described above, is commonly used in the range of 3-20% by weight, based on the total weight of the composition.

In order to confer both the softening property and water-absorbency, it is necessary that both the cis-isomer and the trans-isomer exist together and, furthermore, that the ratio is within a certain range as discussed above.

The inventors suggest that when the quaternary ammonium salt of the present invention is adsorbed onto clothing, the orientation of the salts is disturbed due to this mixture of the cis-isomer and the trans-isomer, and it is this disturbed orientation which results in a decrease in water-repellency while increasing the water absorbency.

If the ratio of the cis-isomer to the trans-isomer is less than 25/75, water-absorbency decreases considerably.

If the ratio of the cis-isomer to the trans-isomer is greater than 90/10, both water-absorbency and the softening property decrease.

In practicing the present invention, dimethylpolysiloxane (silicone) or modified silicone can be added to the composition, in the range of from 0.5-10% by weight, based on the weight of compound in formula (I)-(III) in order to enhance the softening property and water-absorbency of the unsaturated quaternary ammonium salt of formula (I)-(III).

Silicone is known as an ingredient which enhances the softening effect and ironing characteristics of a fabric (see Japanese patent laid-open No. 52-53094).

It is also known that silicone itself has water-repellency and adversely affects water-absorbency.

The fact that silicone enhances water-absorbency when used in conjunction with the specific unsaturated quaternary ammonium salt of the present invention is surprising since it is contrary to what would be expected from the prior art.

More specifically, dimethylpolysiloxane or a modified silicone, having a viscosity of 20-10 000 mPa.s (20-10000 cps) at 25 °C is preferred.

Modified silicones useful in the present invention include, for example, polyoxyethylene modified silicone and amino-modified silicone.

It is preferable that the amount of modification is less than 10%.

It is preferable that dimethylpolysiloxane or modified silicones are emulsified with a polyoxyethylene-type nonionic surfactant or a monoalkylcationic-type or dialkylcationic-type cationic surfactant prior to their use.

In addition to the quaternary ammonium salts of formula (I)-(III), the following substances may be incorporated in any amount which will not impede the effects of the softener composition of the present invention; other known quaternary ammonium salts; polyoxyethylene alkyl or alkenyl ether, polyoxyethylene alkylphenyl ether, polyoxyethylene oxypropylene polyalkylenepolyamine, nonionic surfactants such as glycerine or pentaerythritol which has been partially esterified with higher fatty acids such as stearic acid or oleic acid, or 2-ethylhexanoic acid; water-soluble salts such as sodium chloride, ammonium chloride and calcium chloride; solvents such as ethyl alcohol, isopropyl alcohol, propylene glycol and ethylene glycol; urea; germicides; antioxidants; pigments, dyes, perfumes, etc.

The invention will now be further described with reference to the following illustrative examples.

Example

The softening effects and water-absorbency of the compositions set forth in Table 2 on various fibers were examined.

As the unsaturated quaternary ammonium salt of the present invention, those having the formula set forth in Table 1 were used.

TABLE 1

FORMULA OF QUATERNARY AMMONIUM SALT							
5	COMPOUND NO.	FORMULA	R ¹ ,R ² or R ⁵ ,R ⁶		R ³	R ⁴	X
			CARBON NO.	CIS-ISOMER/TRANS-ISOMER			
10	1 -1*	1	18	95/5	CH ₃	CH ₃	Cl
	1 -2	1	18	65/35	CH ₃	CH ₃	Cl
	1 -3	1	18	50/50	CH ₃	CH ₃	Cl
	1 -4	1	22	70/30	CH ₃	CH ₃	Cl
	1 -5*	1	18	20/80	CH ₃	CH ₃	Cl
15	2 -1	2	17	70/30	CH ₃	-	CH ₃ SO ₄
	2 -2	2	17	50/50	CH ₃	-	CH ₃ SO ₄
	3 -1	3	17	80/20	CH ₃	-	CH ₃ SO ₄

20 *Comparative Example.

The ratio of the cis-isomer to the trans-isomer was calculated by comparing the integration of the cis-olefinic proton with the integration of the trans-olefinic proton measured by using 400 MHz NMR (Nihon Electron Co. Ltd.) for example, as seen in Fig. 1.

(1) Softening Treatment

A commercially available cotton towel and cotton knitwork underwear were washed repeatedly 5 times with a commercially available detergent, Zab (a registered trademark for a product of Kao Corporation), and fiber treating agents were removed from the thus-washed fiber products. The fiber products were then treated in a 0.1% aqueous solution of the softener composition (water having a hardness of 3.5° DH being used) at a temperature of 25°C and a bath ratio of 1/30 for 5 minutes under agitation.

(2) Evaluation

The clothes treated according to the above-mentioned method were air-dried in a room and were allowed to stand still in a thermostat chamber maintained at a temperature of 25°C and a relative humidity of 65% for 24 hours.

The softness and water-absorbency of each cloth was evaluated in the following manner:

(a) softness

The softness was evaluated according to the paired comparison testing method using, as a control, a cloth treated with a comparative softener composition (which contains 5% of Di-(hydrogenated beef tallow alkyl) dimethyl ammonium chloride).

The evaluation scale is as follows:

+2 soft

+1 relatively soft

0 same as control

-1 relatively hard

-2 hard

(b) water-absorbency

The cotton towel and the cotton knitwork underwear were cut into 3 cm x 20 cm rectangular strips.

One end of the cloth was dipped into water to a depth of 2 cm.

After 15 minutes, the rise in water, on each strip was measured in centimeters.

(3) Results

The results obtained are shown in Table 2. As will be apparent from the results shown in Table 2, in the case of the softener of the present invention, water-absorbency was substantially enhanced while sufficient softness was retained.

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TABLE 2

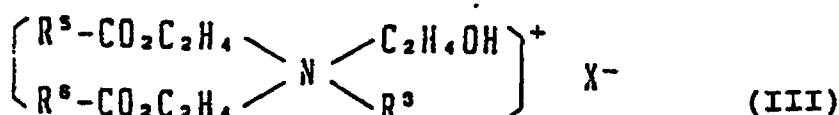
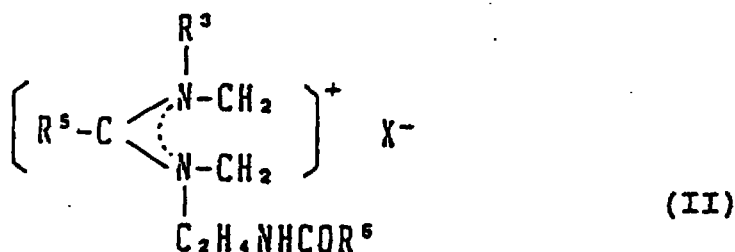
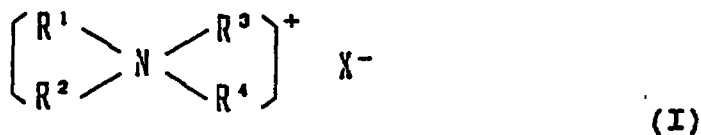
COMPOSITION NO.	COMPOSITION OF QUATERNARY AMMONIUM SALT	(WEIGHT %)	SILICON (WEIGHT%)	COTTON TOWEL		COTTON KNITWORK UNDERWEAR	
				WATER-SOFTNESS	ABSORPTIVITY	WATER-SOFTNESS	ABSORPTIVITY
1*	Di-(hydrogenated beef tallow alkyl) dimethyl ammonium chloride	(5)	--	Standard	6.1	Standard	4.3
2*	dioleyl dimethyl ammonium chloride	(5)	--	-1	9.0	-1	7.0
3*	Di-(hydrogenated beef tallow alkyl) dimethyl ammonium chloride	(2.5)	--	-0.5	6.5	-0.5	4.5
	Dioleyl dimethyl ammonium chloride	(2.5)					
4*	1 - 1	(5)	0.4	0	6.3	0	5.8
5	1 - 2	(5)	--	0	10.8	0	8.2
6	1 - 2	(5)	0.4	0	12.3	0	9.0
7	1 - 3	(5)	0.2	0	12.0	0	9.2
8	1 - 4	(5)	0.4	0	11.8	0	9.2
9*	1 - 5	(5)	--	0	6.2	-1	5.9
10	2 - 1	(5)	--	0	11.0	0	8.3
11	2 - 2	(5)	0.2	0	12.0	0	9.2
12	3 - 1	(5)	0.4	0	12.0	0	9.4

*Comparative Example.



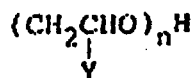
Claims

1. A softener composition comprising at least one quaternary ammonium salt having any of the following formulae (I)-(III):



wherein R^1 and R_2 each independently represents a hydrocarbon radical having 12-22 carbon atoms and one unsaturated bond;

R^3 and R^4 each represents a methyl, ethyl or



group, wherein n is an integer from 1 to 5, and Y is H or methyl;

R^5 and R^6 each represents a hydrocarbon radical having 11-21 carbon atoms and one unsaturated bond;

X represents a halogen, CH_3SO_4 or $C_2H_5SO_4$;

Wherein each salt having any of the formulae (I)-(III) includes both cis-isomer and trans-isomer with the cis-isomer and the trans-isomer ratio being in a molar ratio from 25/75 to 90/10.



2. A softener composition according to claim 1 wherein R¹ and R² each independently has 16-22 carbon atoms.
- 5 3. A softener composition according to claim 1 or 2 wherein the cis-isomer/trans-isomer ratio is in the range of from 50/50 - 80/20.
4. A softener composition according to any preceding claim further comprising dimethylpolysiloxane or modified silicone.
- 10 5. A softener composition according to claim 4 wherein dimethylpolysiloxane or modified silicone has a viscosity of 20-10,000 mPa.s (20-10,000 CPS) at 25° C.
- 15 6. A softener composition according to claim 4 wherein the amount of dimethylpolysiloxane or modified silicone is in the range of from 0.5-10% by weight, based on the weight of compound in the formula (I)-(III).
7. A softener composition according to claim 1, wherein said quaternary ammonium salt of formula (I)-(III) is present in an amount of from 3-20% by weight based on the total weight of the composition.
- 20 8. A method of softening clothes which comprises treating clothes with an aqueous solution of a softener composition according to any preceding claim.

Patentansprüche

- 25 1. Weichmacherzusammensetzung, umfassend wenigstens ein quaternäres Ammoniumsalz gemäß einer der folgenden Formeln (I) bis (III):

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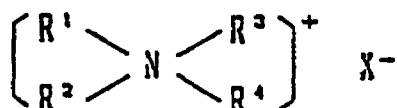
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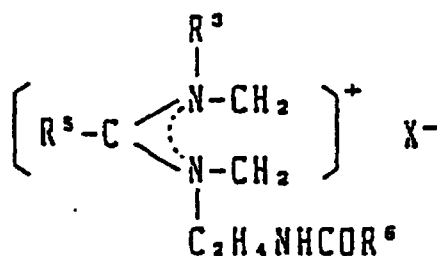
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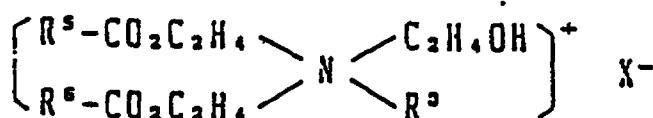
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(I)



(II)

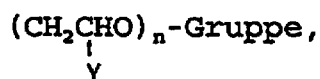


(III)

worin bedeuten:

R¹ und R² jeweils unabhängig ein Kohlenwasserstoffradikal mit 12 bis 22 Kohlenstoffatomen und einer ungesättigten Bindung;

R³ und R⁴ jeweils eine Methyl-, Ethyl- oder



worin n eine ganze Zahl von 1 bis 5 ist und Y steht für Y oder Methyl;

R⁵ und R⁶ ein Kohlenwasserstoffradikal mit 11 bis 21 Kohlenstoffatomen und einer ungesättigten Bindung;

X ein Halogen, CH₃SO₄ oder C₂H₅SO₄;

worin jedes Salz gemäß der Formeln (I) bis (III) sowohl das cis-Isomere als auch das trans-Isomere einschließt, wobei das Verhältnis von cis-Isomer und trans-Isomer ein molares Verhältnis von 25/75 bis 90/10 ist.

2. Weichmacherzusammensetzung nach Anspruch 1, worin R¹ und R² jeweils unabhängig 16 bis 22 Kohlenstoffatome besitzen.

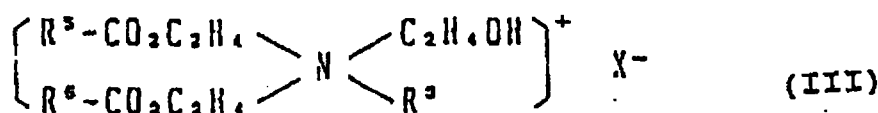
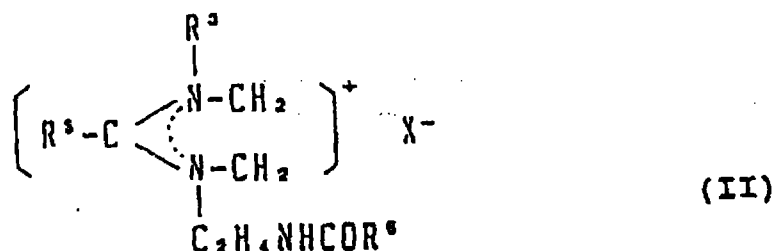
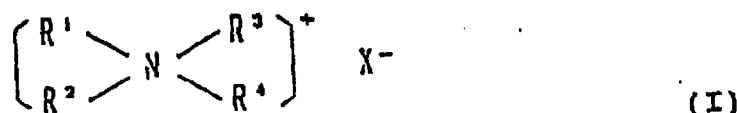
3. Weichmacherzusammensetzung nach Anspruch 1 oder 2, worin das Verhältnis von cis-Isomer/trans-Isomer im Bereich von 50/50 bis 80/20 liegt.



4. Weichmacherzusammensetzung nach einem der vorhergehenden Ansprüche, umfassend weiterhin Dimethylpolysiloxan oder modifiziertes Silikon.
5. Weichmacherzusammensetzung nach Anspruch 4, worin Dimethylpolysiloxan oder modifiziertes Silikon eine Viskosität von 20 bis 10 000 mPa·s (20 bis 10 000 CPS) bei 25 °C besitzt.
6. Weichmacherzusammensetzung nach Anspruch 4, worin die Menge an Dimethylpolysiloxan oder modifiziertem Silikon im Bereich von 0,5 bis 10 Gew.-%, bezogen auf das Gewicht der Verbindung gemäß Formel (I) bis (III), liegt.
7. Weichmacherzusammensetzung nach Anspruch 1, worin das quaternäre Ammoniumsalz gemäß der Formeln (I) bis (III) in einer Menge von 3 bis 20 Gew.-%, bezogen auf das Gesamtgewicht der Zusammensetzung, enthalten ist.
8. Verfahren zum Weichmachen von Stoffen, umfassend das Behandeln von Stoffen mit einer wässrigen Lösung einer Weichmacherzusammensetzung gemäß einem der vorhergehenden Ansprüche.

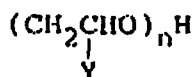
Revendications

1. Composition d'assouplissant comprenant au moins un sel d'ammonium quaternaire ayant l'une quelconque des formules (I) à (III) suivantes :



où R¹ et R² représentent chacun indépendamment un radical hydrocarboné ayant 12 à 22 atomes de carbone et une seule liaison insaturée ;

R³ et R⁴ représentent chacun un groupe méthyle, éthyle ou un groupe



où n est un nombre entier de 1 à 5 et Y est H ou un groupe méthyle ;

R⁵ et R⁶ représentent chacun un radical hydrocarboné ayant 11 à 21 atomes de carbone et une seule liaison insaturée ;

X représente un halogène, CH₃SO₄ ou C₂H₅SO₄ ;

dans laquelle chaque sel ayant l'une quelconque des formules (I) à (III) comprend à la fois l'isomère *cis* et l'isomère *trans*, le rapport molaire de l'isomère *cis* à l'isomère *trans* étant de 25/75 à 90/10.



2. Composition d'assouplissant selon la revendication 1, dans laquelle R¹ et R² ont chacun indépendamment 16 à 22 atomes de carbone.
- 5 3. Composition d'assouplissant selon la revendication 1 ou 2, dans laquelle le rapport isomère *cis*/isomère *trans* se situe dans l'intervalle de 50/50 à 80/20.
4. Composition d'assouplissant selon l'une quelconque des revendications précédentes, comprenant de plus un diméthylpolysiloxane ou une silicone modifiée.
- 10 5. Composition d'assouplissant selon la revendication 4, dans laquelle le diméthylpolysiloxane ou la silicone modifiée a une viscosité de 20 à 10 000 mPa.s (20 à 10 000 cPs) à 25 °C.
- 15 6. Composition d'assouplissant selon la revendication 4, dans laquelle la quantité de diméthylpolysiloxane ou de silicone modifiée se situe dans l'intervalle de 0,5 à 10 % en poids par rapport au poids du composé de formule (I), (II) ou (III).
- 20 7. Composition d'assouplissant selon la revendication 1, dans laquelle ledit sel d'ammonium quaternaire de formule (I), (II) ou (III) est présent en une quantité de 3 à 20 % en poids par rapport au poids total de la composition.
8. Procédé pour assouplir de linge, qui consiste à traiter le linge avec une solution aqueuse d'une composition d'assouplissant selon l'une quelconque des revendications précédentes.

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