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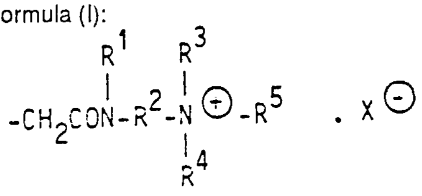
(54) **Nitrogen-containing derivatives of carboxymethylcellulose**

(57) A compound is disclosed, having the structure of carboxymethylcellulose in which at least one carboxymethyl group is replaced by a group of the general formula (I):

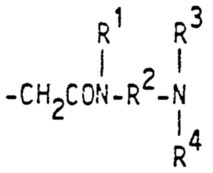


$$-CH_2CO\overset{\overset{\displaystyle R^1}{|}}{N}-R^2-\underset{\underset{\displaystyle R^4}{|}}{\overset{\overset{\displaystyle R^3}{|}}{N}}{}^{\oplus}-R^5 \quad . \; X^{\ominus}$$

(I)

wherein $R^1$ is hydrogen or a methyl group, $R^2$ is a straight chain or branched divalent aliphatic $C_2$-$C_5$ hydrocarbon group, $R^3$ and $R^5$ are each, independently, a straight chain or branched $C_1$-$C_4$ alkyl group, $R^5$ is a straight chain or branched $C_1$-$C_4$ alkyl group or a benzyl group and X is a halogen atom, a sulphate ester group or a sulphonic acid group, with the proviso that at least 0.1 groups of formula (I) are present on average per anhydroglucose unit of the compound's structure.

These compounds are prepared by a process which involves, as intermediate, a derivative of carboxymethyl-cellulose in which at least one carboxymethyl group is replaced by a group of the general formula (II):



$$-CH_2CO\overset{\overset{\displaystyle R^1}{|}}{N}-R^2-\underset{\underset{\displaystyle R^4}{|}}{\overset{\overset{\displaystyle R^3}{|}}{N}}$$

(II)

The compounds are used in cosmetic compositions for application to the hair and in the production of paper and textiles.

GB 2 219 587 A

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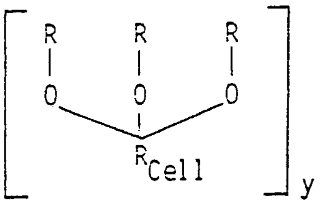
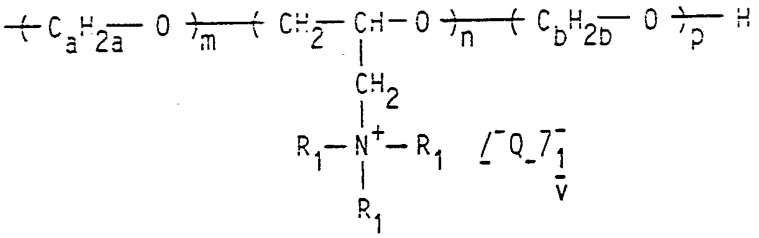
# Nitrogen-containing derivatives of carboxymethylcellulose, their preparation and their use in cosmetic formulations

The invention relates to derivatives of carboxymethylcellulose having quaternary ammonium groups and to a process for the preparation of these compounds and their use in cosmetic formulations, in particular for hair care. The invention furthermore relates to derivatives of carboxymethylcellulose having tertiary amino groups as intermediates for the preparation of the derivatives of carboxymethylcellulose having quaternary ammonium groups.

Quaternary nitrogen-containing cellulose ethers are known from DE-PS 15 93 657. These correspond to the structural formula



wherein $R_{Cell}$ represents the radical of an anhydroglucose unit, y represents an integer from 200 to 5000 and each radical R represents a substituent group of the following general formula:



$$-\!\left(C_aH_{2a}-O\right)_m\!\left(CH_2-\underset{\substack{|\\CH_2\\|\\R_1-N^+-R_1\\|\\R_1}}{CH}-O\right)_n\!\left(C_bH_{2b}-O\right)_p H \quad [Q]^-_{\frac{1}{v}}$$

in which a and b each represent 2 or 3, m and p represent an integer from 0 to 10, n represents an integer from 0 to 3, $R_1$ represents a methyl or ethyl group, Q represents an anion and v represents an integer which corresponds to the valency of Q, and in which the average value, per anhydroglucose unit of the cellulose ether, of n is 0.1 to 0.5 and of m + n + p is 0.1 to 2.5, excluding the cellulose ethers for which the average value of m + p is zero.

According to the information in the patent specification, these ethers have an improved substantivity towards various substrates in comparison with the non-modified cellulose ethers. They can therefore be used for purposes for which the customary cellulose ethers are only poorly suitable, if at all, because of their non-ionic or anionic character. The compounds can be employed in cosmetic formulations.

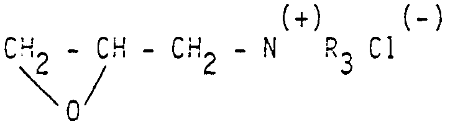
DE-OS 33 01 667 relates to a process for the preparation of cationic cellulose derivatives, with the distinctive feature that

a) an alkali metal cellulose suspended in an aqueous organic solvent which is at least partly watermiscible is reacted with a non-ionic etherifying agent from the group comprising glycidol, glycidyl acetate or glycerol chlorohydrin in an amount of 2 - 10 mol/mol of anhydroglucose unit, and

b) during the reaction or when the reaction has ended, the reaction mixture is reacted with a cationic etherifying agent of the general formulae

$$Cl\text{-}CH_2\text{-}CHOH\text{-}CH_2 - N^{(+)} R_3 Cl^{(-)}$$

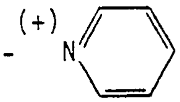
or



$$\underset{\diagdown O \diagup}{CH_2 - CH} - CH_2 - N^{(+)} R_3 Cl^{(-)}$$

,

in which R represents a lower alkyl group having 1 - 4 C atoms, or the group

$- N^{(+)} R_3 Cl^{(-)}$ is replaced by a group -  $Cl^{(-)}$

in an amount of 0.5 to 2.0 mol/mol of anhydroglucose unit.

It is pointed out in this Offenlegungsschrift that the known cationic conditioning active compounds (which also include the products of DE-PS 15 93 657) have been said to have numerous deficiencies. Products of good water-solubility and adequate compatibility with anionic detergent bases are thus said usually to have too weak an action, which would make a high dosage necessary. Other products of limited water-solubility would be too substantive and would be absorbed almost completely onto the hair. If the hair were treated several times, this would lead to accumulation and to a reduction in the fullness and the set of the dried hair. The products of DE-OS 33 01 667 would have these disadvantages to a considerably lesser degree, if at all.

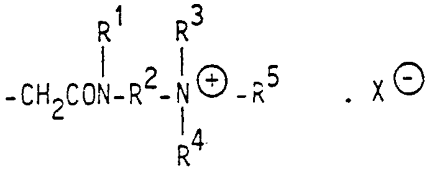
A cosmetic agent for the treatment of hair or skin which contains a quaternary macromolecular polymeric compound derived from chitosan is known from DE-OS 35 02 833. The compounds are prepared by reacting a chitosan consisting to the extent of 50 to 100% of deacetylated chitin with a glycidyltrialkylammonium halide and ethylene oxide in a suitable ratio in the presence of a solvent. Chitosan purified by reprecipitation is employed in particular as the starting material.

Water-soluble cationic polysaccharides based on cellulose ethers are described in published European Patent Application 0,189,935 and essentially differ from the compounds of DE-PS 15 93 657 in that they additionally contain an alkyl radical having at least 8 carbon atoms and are therefore substituted by hydrophobic substituents.

The present invention is based on the object of discovering nitrogen-containing products based on cellulose which exhibit better solution properties in water and which have better technological properties, in particular when used in cosmetic formulations for the hair. The term better solution properties is to be understood here as meaning avoiding, or at least largely excluding, the formation of gelatinous intermediate states when the products are dissolved in water. It should be possible for the products to be brought rapidly into aqueous solutions without particular mechanical aids. The improved cosmetic properties of the new products should comprise, in particular, an improvement in the shine, handle and/or combability of hair. The substantivity of the products should be balanced so that enrichment of the active compounds on the hair is avoided, even when they are used several times. It should be possible to prepare the compounds from readily accessible raw materials.

It has been found, surprisingly, that certain derivatives of carboxymethylcellulose meet these requirements.

The invention thus relates to derivatives of carboxymethylcellulose having quaternary ammonium groups, with the distinctive feature that all the carboxymethyl groups or some of these groups are replaced by groups of the general formula



$$-CH_2CO\overset{\overset{\displaystyle R^1}{|}}{N}-R^2-\underset{\underset{\displaystyle R^4}{|}}{\overset{\overset{\displaystyle R^3}{|}}{N}}{}^{\oplus}-R^5 \quad . \; X^{\ominus} \qquad \text{I}$$

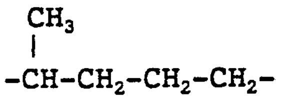
wherein $R^1$ is a hydrogen or methyl radical, $R^2$ is a divalent aliphatic hydrocarbon radical having 2 to 5 carbon atoms, $R^3$ and $R^4$ are an alkyl radical having 1 to 4 carbon atoms, $R^5$ is an alkyl radical having 1 to 4 carbon atoms or a benzyl radical and X is a halogen or sulphate ester radical or a sulphonic acid radical, with the proviso that on average at least 0.1 quaternary ammonium group is present per anhydroglucose unit of the polymeric molecule.

Those derivatives of carboxymethylcellulose which contain on average 0.3 to 0.8, in particular 0.3 to 0.6, quaternary ammonium groups per anhydroglucose unit are preferred.

The number of anhydroglucose units in the polymeric molecule should be about 400 to 10,000.

In formula I, $R^1$ denotes a hydrogen or methyl radical. $R^1$ is preferably a hydrogen radical.

$R^2$ is a divalent aliphatic hydrocarbon radical having 2 to 5 carbon atoms. This alkylene radical can optionally be branched, but straight-chain alkylene radicals, and in particular those with 2 to 4 carbon atoms, are preferred. Examples of such radicals $R^2$ are

$-CH_2-CH_2-$, $-CH_2-CH_2-CH_2-$ and  $\overset{\displaystyle CH_3}{\overset{|}{-CH}}-CH_2-CH_2-CH_2-$ radicals.

The radicals $R^3$ and $R^4$ can be identical or different and denote alkyl radicals having 1 to 4 carbon atoms. The methyl radical is preferred.

$R^5$ is an alkyl radical having 1 to 4 carbon atoms or a benzyl radical. The methyl radical is the preferred alkyl radical.

X is a halogen, sulphate ester or sulphonate radical, which is present in the anionic form. The halogen radical, in particular the chlorine radical, is preferred. Examples of suitable sulphate ester or sulphonate radicals are
$CH_3CH_2OSO_3^{\ominus}$, $CH_3C_6H_4SO_3^{\ominus}$ and $CH_3SO_3^{\ominus}$ radicals.

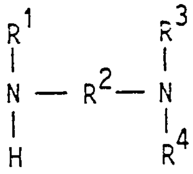
However, in principle other physiologically acceptable radicals present in the anionic form are also suitable, since the properties of the products are influenced only little, if at all, by the anionic radical.

The invention furthermore relates to the process for the preparation of the compounds according to the invention of Patent Claim 1. This process according to the invention is carried out in three stages, in the simplified description alkali metal salts of carboxymethylcellulose being esterified with alkyl chloride in the 1st stage, the resulting ester being converted into a derivative with tertiary amino groups in the 2nd stage and the resulting intermediate being quaternized in the 3rd stage.

The process according to the invention is thus characterized in that

a) an alkali metal salt of carboxymethylcellulose is esterified with, based on the carboxymethyl groups, up to a 10-fold molar excess of alkyl chloride, wherein the alkyl radical has 1 to 3 carbon atoms, at temperatures of 80 to 170°C under a pressure of 5 to 100 bar over a reaction time of 1 to 24 hours in a manner which is known per se, and, after the esterification, the excess alkyl chloride is removed from the reaction mixture in a manner which is known per se,

b) the resulting ester of the carboxymethylcellulose is reacted with amines of the general formula



$$\underset{H}{\overset{R^1}{N}}-R^2-\underset{R^4}{\overset{R^3}{N}}$$

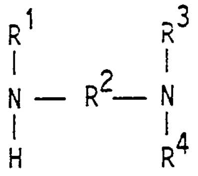
III

wherein $R^1$, $R^2$, $R^3$and $R^4$ are as defined in Claim 1, at temperatures of 80 to 150°C over a reaction time of 1 to 10 hours if appropriate under reduced pressure, in amounts such that 1 to 10 mol of the amine are employed per mol of ester group, and, after the reaction, the excess amine is separated off from the reaction mixture in a manner which is known per se, and

c) the resulting carboxymethylcellulose derivative containing tertiary amino groups is then reacted with, based on the tertiary amino groups, at least equimolar amounts of the compound $R^5$-X, wherein $R^5$ and X are as defined in Claim 1, if appropriate at elevated temperature and if appropriate under increased pressure over a reaction time of 0.5 to 8 hours.

The esterification in the 1st stage is carried out in a manner which is known per se using an alkyl chloride in which the alkyl radical has 1 to 3 carbon atoms. Methyl chloride is preferably used for the esterification. The reaction is carried out at an elevated temperature of 80 to 170°C, a temperature range from 80 to 110°C being preferred. The reaction is carried out under an increased pressure of 5 to 100 bar, preferably under a pressure of 5 to 50 bar. Depending on the alkyl chloride used, the reaction is complete within 1 to 24 hours, it being possible for yields of up to about 95% of theory to be achieved. At least equimolar amounts of alkyl chloride are used. It is advisable to use an excess of alkyl chloride, but for economic reasons a more than 10-fold molar excess will be avoided. After the reaction, the excess amount of alkyl chloride is removed in a manner which is known per se, preferably by distillation.

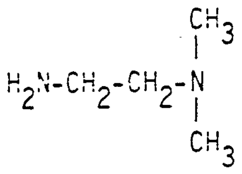
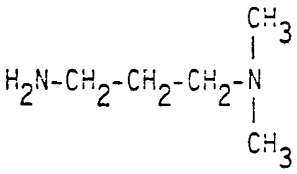
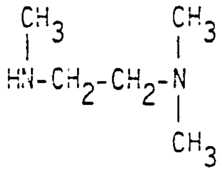
In the 2nd stage, the resulting alkyl ester of the carboxymethylcellulose is reacted with amines of the general formula

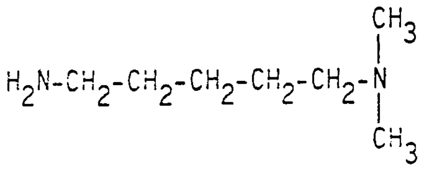
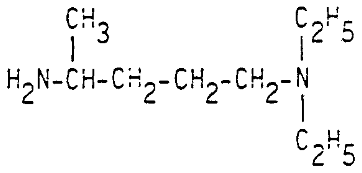


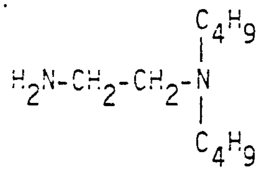
$$\overset{R^1}{\underset{H}{N}} - R^2 - \overset{R^3}{\underset{R^4}{N}}$$

III

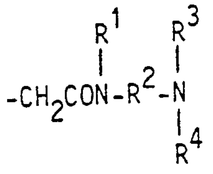
The definition of the radicals $R^1$, $R^2$, $R^3$ and $R^4$ corresponds to the definitions of Patent Claim 1. A range from 80 to 150°C, preferably 100 to 140°C, is chosen as the reaction temperature. If appropriate, the reaction can be carried out under increased pressure. This largely depends on the boiling point of the amine used. The reaction has ended in 1 to 10 hours, with a yield of about 90%. 1 to 10 mol of the amine are employed per ester group, the excess amount of amine being separated off after the reaction in a manner which is known per se. This can be effected by filtering off the reaction product from the reaction mixture, precipitation of the reaction product being brought to completion by addition of polar organic solvents, such as, for example, acetone, isopropanol or methanol. The reaction is preferably carried out in suspension with addition of an inert polar organic solvent, such as, for example, methanol or isopropanol, in a pressure-resistant reaction vessel. For this, 1 to 3 mol of the amine are preferably employed per ester group. Examples of suitable amines of the formula III are


$H_2N-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{N}}$ ,

$H_2N-CH_2-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{N}}$ ,

$\overset{CH_3}{HN}-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{N}}$ ,


$H_2N-CH_2-CH_2-CH_2-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{N}}$ ,

$H_2N-\overset{CH_3}{CH}-CH_2-CH_2-CH_2-\underset{C_2H_5}{\overset{C_2H_5}{N}}$ and


$H_2N-CH_2-CH_2-\underset{C_4H_9}{\overset{C_4H_9}{N}}$ .

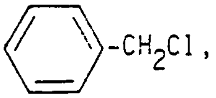
The intermediates obtained in the 2nd stage are in turn new compounds, the properties of which are causal for the properties of the end products according to the invention. The invention therefore furthermore relates to these new intermediates in the form of the derivatives of carboxymethylcellulose having tertiary amino groups, which are characterized in that all the carboxymethyl groups or some of these groups are replaced by groups of the general formula


$$-CH_2CO\overset{R^1}{N}-R^2-\underset{R^4}{\overset{R^3}{N}} \qquad II$$

wherein the substituents $R^1$, $R^2$, $R^3$ and $R^4$ have the meaning given in Claim 1, with the proviso that on average at least 0.1 tertiary amino group is present per anhydroglucose unit of the polymeric molecule.

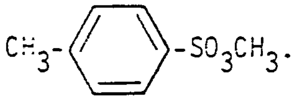
In the third stage of the process according to the invention, these new intermediates are now reacted with, based on the tertiary amino groups, at least equimolar amounts of the compound $R^5$-X. Examples of suitable compounds $R^5$-X are

$CH_3Cl$, $C_2H_5Cl$, $C_4H_9Br$,



$(CH_3O)_2SO_2$,

$(C_2H_5O)_2SO_2$, $CH_3SO_3CH_3$ and



The quaternization reaction is carried out in a manner which is known per se. It can be carried out at a low boiling point of the compounds $R^5$-X, if appropriate under increased pressure. Although the reaction already takes place at 0°C, for example with methyl chloride, it is advisable to operate at an elevated temperature in order to accelerate the reaction. When the reaction has ended, the excess amount of $R^5$-X is removed by distillation or by filtration and washing the cellulose derivative with a polar organic solvent, such as isopropanol or acetone.

The reaction of stage 3 can be carried out in a two-phase system, the derivative of carboxymethylcellulose obtained in the 2nd stage being suspended in a suitable liquid organic phase, for example methanol. Although a reaction in the aqueous phase is possible, because of the high viscosity of the solution it is only preferred if the end product is to be further used directly in the form of an aqueous solution.

Mixed carboxymethyl-hydroxyalkyl-cellulose ethers are also commercially available. They can likewise be used as starting compounds. In this case, the carboxymethylcellulose derivatives according to the invention can additionally optionally contain ether radicals, such as, for example, $(C_2H_4O)_pH$ and $(C_3H_6O)_pH$, wherein p can assume an average value from 1 to 5.

The compounds prepared by the process according to the invention dissolve both in cold and in hot water without or largely without the formation of gelatinous intermediate stages.

The invention furthermore relates to the use of the compounds according to the invention in cosmetic formulations, in particular for hair care. The compounds according to the invention have the properties required above to a particularly high degree. If hair is treated with aqueous formulations of the compounds according to the invention, the hair is given the desired shine and a pleasantly flexible handle and can easily be combed. The products have proved to be particularly suitable for the care of damaged hair. The aqueous formulations should contain the compounds according to the invention here in an amount of 0.1 to 2.5% by weight. No skin irritation or hair damage has been observed with the compounds according to the invention.

The compounds according to the invention can moreover be used for thickening aqueous solutions or aqueous suspensions. They are suitable for the treatment of textile fibres or yarns or sheet-like textiles produced therefrom, the improvement in handle coupled with a reduction in the electrostatic charging in turn being of prime importance. The compounds according to the invention can furthermore be added to the pulp in the production of paper. The compounds can furthermore be used for thickening aqueous binders.

The following examples show the preparation of the compounds according to Patent Claim 1 and 2. The technological properties of the compounds are furthermore shown in comparison with products of the prior art.

## I Preparation of the compounds according to the invention

### 1. Preparation of carboxymethylcellulose methyl ester (Process stage a))

1 a) 30 g of sodium carboxymethylcellulose with a degree of modification DS = 0.9, a saponification number SN < 4 and a purity of 99.5%, a 1% strength aqueous solution of which has a Brookfield viscosity of about 2000 mPas, and 87 g of chloromethane are heated at 100°C for 10 hours in a 250 ml laboratory autoclave in

accordance with JP-OS 49-18981. A pressure of about 40 bar builds up during this time. The chloromethane is then evaporated off. The product is heated at 50°C under 60 mbar for complete removal of the chloromethane. 34 g of carboxymethylcellulose methyl ester mixed with the sodium chloride formed as a by-product by the reaction are obtained. The methyl ester has a saponification number of SN = 225, which corresponds to a conversion of 90% of the carboxyl groups.

1 b) 30 g of carboxymethylcellulose (sodium salt) with a degree of modification DS = 0.7, a saponification number SN < 4 and a purity of 99.5%, a 1% strength aqueous solution of which has a Brookfield viscosity of about 1500 mPas, are reacted with chloromethane in the same manner. The carboxymethylcellulose methyl ester obtained has a saponification number of SN = 200, which corresponds to a conversion of 86% of the carboxyl groups.

2. Preparation of the aminoamide of carboxymethylcellulose
(Process stage b))

2 a) 30 g of carboxymethylcellulose methyl ester obtained according to Section 1 a) are heated under reflux with 200 g of dimethylaminopropylamine for 6 hours, while stirring. After cooling, 1000 g of isopropanol are added for complete precipitation of the reaction product. The carboxymethylcellulose aminoamide is

isolated by filtration with suction and extracted with isopropanol in a Soxhlet apparatus. The amine nitrogen content of the product is determined as 2.2% of N by titration, which corresponds to a reaction of 60%. The product is readily water-soluble.

2 b) 30 g of carboxymethylcellulose methyl ester obtained according to Section 1 a) are heated at 150°C for 1 hour together with 24 g of dimethylaminopropylamine and 100 g of methanol in a 250 ml laboratory autoclave, while stirring, a pressure of about 18 bar developing. After cooling, the product is filtered off with suction and washed with methanol. After drying, the amine nitrogen content is determined as 3.4% of N by titration, which corresponds to a conversion of 92%, based on the ester groups. The $^1$H-NMR spectrum recorded in $D_2O$ shows the signal of the methyl substituent of the tertiary amino group at 2.4 ppm as the characteristic peak.

2 c) 30 g of the same carboxymethylcellulose methyl ester are reacted with 21 g of dimethylaminoethylamine in accordance with Section 2 b). The amine nitrogen content of the resulting carboxymethylcellulose aminoamide determined by titration is 3.3%, which corresponds to a conversion of 85% of the ester groups.

2 d) 30 g of the same carboxymethylcellulose methyl ester are reacted with 24 g of N,N,N′-trimethylethylenediamine in the same manner. The amine nitrogen content of the resulting carboxymethylcellulose aminoamide

determined by titration is 2.9%, which corresponds to a conversion of 79% of the ester groups.

2 e) 30 g of the same carboxymethylcellulose methyl ester are reacted with 37 g of 1-diethylamino-4-aminopentane in the same manner. The amine nitrogen content of the resulting carboxymethylcellulose aminoamide determined by titration is 2.6%, which corresponds to a conversion of 83% of the ester groups.

2 f) 30 g of the same carboxymethylcellulose methyl ester are reacted with 40 g of dibutylaminoethylamine in the same manner. The amine nitrogen content of the resulting carboxymethylcellulose aminoamide determined by titration is 2.4%, which corresponds to a conversion of 80% of the ester groups.

2 g) 30 g of carboxymethylcellulose methyl ester obtained according to Section 1 b) are heated at 150°C for 1 hour together with 24 g of dimethylaminopropylamine and 100 g of isopropanol in a 250 ml laboratory autoclave, while stirring, a pressure of about 10 bar developing. After cooling, the product is filtered off with suction and washed with isopropanol. After drying, the amine nitrogen content is determined as 2.4% by titration, which corresponds to a conversion of 65% of the ester groups. The Brookfield viscosity of a 2% strength aqueous solution of the carboxymethylcellulose aminoamide prepared is 500 mPas.

3. Quaternization of the aminoamide of carboxymethylcellulose
(Process stage c))

3 a) 25 g of carboxymethylcellulose aminoamide obtained according to Section 2 b) are suspended in 400 ml of methanol. A slow stream of chloromethane is passed into the suspension at room temperature; this procedure is continued until no further chloromethane is absorbed. This can easily be determined by condensation of the excess chloromethane in a cold trap downstream. The reaction has ended after about 5 hours. The product is filtered off with suction. Amine nitrogen is no longer clearly detectable in the resulting quaternary ammonium derivative of the cellulose by titration of an aqueous solution of the polymer with perchloric acid. The chloride content is 7.2%. The $^1$H-NMR spectrum recorded in $D_2O$ shows the signals of the methyl substituents of the tertiary amino group at 2.9 ppm and of the quaternary ammonium group at 3.2 ppm as characteristic peaks. The intensity ratio of these signals indicates a conversion of about 90%. On the basis of a carboxymethylcellulose with a degree of substitution DS = 0.9, a conversion in the esterification reaction of about 90% and a conversion in the amidation reaction of 92%, a degree of substitution, based on the quaternary groups, of DS = about 0.67 results.

3 b) 25 g of carboxymethylcellulose aminoamide, the preparation of which is described in Section 2 c) are reacted with chloromethane in accordance with Section 3 a). Amine nitrogen is no longer clearly detectable in the resulting quaternary ammonium derivative of the cellulose by titration with perchloric acid. The chloride content of the product is 6.8%.

3 c) 25 g of cellulose aminoamide, the preparation of which is described in Section 2 d), are reacted with chloromethane in accordance with Section 3 a). Amine nitrogen is no longer clearly detectable in the resulting quaternary ammonium derivative of the cellulose by titration with perchloric acid. The chloride content of the product is 6%.

3 d) 25 g of carboxymethylcellulose aminoamide, the preparation of which is described in Section 2 e), and 120 ml of methanol are introduced into a 250 ml laboratory autoclave. About 6 g of chloromethane are added, by passing in and by condensation. The mixture is then heated at 80°C for 5 hours. After cooling, the excess chloromethane and some of the methanol are removed under reduced pressure. The product is filtered off and dried. Amine nitrogen is no longer clearly detectable by titration with perchloric acid; the chloride content is 5.5%.

3 e) 25 g of the carboxymethylcellulose aminoamide, the preparation of which is described in Section 2 f), are quaternized with an excess of chloromethane in accor-

dance with Section 3 d). The chloride content is 4.6%.

3 f) 25 g of carboxymethylcellulose aminoamide corresponding to Section 2 b) are suspended in 300 ml of solvent consisting of 9 parts of isopropanol and 1 part of water, 36.6 g of butyl bromide are added and the mixture is heated at 60°C for 5 hours, while stirring intensively. After cooling, the product is filtered off, washed with isopropanol and dried. The bromide content is 12.5%.

3 g) 25 g of carboxymethylcellulose aminoamide corresponding to Section 2 b) are suspended in 300 ml of solvent consisting of 9 parts of isopropanol and 1 part of water, 33.8 g of benzyl chloride are added and the mixture is heated at 60°C for 5 hours, while stirring intensively. After cooling, the product is filtered off, washed with isopropanol and dried. The chloride content is 6.8%.

3 h) 25 g of carboxymethylcellulose aminoamide corresponding to Section 2 b) are suspended in 300 ml of solvent consisting of 9 parts of isopropanol and 1 part of water, 41 g of diethyl sulphate are added and the mixture is heated at 60°C for 8 hours, while stirring intensively. After cooling, the product is filtered off, washed with isopropanol and dried. The $^1$H-NMR spectrum recorded in $D_2O$ shows the signals of the methyl substituents of the tertiary amino group at 2.9 ppm and of the quaternary ammonium group at 3.2 ppm as characteristic

peaks. The intensity ratio of these signals indicates a conversion of about 80%.

II Investigation of the solution properties of quaternary cellulose derivatives according to the invention in water in comparison with that of other quaternary cellulose derivatives of the prior art.

The solution properties of the following quaternary cellulose derivatives are investigated:

A: A low-viscosity hydroxyethylcellulose modified with 3-chloro-2-hydroxypropyltrimethylammonium chloride, corresponding to DE-PS 15 93 657. The product has a nitrogen content of 1.7% and is commercially available under the name Polymer JR 400.

B: A relatively high-viscosity hydroxyethylcellulose modified with 3-chloro-2-hydroxypropyltrimethylammonium chloride, corresponding to DE-PS 15 93 657. The product has a nitrogen content of 1.7% and is commercially available under the name Polymer JR 30 M.

C: A cellulose modified with glycidol and then with 3-chloro-2-hydroxypropyltrimethylammonium chloride, corresponding to Example S 7 of DE-OS 33 01 667. The product has a nitrogen content of 2.2%.

D: A cellulose derivative, according to the invention, containing quaternary ammonium groups. Its preparation is described in Section 3 a).

In each case 1 g of the cellulose derivatives A, B, C and D is introduced into 99 g of water at 20°C, while stirring with a magnetic stirrer (about 300 revolutions per minute). The time taken for complete solution of the products is measured. The solutions formed are evaluated in respect of their nature. The results are summarized in the following table:

| Product | Time required for complete dissolution [min] | Consistency of the solution | Brookfield viscosity of the solution [mPas] |
|---|---|---|---|
| A | 75 | clear | 400 |
| B | 75 | clear | 1200 |
| C | > 75 | cloudy | 100 |
| D | 20 | clear | 300 |

III

1. Treatment of hair with quaternary cellulose derivatives according to the invention and quaternary cellulose derivatives of the prior art

In each case 0.1% strength by weight aqueous solutions of the quaternary cellulose derivatives A, B and C, which correspond to the prior art, and five different quaternary cellulose derivatives according to the invention are prepared. For simplification, the quaternary cellulose derivatives according to the invention are identified as follows:

D Preparation described in Section 3 a)
E Preparation described in Section 3 b)
F Preparation described in Section 3 c)
G Preparation described in Section 3 d)
H Preparation described in Section 3 g)

The aqueous solutions of the cellulose derivatives A, B and C which are not according to the invention are described in Section II.

Fine Chinese hair 15 cm long is bleached with a commercial bleaching agent for 1 hour in accordance with the prescribed instructions and is then dried. The conditioner included with the bleaching agent is not used. The now lightened and damaged hair is tied into hanks of about 1 g each. The hanks are left in the solutions described above at 30°C for 10 minutes. They are then rinsed thoroughly with lukewarm running water for 3 minutes, dried in air for 12 hours and combed. In each case 3 hanks of hair are treated with each of the solutions.

The shine of the treated hanks of hair is generally significantly improved and good to very good. As regards handle and combability, there are significant differences between the variously treated hanks of hair, on the basis of which the cellulose derivatives A to H can be arranged in a sequence, the cellulose derivatives which give the best result being mentioned first. The following results are obtained:

Wet combability: E > D > F > A = H > G > C = B >> bleached, non-treated hair

Dry combability: H = D > F > E > G > C > B > A >> bleached, non-treated hair

Handle: E > D > G > H > C = F > B > A >> bleached, non-treated hair

According to these results, the cellulose derivatives D and E according to the invention are to be evaluated as especially suitable for this use.

2. Treatment of hair with shampoo formulations which contain quaternary cellulose derivatives according to the invention and quaternary cellulose derivatives of the prior art

Shampoo formulations consisting of 1% of cellulose derivative, 20% of sodium lauryl sulphate, 4% of sodium chloride and 75% of water are prepared with the quaternary cellulose derivatives A to H described in the above section.

Fine Chinese hair is bleached and tied into hanks as described.

For the treatment, the hanks of hair are immersed in the shampoo formulations, diluted with 9 parts of water, at 20°C for 10 minutes and then rinsed thoroughly with lukewarm running water for 3 minutes, dried in air for 12 hours and combed. In each case 3 hanks of hair are treated with each of the shampoo solutions.

The shine of the treated hanks of hair is generally significantly improved and good to very good. There are significant differences in respect of handle and combability. The following results are obtained:

Wet combability: E > D > F = H = G = A > C > B >> bleached, non-treated hair

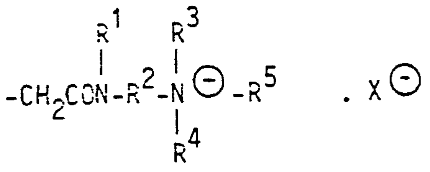
Dry combability: H > G > E > D > C > F > B > A >> bleached, non-treated hair

Handle: E > D > G > C > F > H > B > A >> bleached, non-treated hair

The shampoo formulations prepared with the cellulose derivatives C, D, E and G have the effect of a particularly pleasant handle of the hair, although cellulose derivative C also produces an increased static friction (tackiness). The shampoo formulations prepared with the other cellulose derivatives have the effect of a less smooth, less flexible handle, but the handle of this hair is also significantly improved in comparison with that of the untreated hair.

CLAIMS

1. A compound having the structure of carboxymethylcellulose in which at least one carboxymethyl group is replaced by a group of the general formula (I):

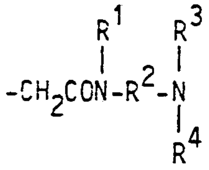


$$-CH_2CO\overset{R^1}{\overset{|}{N}}-R^2-\underset{R^4}{\underset{|}{\overset{R^3}{\overset{|}{N}}}}{}^{\ominus}-R^5 \quad . X^{\ominus}$$

(I)

wherein $R^1$ is hydrogen or a methyl group, $R^2$ is a straight chain or branched divalent aliphatic $C_2$-$C_5$ hydrocarbon group, $R^3$ and $R^5$ are each, independently, a straight chain or branched $C_1$-$C_4$ alkyl group, $R^5$ is a straight chain or branched $C_1$-$C_4$ alkyl group or a benzyl group and X is a halogen atom, a sulphate ester group or a sulphonic acid group, with the proviso that at least 0.1 quaternary ammonium groups are present on average per anhydroglucose unit of the compound's structure.

2. A compound having the structure of carboxymethylcellulose in which at least one carboxymethyl group is replaced by a group of the general formula (II):



$$-CH_2CO\overset{R^1}{\overset{|}{N}}-R^2-\underset{R^4}{\underset{|}{\overset{R^3}{\overset{|}{N}}}}$$

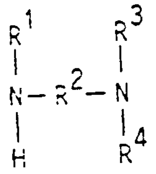
(II)

wherein $R^1$, $R^2$, $R^3$ and $R^4$ are as defined in Claim 1, with the proviso that at least 0.1 groups of formula (II) are present on average per anhydroglucose unit of the polymer's structure.

3. A process for the preparation of a compound as claimed in claim 2 which comprises:

(a) esterifying an alkali metal salt of carboxymethylcellulose with, based on the carboxymethyl groups, up to a 10-fold molar excess of a $C_1$-$C_3$ alkyl chloride, at a temperature of from 80 to 170°C under a pressure of from 5 to 100 bar over a reaction time of 1 to 24 hours, and after the esterification has taken place, removing the excess alkyl chloride from the reaction mixture; and

(b) reacting the ester of the carboxymethylcellulose produced in step (a) with an amine of the general formula (III):



$$\underset{\displaystyle H}{\overset{\displaystyle R^1}{N}}-R^2-\underset{\displaystyle R^4}{\overset{\displaystyle R^3}{N}}$$

(III)

wherein $R^1$, $R^2$, $R^3$ and $R^4$ are as defined in Claim 1, at a temperature of from 80 to 150°C over a reaction time of 1 to 10 hours, under reduced pressure if appropriate, in an amount such that 1 to 10 moles of the amine are employed per mole of ester group.

4. A process according to claim 3 which comprises, after the reaction of step (b) has taken place, separating excess

amine from the reaction mixture.

5. A process according to claim 3 and substantially as hereinbefore described in the Examples.

6. A process for the preparation of a compound as claimed in claim 1 which comprises reacting a compound as claimed in claim 2 with, based on tertiary amino groups, at least an equimolar amount of a compound $X-R^5-COOM$, in which X is a halogen atom, M is an alkali metal or an ammonium ion and $R^5$ is as defined in Claim 1, at a temperature of from 40 to 125°C over a reaction time of 0.5 to 8 hours.

7. A process according to claim 6 wherein the compound as claimed in claim 2 is produced by the process as claimed in claim 3.

8. A process according to claim 6 and substantially as hereinbefore described in the Examples.

9. A process according to any one of claims 6 to 8 in which the product is purified by removing excess alkyl chloride by distillation or by filtering and washing the product in a polar organic solvent.

10. A compound according to claim 1 or 2 and specifically as hereinbefore mentioned.

11. A composition suitable for application to the hair which comprises, in a cosmetically acceptable aqueous vehicle, from 0.1 to 2.5 % by weight of a compound as claimed in claim 1.

12. A composition according to claim 11 and substantially

as hereinbefore described in the Examples.

13. A method for the cosmetic treatment of hair which comprises applying to the hair a compound as claimed in claim 1 or a composition as claimed in claim 11 or 12.

14. A method of thickening an aqueous solution or an aqueous suspension suitable for use in the treatment of textile fibres, textile yarns or sheet-like fibres, or of thickening an aqueous binder, which comprises adding to the solution, suspension or binder a compound as claimed in claim 1.

15. A method for producing paper from pulp which comprises adding to the pulp a compound as claimed in claim 1.

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