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(54) Title: ACRYLAMIDE AND TRIALKYLAMMONIUM SALT COPOLYMER, METHOD FOR OBTAINING SAME AND COATED TEXTILE (54) Titre: COPOLYMERE D'ACRYLAMIDE ET DE SELS DE TRIALKYLAMMONIUM, PROCEDE D'OBTENTION ET TEXTILE ENDUIT (57) Abstract The invention concerns an acrylamide or acrylamide derivative and trialkylammonium salt copolymer capable of being obtained by radical copolymerisation, in the presence of an initiator, of at least a first monomer selected among acrylamide and its derivatives, and of a second monomer, selected among trialkylammonium salts corresponding to the following formula (I): $[H_2C = C(R_1) - (CH_2)_n - A - (CH_2)_{n'} - N^+(R_2)(R_3)(R_4)]X^-$ wherein: R_1 represents H or an alkyl group with 1 to 3 carbon atoms; R_2, R_3 and R_4, identical or different, represent each an alkyl group with 1 to 3 carbon atoms; n and n' represent each, independently of one another, a non-null integer not more than 15; A represents a carboxyl or amide bivalent function; and X^- represents a counter-ion. The invention also concerns a method for obtaining said copolymer, one use thereof for obtaining a textile support biocide by contact, and such a coated textile. (57) Abrégé L'invention concerne un copolymère d'acrylamide ou de dérivés d'acrylamide et de sels de trialkylammonium susceptible d'être obtenu par copolymérisation radicalaire, en présence d'un amorceur, d'au moins un premier monomère choisi parmi l'acrylamide et ses dérivés, et d'un second monomère, choisi parmi les sels de trialkylammonium répondant à la formule (I) suivante: $[H_2C = C(R_1) - (CH_2)_n - A - (CH_2)_{n'} - N^+(R_2)(R_3)(R_4)]X^-$ dans laquelle R_1 représente H ou un groupe alkyle ayant de 1 à 3 atomes de carbone, R_2, R_3 et R_4 identiques ou différents, représentent chacun un groupe alkyle ayant de 1 à 3 atomes de carbone, n et n' représentent chacun, indépendamment l'un de l'autre, un entier non nul au plus égal à 15, A représente une fonction bivalente carboxyle ou amide, et X^- représente un contre-ion. L'invention concerne aussi un procédé d'obtention d'un tel copolymère, une utilisation de ce dernier pour obtenir un support textile biocide par contact, et un textile ainsi enduit.		

COPOLYMER OF ACRYLAMIDE AND OF TRIALKYLAMMONIUM SALTS,
PREPARATION PROCESS AND COATED TEXTILE

The present invention relates to a copolymer
5 of acrylamide or acrylamide derivative and of
trialkylammonium salts which exhibits a biocidal nature
and is intended in particular for the coating of
substrates.

In the following description, the invention
10 is more particularly set out with reference to a
copolymer for the impregnation of a textile substrate,
but, of course, it should not be regarded as being
limited thereto, it being possible for the copolymer of
the invention to be applied to other substrates, such
15 as leather, wood or plastic substrates.

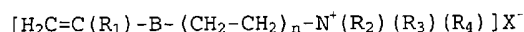
The term "biocidal" is understood to mean the
property which consists in destroying a microorganism,
such as fungi, yeasts or bacteria. More specifically,
the copolymer which is the subject-matter of the
20 invention exhibits, and confers on the substrate to
which it is applied, a contact biocidal nature, which
means that it directly brings about the death of the
microorganisms by simple contact.

The present invention is mainly of advantage
25 in the medical field, where the need to have available
means for protecting against pathogenic agents is
ceaselessly increasing.



The properties required for a textile for medical use are, first, a biocidal effect and good absorption of liquids.

A biocidal or antiseptic compound
5 corresponding to the following formula:



in which,

- 10 R_1 represents H or CH_3 ,
 R_2 , R_3 and R_4 each represent an alkyl group
such that the total number of carbon atoms of R_2 , R_3 and
 R_4 varies from 6 to 15,
 n varies from 1 to 3,
15 B represents CH_2 , a carboxyl functional group
or an amide functional group, and
 X^- represents a counterion,
is known according to the document FR-A-2,695,800.

The compound disclosed is used for the
20 preparation of biocidal fabric cotton textile under
conditions of grafting the said compound by radical
activation under the effect of ionizing radiation, such
as γ radiation.

The manufacture on an industrial scale of a
25 biocidal textile as disclosed according to FR-A-2, 695,
800, and more particularly the stage of grafting the
compound to the substrate, represents a very heavy
technological investment and, furthermore, requires a



workforce necessarily trained in nuclear techniques, due to the harmful effects of such radiation.

The Applicant Company has discovered a biocidal product which makes it possible to solve the problem posed by known biocidal compounds by introducing a product which
 5 can be attached to a substrate by simple impregnation. In particular, when the substrate is textile, the attachment of the product can be carried out by standard techniques of this industry, in particular padding.

According to a first aspect, the present invention consists in a copolymer of acrylamide or acrylamide derivative and of trialkylammonium salts which can be
 10 obtained by radical copolymerization, in the presence of an initiator,

- of at least of a first monomer chosen from acrylamide and its derivatives of formula



in which n" is an integer which can vary from 1 to 5, and advantageously from 1 to 3

- and of a second monomer chosen from trialkylammonium salts corresponding to the
 15 following formula (I)



in which,

R₁ represents H or an alkyl group having from 1 to 3 carbon atoms,

R₂, R₃ and R₄, which are identical or different, each represent an alkyl group having
 20 from 1 to 3 carbon atoms,

n and n' each represent, independently of one another, a non-zero integer at most equal to 15,

A represents a divalent carboxyl or amide functional group, and

X⁻ represent a counterion.

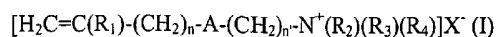
25 According to a second aspect, the present invention consists in a process for preparing the copolymer according to the first aspect, which process comprises the stages consisting in reacting

- at least a first monomer chosen from acrylamide and its derivatives of formula



30 in which n" is an integer which can vary from 1 to 5,

- and of a second monomer chosen from trialkylammonium salts corresponding to the following formula (I)



in which,

R₁ represents H or an alkyl group having from 1 to 3 carbon atoms,

R_2 , R_3 and R_4 , which are identical or different, each represent an alkyl group having from 1 to 3 carbon atoms,

n and n' each represent, independently of one another, a non-zero integer at most equal to 15,

5 A represents a divalent carboxyl or amide functional group, and

X^- represent a counterion,

in a solvent at reflux temperature, in the presence of an initiator.

According to a third aspect, the present invention consists in textile coated with a copolymer according to the first aspect.

10 According to a fourth aspect, the present invention consists in use of a copolymer according to the first aspect for preparing a textile substrate which is biocidal by contact.

According to a sixth aspect, the present invention consists in a substrate coated with a copolymer of the first aspect.

15 Preferably, the first monomer is acrylamide or else the second monomer corresponds to the abovedescribed formula (I) in which n varies from 7 to 9, n' varies from 2 to 4 and X^- represents Cl^- , F^- or an alkyl sulphate ion.

The second monomer advantageously corresponds to the abovedescribed formula (I) in which R_1 represents H; R_2 , R_3 and R_4 are identical and each represent the methyl group; n is equal to 8 and n' is equal to 3; A represents the amide functional group; and X^- 20 represents the methyl sulphate ion.

As will be illustrated in the examples at the end of the description, a particularly advantageous copolymer according to the invention is that which can result from the copolymerization between the preferred first monomer and the preferred second monomer identified above.



More advantageously still, the weight-average molecular weight (Mw) of the copolymers is between 6000 and 10,000.

According to an alternative form of the invention, a copolymer can consist of a terpolymer which can be obtained by radical copolymerization at least of the said first monomer, of the said second monomer and, in addition, of a third monomer chosen from acrylic acid and vinyl esters. Mention may be made, by way of example of such esters, of vinyl acetate, vinyl propionate and vinyl butyrate.

Another subject-matter of the invention is a process for preparing a copolymer defined above. It comprises the stages consisting in reacting at least a first monomer, a second monomer and optionally a third monomer, as have been defined above, in a solvent at the reflux temperature, in the presence of an initiator.

Preferably, the first monomer is acrylamide and/or the second monomer corresponds to the formula (I) in which n varies from 7 to 9, n' varies from 2 to 4 and X^- represents Cl^- , F^- or an alkyl sulphate ion.

The second monomer advantageously corresponds to the formula (I) in which R_1 represents H; R_2 , R_3 and R_4 are identical and each represent the methyl group; n is equal to 8 and n' is equal to 3; A represents the amide functional group; and X^- represents the methyl



sulphate ion. If appropriate, the third monomer is acrylic acid.

Moreover, the process of the invention exhibits the following preferred characteristics, considered alone or in combination:

- the molar concentration of the second monomer is at least equal to 20% with respect to the final molar concentration of the first and second monomers and of the third monomer, if necessary; this concentration is advantageously at least equal to 25% and at most equal to 40%;
- the solvent in which the monomers are reacted is a water/ethanol mixture in a molar ratio preferably varying from 25/75 to 50/50;
- the initiator is chosen from 2,2'-azobis(2-amidinopropane) hydrochloride and potassium persulphate;
- the first, second and optionally third monomers are reacted under a nitrogen flow.

Another subject-matter of the invention is a textile coated with a copolymer of the invention. This textile is preferably chosen from cotton fabrics and polyester nonwovens, which are the most frequently employed textiles, in particular in the medical field.

The invention also relates to the use of a copolymer defined above for preparing a textile which is biocidal by contact.



The characteristics and advantages of the subject-matters of the invention are demonstrated in the following Examples 1 to 4.

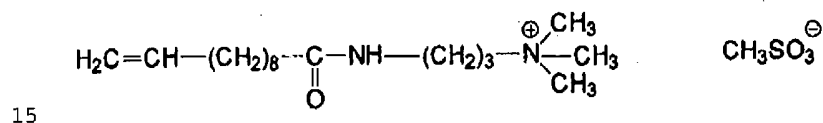
5 **EXAMPLE 1: Preparation of a preferred copolymer according to the invention**

1/ Products involved

- Monomers:

First monomer: acrylamide

10 Second monomer:
trimethyl(undecylamidepropyl)ammonium methyl
sulphate (Noranium[®] MU 50; Elf Atochem S.A.)
of formula:



Third monomer: acrylic acid

- Initiator : 2,2'-azobis(2-amidinopropane)
hydrochloride (V50[®]; Wako) or potassium
20 persulphate
- Solvent : water/methanol mixture.

2/ Principle

The copolymerization is carried out under
25 pad-batch conditions, that is to say by simultaneous
introduction in a single step of the monomers into the

reactor, under a nitrogen flow (in order to remove the dissolved oxygen, which is a polymerization inhibitor) and at 70°C (reflux temperature of the methanol).

The formulations are prepared for a volume of
5 solution of 1 litre (synthesis on a laboratory scale)
and 100 litres (synthesis on an industrial scale).

3/ Equipment

Synthesis on a laboratory scale is carried
out in a two-litre reactor comprising a jacket, which
10 jacket is connected to a thermostatically-controlled
bath, and equipped with a reflux condenser terminated
by a bubbler, with a mechanical stirrer indicating the
rotational speed and with an inlet for the introduction
of the various products.

15 Use is made, for synthesis on an industrial
scale, of a 300-litre reactor equipped with similar
facilities and with a nitrogen inlet.

4/ Synthesis of the copolymer

- *Synthesis on a laboratory scale*

20 Various copolymers are prepared: copolymers
based on acrylamide and on Noranium® MU 50 and
terpolymers based on acrylamide, on Noranium® MU 50 and
on acrylic acid, while varying, for each synthesis, the
following parameters: proportions of the various
25 monomers (Norianium® MU 50/acrylamide/acrylic acid,
abbreviated to Nor/Acry/AcryAc), overall monomer
concentration, and methanol concentration.

The concentration of initiator V50[®] is constant (1 g/l).

The parameters chosen for the syntheses and the results are collated in Table 1.

5 - *Synthesis on an industrial scale*

The two copolymer solutions prepared correspond to the above copolymer solutions 19 and 26. They are obtained under the conditions of Table 1, with the exception of the fact that the initiator employed is potassium persulphate. The copolymers obtained (19' and 26', respectively) are identical.

5/ Characterization of the copolymer

The copolymer obtained is characterized by its final appearance (homogeneous solution, heterogeneous solution or gel), by the number-average molecular mass (M_n) and the weight-average molecular mass (M_w), and by the polydispersity index ($PI = M_w/M_n$), determined by gel permeation chromatography. These parameters appear in Table 1.

TABLE 1

Water/Methanol Solvent Ratio	Monomers		No.	Physical appearance of the product	Mn $\pm$ 5%	Mw $\pm$ 5%	PI
	Nor/Acry/AcryAc Ratio	Concentration of (%)					
50/50	10/90/0	10	14	Solution	29,000	33,700	1.2
	25/75/0	10	19	Solution	6500	13,500	2.1
	50/50/0	10	16	Solution	1000	5800	5.7
	10/88/2	10	24	Solution	18,000	30,700	1.7
	10/88/2	25	23	Gel	20,000	31,500	1.6
	25/73/2	10	27	Solution	13,000	22,600	1.8
75/25	25/65/10	10	26	Solution	9000	17,200	1.9
	10/88/2	25	22	Gel	16,700	28,200	1.7
100/0	25/73/2	10	25	Solution	11,700	21,200	1.8
	10/88/2	10	20	Solution	7600	17,100	2.2
	10/88/2	25	21	Gel	17,000	27,000	1.6

**EXAMPLE 2: Bactericidal power of the
copolymers**

1/ Principle

The copolymer solution is brought into
5 contact with a known population of *Pseudomonas*
aeruginosa ATC 9027 or *Staphylococcus aureus* ATCC 6538
which has been grown for approximately 12 hours in an
oven at 30°C in an initially sterile nutrient medium.

If N_0 (bacteria/cm³) is the initial bacterial
10 population and N_t (bacteria/cm³) is the population at
time t , the bacterial power is measured by calculating
 $\log(N_t/N_0)$.

The following effect is attributed to the
values of $\log(N_t/N_0)$:

15

$\log(N_t/N_0)$	Effect
Zero	bacteriostatic
Negative	bactericidal
Positive	no

2/ Counting of the bacteria

Use is made of the dilution method known as
"Microbiological tests" described in "United States
20 Pharmacopeia XIX".

The bacteria are counted according to the
method known under the name "Most Probable Total Count
by Multiple-tube Method".

3/ Results

The bactericidal power of the copolymer solutions 14, 16 and 19, calculated according to a contact time varying from 1 to 24 hours, is given in

5 Table 2.

The concentration as Noranium[®] MU 50 (Nor) equivalent of each copolymer solution is expressed in mol/l.

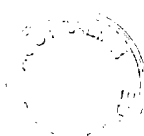


TABLE 2

Copolymer Solution No.	T (hours)	Pseudomonas aeruginosa		Staphylococcus aureus	
		Population N (bacteria/ml)	Log N_t/N_0	Population N (bacteria/ml)	Log N_t/N_0
14 (Nor = 0.10)	0	2.5×10^7	-	4.5×10^6	-
	1	9×10^3	- 3.44	ND	ND
	4	5×10^3	- 3.70	4.5×10^2	-4.00
	7	9×10^2	- 4.44	ND	ND
	24	3×10^2	- 4.92	2.5×10^2	-4.25
19 (Nor = 0.17)	0	2.5×10^7	-	4.5×10^6	-
	1	5×10^3	- 3.70	ND	ND
	4	5×10^2	- 4.44	3×10^2	-4.17
	7	3×10^2	- 4.92	ND	ND
	24	3×10^2	- 4.92	2.5×10^2	-4.25
16 (Nor = 0.20)	0	2.5×10^7	-	4.5×10^6	-
	1	9×10^2	- 4.44	ND	ND
	4	3×10^2	- 4.92	2.5×10^2	-4.25
	7	3×10^2	- 4.92	ND	ND
	24	3×10^2	- 4.92	0.9×10^2	-4.69

ND = not determined

It is observed that the biocidal activity is
 5 very high for all the copolymer solutions, from the
 first hour.

When the Noranium[®] MU 50 concentration in the
 solution increases, the biocidal activity of the
 polymer increases.

10 **EXAMPLE 3: Preparation of a textile with a
 biocidal nature**

1/ Textile

Use was made of a cotton textile and of a
 70 g/m² polyester nonwoven.

2/ Impregnation

The trials are carried out with the copolymers 14, 16, 19, 20, 24, 25 and 26.

For the impregnation, the following

5 conditions are:

- Horizontal padding mangle from Laboratoire Werner Mathis,

- rolls: hardness of the rubber 70° Shore,
width 350 mm, diameter 110 mm,
- 10 • pressure between the rolls: 100%, i.e.
40-45 kg/cm,
- depth of immersion in the bath: 40 mm,
- Thermosetting treatment (vaporizing of water),
- Drying on a stenter at 50°C,
- 15 - Direct impregnation, according to which the
copolymer solution is placed between the rolls of
the padding mangle,
- One or two passes in the padding mangle.

The various trials are compared according to:

- 20 - the level of the loading,
- the quality of the feel, with the following key:
-- means a very poor feel (pronounced "cardboard"
effect), - means a poor feel (stiff textile),
+ means an average feel and ++ means a pleasant
25 feel (virtually identical to that of the untreated
textile).

The results are collated in Table 3.

TABLE 3

Type of Textile	Copolymer Solution No.	Number Passes Padding mangle	Level of loading on a dry basis (%)	Quality of the feel
Cotton fabric	14	1	11	-
		2	11	-
	19	1	9.7	+
		2	8.8	+
	16	1	7.6	+
		2	6.9	+
	24	1	12.4	-
	27	1	10.8	+
	26	1	12.2	+
	25	1	10.4	+
	20	1	10.7	-
Nonwoven	14	1	17.5	--
		2	19.4	-
	19	1	15	+
		2	16.7	+
	16	1	55.6	+
		2	12.8	+
	24	1	20	-
	27	1	14.2	+
	26	1	19.5	+
	25	1	1.3	+
	20	1	17.8	-

As regards the level of loading, that is to say the amount of polymer attached to the substrate,

5 the results are relatively close, whatever the solutions used (with or without acrylic acid).

The results of the textile application are entirely acceptable.

It should be noted that trials carried out on a cotton fabric and on a nonwoven with all the
5 abovementioned copolymer solutions gave similar results in terms of quality to the feel.

EXAMPLE 4: Bactericidal power of an impregnated textile

1/ Principle

10 The principle of this test, disclosed in the document FR-A-2,695,800, is restated hereinbelow.

Samples with an identical size (discs with a diameter of 34 mm) of each of the substrates are introduced into sterile flasks (diameter substantially
15 identical to the disc), so as to completely cover the lower surface.

A suspension of *Pseudomonas aeruginosa* ATCC 9027 is prepared (0.4 ml in nutrient medium) and introduced into an oven at 30°C for a few hours.

20 The following are prepared for each type of textile tested:

- a sample of each trial,
- two control samples (before impregnation):
one in order to determine the number of
25 bacteria at the start ("Control 0") and the other in order to know the number of bacteria which are growing after 24 hours ("Control 24").

The samples are inoculated with:

- 0.2 ml of bacterial suspension for the samples of 70 g/m² nonwoven,
- 0.6 ml of bacterial suspension for the samples of cotton fabric.

5

A first counting of bacteria is carried out on the "Controls 0". The other flasks ("Controls 24" + various trials) are introduced into an oven at 30°C and, after 24 hours, the number of bacteria present in the medium is determined.

10

The bacteria are counted by the method of Example 2, paragraph 2.

2/ Results

The bacteriological tests were carried out on samples of cotton fabrics (solely the fabrics after attachment) and of polyester nonwovens which are impregnated with the copolymer solutions 14, 16, 19, 25, 26 and 27.

15

The results are collated in the following Table 3.

20

TABLE 4

Textile	Copolymer Solution No.	Nor (mol/l)	Level of loading (%)	Time (Hour)	Control	Impregnated
Cotton fabric	14	0.1	11.0	0	2.5×10^4	ND
				24	2.5×10^7	3×10^1
	19	0.17	9.7	0	4.5×10^3	ND
				24	$> 1 \times 10^8$	2.5×10^1
	16	0.20	7.6	0	4.5×10^3	ND
				24	$> 1 \times 10^8$	4.5×10^1
Nonwoven	25	-	10.4	0	0.7×10^4	ND
				24	$> 1 \times 10^9$	2.5×10^1
	26	-	12.2	0	0.7×10^4	ND
				24	$> 1 \times 10^9$	2.5×10^1
	27	-	10.8	0	0.7×10^4	ND
				24	$> 1 \times 10^9$	2.5×10^1
Nonwoven	14	0.1	17.5	0	2.5×10^4	ND
				24	4.5×10^6	1.5×10^2
	19	0.17	15	0	2.5×10^3	ND
				24	4.5×10^5	2.5×10^1
	16	0.20	55.6	0	2.5×10^3	ND
				24	4.5×10^5	4.5×10^1
Nonwoven	25	-	1.3	0	1.5×10^2	ND
				24	9.5×10^7	2.5×10^1
	26	-	19.5	0	1.5×10^2	ND
				24	9.5×10^7	1.1×10^1
	27	-	14.2	0	1.5×10^2	ND
				24	9.5×10^7	2.5×10^1

ND = Not Determined

5 The results obtained are excellent.

The amount of acrylic acid in the solution
apparently does not influence the results.

The antimicrobial power of the nonwoven polyester substrates is generally slightly less than that of the woven cotton substrates.

The claims defining the invention are as follows:

1. Copolymer of acrylamide or acrylamide derivative and of trialkylammonium salts which can be obtained by radical copolymerization, in the presence of an initiator,

- of at least of a first monomer chosen from acrylamide and its derivatives of formula



in which n'' is an integer which can vary from 1 to 5,

- and of a second monomer chosen from trialkylammonium salts corresponding to the following formula (I)



in which,

R_1 represents H or an alkyl group having from 1 to 3 carbon atoms,

R_2 , R_3 and R_4 , which are identical or different, each represent an alkyl group having from 1 to 3 carbon atoms,

n and n' each represent, independently of one another, a non-zero integer at most equal to 15,

A represents a divalent carboxyl or amide functional group, and

X^- represent a counterion.

2. Copolymer according to claim 1, wherein n varies from 7 to 9, n' varies from 2 to 4 and X^- represents Cl^- , F^- or an alkyl sulphate ion.

3. Copolymer according to claim 2, wherein R_1 represents H; R_2 , R_3 and R_4 are identical and each represent the methyl group; n is equal to 8 and n' is equal to 3; A represents the amide functional group; and X^- represents the methyl sulphate ion.

4. Copolymer according to claim 2 or 3, wherein the first monomer is acrylamide.

5. Copolymer according to any one of claims 1 to 4, which can be obtained by radical copolymerization at least of the said first monomer, of the said second monomer and, in addition, of a third monomer chosen from acrylic acid and vinyl esters.

6. Process for preparing a copolymer according to claim 1, which process comprises the stages consisting in reacting

- at least a first monomer chosen from acrylamide and its derivatives of formula



in which n'' is an integer which can vary from 1 to 5,

- and of a second monomer chosen from trialkylammonium salts corresponding to the following formula (I)



in which,

R_1 represents H or an alkyl group having from 1 to 3 carbon atoms,

R_2 , R_3 and R_4 , which are identical or different, each represent an alkyl group having from 1 to 3 carbon atoms,

5 n and n' each represent, independently of one another, a non-zero integer at most equal to 15,

A represents a divalent carboxyl or amide functional group, and

X^- represent a counterion,

in a solvent at reflux temperature, in the presence of an initiator.

10 7. Process according to claim 6, wherein the first monomer is acrylamide and the second monomer corresponds to the formula (I) in which n varies from 7 to 9, n' varies from 2 to 4 and X^- represents Cl^- , F^- or an alkyl sulphate ion.

8. Process according to claim 6 or 7, wherein the second monomer corresponds to the formula (I) in which R_1 represents H; R_2 , R_3 and R_4 are identical and each represent
15 the methyl group; n is equal to 8 and n' is equal to 3; A represents the amide functional group; and X^- represents the methyl sulphate ion.

9. Process according to any one of claims 6 to 8, wherein the molar concentration of the second monomer is at least equal to 20% with respect to the molar concentration of the first and second monomers.

20 10. Process according to claim 9, wherein the molar concentration of the second monomer is at least equal to 25% and at most equal to 40% with respect to the final molar concentration of the first and second monomers.

11. Process according to claim 6, wherein a third monomer chosen from acrylic acid and vinyl esters is additionally reacted.

25 12. Process according to claim 6, wherein the solvent is a water/methanol mixture in a molar ratio varying from 25/75 to 50/50.

13. Process according to claim 6, wherein the initiator is chosen from 2,2'-azobis (2-amidinopropane) hydrochloride and potassium persulphate.

30 14. Process according to claim 6 or 11, wherein the first, second and optionally a third monomer are reacted under nitrogen flow.

15. Textile coated with a copolymer according to any one of claims 1 to 5 or prepared by the process of any one of claims 6 to 14.

16. Textile according to claim 15, which is chosen from cotton fabrics and polyester nonwovens.

17. Use of a copolymer according to any one of claims 1 to 5 or prepared by the process of any one of claims 6 to 14, for preparing a textile substrate which is biocidal by contact.

18. Copolymer according to claim 1 substantially as hereinbefore described with
5 reference to any one of the examples.

19. Copolymer of acrylamide or of acrylamide derivative and or trialkylammonium salts substantially as described in Example 1 or 2.

20. Process according to claim 6, said process being substantially as hereinbefore described with reference to any one of the examples.

10 21. Copolymer as defined in claim 1 prepared by the process claimed in any one of claims 6 to 14 or 20.

22. A substrate coated with a copolymer as claimed in any one of claims 1 to 5, 18 or 19 or prepared by the process of any one of claims 6 to 14 or 20.

15 23. A substrate according to claim 22, substantially as hereinbefore described with reference to any one of the examples.

24. Textile coated with a copolymer according to claim 1, substantially as described in Example 3 or 4.

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