United States Patent [19]
Bille et al.

[11] **3,862,073**
[45] **Jan. 21, 1975**

[54] EMULSIFIER COMPOSITIONS FOR CREASEPROOFING TEXTILE MATERIALS WHICH CONTAIN COPOLYMERS OF UNSATURATED CARBOXYLIC ACIDS AND THEIR ESTERS

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[22] Filed: **June 27, 1972**

[21] Appl. No.: **266,608**

[30] **Foreign Application Priority Data**

July 5, 1971 Germany............................ 2133351

[52] U.S. Cl... **260/29.4 UA,** 260/17 R, 260/18 WF, 260/23 EM, 260/28.5 B, 260/29.6 MQ, 260/29.6 ME, 260/29.7 T, 117/139.5 A, 117/161 UT, 117/161 UD

[51] **Int. Cl.**.. **C08f 45/24**

[58] **Field of Search**............260/29.4 UA, 29.6 TA, 260/29.6 SQ, 29.6 MQ, 29.2 N, 29.7 T

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[57] ABSTRACT

Emulsifier compositions containing, apart from water and conventional surfactants, a copolymer of unsaturated carboxylic acids and their esters and optionally other comonomers for creaseproofing cellulosic textile materials with amino resin forming substances.

6 Claims, No Drawings

EMULSIFIER COMPOSITIONS FOR CREASEPROOFING TEXTILE MATERIALS WHICH CONTAIN COPOLYMERS OF UNSATURATED CARBOXYLIC ACIDS AND THEIR ESTERS

This invention relates to novel emulsifier compositions for creaseproofing textile materials containing cellulose and/or regenerated cellulose. The invention particularly relates to the use of such compositions in processes for creaseproofing textile materials in which part of the water is replaced by organic solvents.

Emulsifiers are materials capable of maintaining organic substances, primarily liquids, in a stable mixture with other liquids where such substances are not miscible with each other or soluble in each other. Such emulsifiers are important when it is desired to distribute organic, water-immiscible or water-insoluble substances in water in such a manner that they are uniformly present in the aqueous medium as if they were physically dissolved therein.

Emulsifiers of this kind have hitherto been used for the said purpose in resin finishing processes.

Recently, increaseproofing textiles, one of the most important finishing treatments, a considerable portion of the water has been replaced by organic solvents such as chlorinated hydrocarbons. The advantages of these solvents is, inter alia, that they penetrate the fabric and thus render it wettable.

Where it is desired to treat textiles using organic solvents, it is particularly recommended to exercise great care when selecting the emulsifiers, since it is known that an emulsion of liquids of different densities, particularly for example water and hexachloroethane, tends to be unstable.

German Published Applications **1,594,954** and **1,594,965** describe textile treatment baths based on methylolated amino resin-forming substances which contain organic solvents and include emulsifiers for stabilizing the emulsion, which emulsifiers are based on ethoxylated fatty acid amides and, according to German Published Application **1,594,965,** must also exhibit specific physical characteristics.

These methods, which indisputably provide advantages over previous methods as regards the ability to finish fabrics from oil-in-water emulsions, suffer from the drawback that such characteristics as tensile strength and crease recovery of fabrics creaseproofed thereby do not satisfy the textile consumer. The last-named developments have clearly been based on a very limited class of emulsifiers, namely ethoxylated fatty acid amides, i.e. weakly cationic surfactants intended to make stabilization of the emulsion possible.

However, in order to obviate said drawback, it was necessary to approach the problem from a new angle. It is an object of the invention to provide an emulsifier composition which not only makes it possible to obtain a stable water-in-oil emulsion but also influences known methylolated amino resin-forming substances in such a manner that excellent crease recovery is achieved and, in addition, tensile strength values are obtained which are substantially similar to those measured on untreated textiles.

According to the invention, the above object is achieved using emulsifier compositions for creaseproofing textile materials containing cellulose and/or regenerated cellulose in an aqueous liquor which may or may not contain organic solvents and which contains methylolated amino resin-forming substances and optionally amino resin-forming substances which have been etherified at the methylol group, said emulsifier compositions being characterized by contents of:

A. from 5 to 70 parts by weight of the composition of a copolymer containing polymerized units of the following monomers:
  a. from 1 to 10% by weight of the copolymer of an ethylenically unsaturated carboxylic acid which contains from 3 to 10 carbon atoms and which may or may not be substituted by hetero atoms or groups containing hetero atoms, or a mixture of said carboxylic acids,
  b. from 99 to 70% by weight of the copolymer of an ester of the carboxylic acids defined under (a) above with C_{1-8} alcohols of the aliphatic series, or a mixture of said esters and
  c. from 0 to 20% by weight of the copolymer of some other copolymerizable ethylenically unsaturated compound, which may or may not be capable of providing additional crosslinking, or a mixture of said unsaturated compounds,
B. from 30 to 80 parts by weight of the composition of a known cationic, anionic or non-ionic surface-active compound and
C. from 30 to 70 parts by weight of the composition of water.

Suitable comonomers (a) of component (A) are α,β-ethylenically unsaturated carboxylic acids of the aliphatic and aliphatic/aromatic series having from 3 to 10 carbon atoms. They may also be substituted by hetero atoms such as halogen atoms and in particular chlorine atoms, or by hetero atom-containing groups such as hydroxyl groups and alkoxyl groups. Also of commerical interest are mixtures of two or more of these acids, specific examples of which are acrylic acid, methacrylic acid, chloracrylic acid, crotonic acid, phenylacrylic acid, maleic acid, fumaric acid, itaconic acid and citraconic acid.

Of particular interest commerically are acrylic acid, methacrylic acid and mixtures thereof.

The monomer units (a) are conveniently incorporated in the copolymers in amounts ranging from 1 to 10% and preferably from 2 to 7 % by weight.

The comonomers (b) are esters of said acids (a) or mixtures of said esters. Of commerical interest are ester mixtures containing from 2 to 4 esters. The alcohols from which the esters are derived are of the saturated aliphatic series and contain from 1 to 8 and preferably from 1 to 6 carbon atoms. Particular examples thereof are methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, the amyl alcohols, hexyl alcohols and octyl alcohols, preferably methanol, ethanol, n-propanol, n-butanol and n-hexanol.

Of particular commercial interest are mixtures of methyl, ethyl, propyl, butyl and hexyl acrylates and/or methacrylates. Such esters are conveniently incorporated in the copolymers in amounts ranging from 99 to 70% and preferably from 98 to 75%. Suitable comonomers (c) are copolymerizable monomers which may be present in the copolymers in amounts of up to 20% by weight and which may, if desired, contain materials having a crosslinking effect.

Specific examples thereof are acylonitrile, methacrylonitrile, acrylamide, methacrylamide, styrene, ethylene, propylene, vinyl esters of saturated carboxylic acids such as vinyl acetate and vinyl propionate, vinyl ethers such as vinyl ethyl ether, vinyl chloride, vinylidene chloride, butadiene, isoprene, monomers having crosslinking groups such as N-methylolacrylamide and N-methylolmethacrylamide, 2-chloro-3-hydroxypropyl acrylate, 1,3-butanediol monoacrylate and 1,3-butanediol diacrylate.

These copolymers are prepared by known methods. Thus any of the free radical generating substances normally used for such copolymerization and generally known in the art of the manufacture of dispersions may be used for the present purpose. For example, free radical substances such as benzoyl peroxide, lauroyl peroxide, benzoic peroxide, peracetic acid, azoisobutyronitrile or other free radical substances may be used. Conventional molecular weight regulators and plasticizers, as commonly used for polymerizations, may also be present.

Suitable components (B), which may be present in the composition in amounts ranging from 30 to 80 parts by weight and preferably from 30 to 60 parts by weight, are all cationic, anionic and/or non-ionic surfactants such as have been conventionally used in the textile industry over many years. It is immaterial whether the surface-active agents are anionic, cationic or non-ionic. However, it is more convenient to use non-ionic or anionic compounds. Specific examples are alkali metal or ammonium salts of long-chain fatty acids or long-chain sulfonic acids and sulfuric acid half esters of polyoxyalkylated compounds which have been prepared from alcohols, carboxylic acids, carboxamides and alkylphenols by reaction with from 5 to 90 moles of ethylene oxide and/or propylene oxide. Suitable alcohols and carboxylic acids for this purpose are for example coconut fatty alcohol, sperm oil alcohol, wax alcohol, sperm oil fatty acid, stearic acid, palmitic acid, oleic acid, ricinoleic acid and corresponding products of paraffin oxidation. Apart from said fatty alcohols and acid derivatives, oxyalkylated alkylphenols are also highly suitable surfactants. Thus for example oxyalkylated alkylphenols having a degree of oxyalkylation of between 10 and 60 and in which the alkyl radicals contain from 6 to 14 carbon atoms and may be branched-chain or unbranched, may be used after conversion to the alkali metal or ammonium salts of their sulfuric acid half esters. Suitable alkylphenols from which these compounds are derived are for example iso-octylphenol, decylphenol, dodecylphenol and nonylphenol or the corresponding naphthols.

Instead of the fatty alcohols or the carboxylic acid oxyalkylates, the amides of the carboxylic acids are also highly suitable.

Component (C), which is present in the compositions in amounts ranging from 30 to 70 parts by weight, is water.

The compositions described above constitute excellent emulsifier systems for creaseproofing textile materials containing cellulose or regenerated cellulose.

It is well known that the basic component of a creaseproofing agent consists in a methylolated amino resin-forming substance, in which some or all of the methylol groups may be etherified by lower alcohols. Examples of alcohols which are suitable as etherifying components are preferably those containing from 1 to 5 carbon atoms. By amino resin-forming substances we mean for example ethylene urea, propylene urea, melamine, carbamates, and urone. Examples of methylolated amino resins are as follows: N,N'-dimethylolethylene urea, N,N'-dimethylolpropylene urea, N,N'-dimethylol-4-methoxy-5,5-dimethylpropylene urea, N-methylol-2-methoxyethylene carbamate, hexamethylolmelamine, dimethylol urea and N,N'-dimethylol urone. Examples of etherified or partially etherified methylolated amino resins are N,N'-dimethoxymethylethylene urea, N,N'-dimethoxymethyl-4,5-hydroxyethylene urea, N,N'-methoxymethylpropylene urea, N,N'-dimethoxymethyl-4-methoxy-5,5-dimethylpropylene urea, N,N'-isopropoxymethyl-4-methoxy-5,5-dimethylpropylene urea, N,N',N''-hexamethoxymelamine, N,N-dimethylol-2-methoxyethyl carbamate, N,N'-dimethoxymethyl-2-methoxymethyl carbamate and N,N'-dimethoxymethyl urone.

The finishing bath may additionally include protective colloids derived for example from water-soluble copolymers or saponification products of polymers such as polyvinyl alcohol and methyl cellulose.

A finishing bath containing the emulsifier compositions of the invention generally comprises from about 5 to 60% by weight of one of the aforementioned, optionally partially etherified methylol compounds, from about 0.01 to 20% by weight of the emulsifier of the invention, from about 5 60% by weight of water and from about 5 to 90% by weight of chlorinated hydrocarbon. Suitable hydrocarbons are, for example, carbon tetrachloride, trichloroethylene, perchloroethylene, 1,1,1-trichloroethane, 1,2-dichloropropane and hexachloroethane.

Creaseproofing is carried out in known manner with the addition of so-called curing catalysts. These include all acids and potential acids known to be valuable for this purpose. These are acids or Lewis acids such as zinc chloride, zinc acetate and magnesium chloride. Examples of acids are monochloroacetic acid, secondary diammonium phosphate, benzoic acid, organic sulfonic acids such as p-toluenesulfonic acid and also acid-liberating compounds such as p-toluenesulfonic chloride.

When preparing the finishing baths, the components may generally be added in any order.

A finishing bath containing the emulsifier compositions of the invention is eminently suitable for effecting creaseproofing from organic solvent emulsions.

A smooth emulsion may be obtained simply by stirring one of the methylol compounds with the emulsifier composition of the invention followed by the addition of organic solvents. Surprisingly, even a small amount of emulsifier is sufficient to stabilize such an emulsion. The conventional curing catalyst is added to the liquor simultaneously or subsequently. A liquor of user consistency is obtained from this mixture by further dilution with said organic solvents, which may themselves contain water if desired, to form clear to opalescent solutions of stable water-in-oil emulsions.

The water required for the creaseproofing process may be included in the emulsifier composition of the invention. Alternatively, it may be added when the finishing liquor is prepared.

When carrying out the process using the emulsifier compositions of the invention it is advisable, as is the case when using aqueous methods, to adjust the pH of the finishing liquor so that the dry crease recovery reaches a maximum whilst the loss of tensile strength is kept at a minimum.

Alternatively, by selecting a higher pH (i.e. using a less acidic finishing liquor) it is possible to shift the point of balance toward good wet crease recovery (and away from good dry crease recovery). It is not possible to make a general statement in view of the large number of finishing agents used, but the correct pH may be readily determined by simple experiment in each case.

Conventional plasticizers, fillers or water or oil repellents may also be added to the finishing baths with the catalysts.

The textiles are impregnated with the above liquors, freed from excess liquor and dried and then, advantageously, heated to temperatures between 110° and 190°C. Textiles treated in this manner exhibit considerably higher tensile strength and tear resistance than textiles treated with aqueous emulsifier-free baths or textiles treated in baths containing organic solvents and conventional emulsifiers. In addition, the losses of abrasion resistance are much less in the present case, whilst the crease recovery is at the same level as that obtained when working according to the prior art.

The use of our novel emulsifier compositions permits energysaving drying and the treatment of very sensitive fabrics due to the controlled swelling of the cellulose fibers made possible by varying the amount of water contained in the finishing liquors.

Finishing agents prepared with the compositions of the invention are suitable for finishing textile materials of all kinds, provided they contain cellulose or regenerated cellulose.

The invention is illustrated but not limited by the following Examples.

EXAMPLE 1

A mixture of

60 parts by weight of an approximately 70% emulsifier composition prepared in the manner described in supplement 1 below and

150 parts by weight of a 50% aqueous solution of N,-N'-dimethylol-4,5-dihydroxyethylene urea is emulsified and made up to

970 parts by volume with 1,1,1-trichloroethane with stirring.

To this composition of the invention, which contain 3.47% by weight of emulsifier, 6.2% by weight of methylol compound, 9.3% by weight of water and 83% by weight of 1,1,1-trichloroethane, there are added

20 parts by weight of monochloroacetic acid dissolved in

27 parts by weight of water.

White mercerized and beached cotton poplin weighing about 118 g/m^2 is impregnated with the above liquor. The impregnated fabric is dried, conditioned and then condensed at 150°C for 5 minutes. The fabric thus treated exhibits good crease recovery in both the dry and wet states and shows low losses of tensile strength, tear resistance and abrasion resistance compared with purely aqueous treatments.

Supplement 1

2,100 parts by weight of an approximately 45% polymer dispersion of the following composition:

62% of butyl acrylate,
32% of ethyl acrylate,
4% of acrylic acid and
2% of methacrylamide

are thoroughly mixed with

600 parts by weight of a 40% aqueous solution of the sodium salt of paraffinsulfonic acid and

2,100 parts by weight of an addition product of 25 moles of ethylene oxide with 1 mole of Alphol 16–18 F.

Supplement 2

If the process is repeated using magnesium chloride instead of monochloroacetic acid, similar results are obtained.

EXAMPLE 2

A mixture of

60 parts by weight of an emulsifier composition as described in supplement 1 of Example 1 and

100 parts by weight of a 75% aqueous solution of N,-N'-dimethylol-4,5-dihydroxyethylene urea are emulsified and made up to

940 parts by volume with 1,1,1-trichloroethane with stirring. The pH is then adjusted to 5 with monochloroacetic acid and the mixture is made up to

1,000 parts by volume with water.

This finishing bath is used to treat white cotton poplin as described in Example 1. The treated fabric has good crease recovery, particularly when wet, whilst the losses of tensile strength, tear resistance and abrasion resistance are only slight.

Supplement

If the process is repeated using 150 parts by weight of a 50% aqueous solution of N,N'-dimethylolethylene urea or 150 parts by weight of a similar solution of N,N'-dimethylolpropylene urea instead of 100 parts by weight of a 75% aqueous solution of N,N'-dimethylol-4,5-dihydroxyethylene urea, similar results are obtained.

EXAMPLE 3

120 parts by weight of the approximately 35% emulsifier composition described in supplement 1 below are homogeneously mixed with a solution of

136 parts by weight of N,N'-di(methoxymethyl)ethylene urea in

360 parts by weight of 1,1,1-trichloroethane.

To this mixture, which contains 22% by weight of etherified methylol compound, 6.8% by weight of emulsifier, 12.7% by weight of water and 58.5% by weight of 1,1,1-trichloroethane, there is added a mixture consisting of

25 parts by weight of monochloroacetic acid and

25 parts by weight of water,

and the whole is made up to

1,000 parts by volume with 1,1,1-trichloroethane with stirring.

The resulting stable emulsion is used to impregnate white mercerized and bleached cotton poplin weighing about 118 g/m^2, which is then dried and condensed for 1 minute at 180°C.

The fabric shows very good crease recovery in both the dry and wet states with low losses of tensile strength and tear resistance and very low losses of abrasion resistance.

Supplement 1

A mixture of

54 parts by weight of an approximately 46% polymer dispersion of the following composition:

47% of ethyl acrylate,
46% of butyl acrylate,
5% of methyl methacrylate and
2% of acrylic acid,

14 parts by weight of a 40% aqueous solution of the sodium salt of paraffinsulfonic acid and

132 parts by weight of a 30% aqueous solution of Emulphor OU. Emulphor OU is a polyoxyethylated fatty alcohol having a melting point of 35°–40°C., a drop-forming temperature of 46°–49°C., and a turbidity point (1% aqueous solution) of ca. 100°C. or (2% solution in 10% aqueous NaCl solution) of 73°–78°C.

Supplement 2

If the process is repeated using, instead of 120 parts by weight of the emulsifier composition described in Supplement 1, 120 parts by weight of an emulsifier composition which contains a polymer dispersion of the following composition instead of that given in Supplement 1 above:

40% of ethyl acrylate,
51% of butyl acrylate,
5% of methyl methacrylate and
4% of acrylic acid,

similar results are obtained.

EXAMPLE 4

120 parts by weight of the emulsifier composition described in supplement 1 of Example 1 but containing 3% of acrylic acid in place of 2% thereof are homogeneously mixed with a solution of

172 parts by weight of N,N'-di(methoxymethyl)propylene urea in

470 parts by weight of perchloroethylene.

To this emulsion, which contains 23.2% by weight of etherified methylol compound, 5.5% by weight of emulsifier, 10.3% by weight of water and 61.0% by weight of perchloroethylene, there is added, with stirring, a mixture consisting of

32 parts by weight of monochloroacetic acid and

42 parts by weight of water. The mixture is then made up to 1,000 parts by volume with perchloroethylene with stirring.

The resulting emulsion is used to treat fabric as described in Example 1. The treated fabric shows good crease recovery in both the dry and wet states with moderate losses of tensile strength and tear resistance and very small losses of abrasion resistance.

EXAMPLE 5

120 parts by weight of the emulsifier composition described in Example 2 are mixed to a homogeneous emulsion with a solution of

176 parts by weight of N,N'-di(methoxymethyl)urone in

464 parts by weight of perchloroethylene.

To this mixture, which contains 23.2% by weight of etherified methylol compound, 5.5% by weight of emulsifier, 10.3% by weight of water and 61% by weight of perchloroethylene, there is added a solution of

30 parts by weight of monochloroacetic acid in

42 parts by weight of water. The mixture is then made up to 1,000 parts by volume with perchloroethylene with stirring.

This emulsion is used to impregnate white mercerized and bleached cotton poplin weighing about 118 g/m². The fabric is then dried and condensed for 1 minute at 180°C.

The treated fabric shows good crease recovery in both the dry and wet states with low losses of tensile strength, tear resistance and abrasion resistance.

EXAMPLE 6

146 parts by weight of N,N'-di(methoxymethyl)propylene urea are dissolved in

120 parts by weight of the emulsifier composition described in Example 1, with stirring.

5 parts by weight of p-toluenesulfonic acid, dissolved in

22 parts by weight of water, are added and the mixture is made up to

1,000 parts by volume with 1,1,1-trichloroethane so as to give a stable finishing emulsion.

Cotton fabric is treated with this emulsion, dried and condensed in the manner described in Example 1. It is then rinsed in the usual manner.

The fabric shows good crease recovery in both the wet and dry states with low losses of tensile strength, tear resistance and abrasion resistance.

EXAMPLE 7

100 parts by weight of the emulsifier composition described in Example 1 but containing a polymer dispersion of the following composition:

48% of butyl acrylate,
40% of ethyl acrylate,
5% of methyl methacrylate and
7% of acrylic acid

are stirred with a solution of

160 parts by weight of N,N'-di(methoxymethyl)propylene urea in a little trichloroethylene. The mixture is then made up to

950 parts by volume with trichloroethylene with stirring and

50 parts by volume of an aqueous 50% solution of monochloroacetic acid are then added.

When cotton fabric is treated with this bath in the manner described in Example 4, it shows good crease recovery in both the wet and dry states with low losses of tensile strength, tear resistance and abrasion resistance.

EXAMPLE 8

A solution of

145 parts by weight of N,N'-di(methoxymethyl)ethylene urea in

250 parts by volume of trichloroethylene is stirred with

120 parts by weight of the emulsifier compositions described in

Supplements 1 and 2 of Example 1. To the mixture there is added with stirring a solution of

28 parts by weight of monochloroacetic acid in

32 parts by weight of water, and the shole is made up to 1,000 parts by volume with trichloroethylene with stirring.

These finishing baths may be successfully used for the treatment of textiles.

Supplement

If the process is repeated but using perchloroethylene in place of trichloroethylene, similar finishing baths are obtained.

EXAMPLE 9

A mixture of
1 part by weight of an approximately 70% emulsifier composition described in the Supplement below,
100 parts by weight of water and
217 parts by weight of N,N'-di(methoxymethyl)-4,5-methoxyethylene urea is emulsified with stirring with perchloroethylene which is added to make up to
950 parts by volume.

To this composition of the invention, which contains 0.051% by weight of emulsifier, 15.8% by weight of etherified methylol compound, 7.3% by weight of water and 77% by weight of perchloroethylene, there are added
17 parts by weight of zinc nitrate dissolved in
50 parts by weight of water.

This finishing bath is used to impregnate white mercerized and bleached cotton poplin weighing approximately 118 g/m^2. The fabric is dried and condensed for 1 minute at 180°C. The fabric thus treated shows good crease recovery in both the dry and wet states with low losses of tensile strength, tear resistance and abrasion resistance.

Supplement

2,100 parts by weight of an approximately 45% polymer dispersion of the following composition:
62% of butyl acrylate,
32% of ethyl acrylate,
4% of acrylic acid and
2% of methacrylamide
are thoroughly mixed with
600 parts by weight of a 40% aqueous solution of the sodium salt of paraffinsulfonic acid and
2,100 parts by weight of an addition product of 85 moles of ethylene oxide and 1 mole of Alphol 16–18F.

We claim:

1. A mixture for creaseproofing textile materials containing cellulose and/or regenerated cellulose in an aqueous liquor which may or may not contain organic solvents and which contains methylolated amino resin-forming substances and optionally amino resin-forming substances which have been etherified at the methylol group, and an emulsifier composition comprising

A. from 5 to 70 parts by weight of the emulsifier composition of a copolymer containing polymerized units of the following monomers:
   a. from 1 to 10% by weight of the copolymer of an α,β-ethylenically unsaturated carboxylic acid which contains from 3 to 10 carbon atoms, or a mixture of said carboxylic acids,
   b. from 99 to 70% by weight of the copolymer of an ester of the carboxylic acids defined under (a) above with C_{1-8} alcohols of the aliphatic series, or a mixture of said esters and
   c. from 0 to 20% by weight of the copolymer of at least one copolymerizable ethylenically unsaturated compound selected from the group consisting of acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, styrene, ethylene, propylene, a vinyl ester of a saturated carboxylic acid, vinyl ethyl ether, vinyl chloride, vinylidene chloride, butadiene, isoprene, N-methylolacrylamide, N-methylolmethacrylamide, 2-chloro-3-hydroxypropyl acrylate, 1,3-butanediol monoacrylate and 1,3-butanediol diacrylate

B. from 30 to 80 parts by weight of the emulsifier composition of a surfactant and

C. from 30 to 70 parts by weight of the emulsifier composition of water.

2. A mixture as claimed in claim **1** wherein said copolymer (A) is a copolymer of 1–10% acrylic acid, methacrylic acid or both of said acids, 99–70% of one or more acrylate esters optionally together with a methacrylate ester, and 0–20% of methacrylamide; and the surface active compound (B) is a polyoxyethylated fatty alcohol.

3. A mixture as claimed in claim **1** wherein said copolymer (A) is a copolymer of 1–10% of acrylic acid and 99–70% of butyl acrylate and ethyl acrylate optionally together with methylmethacrylate, and 0–20% of methacrylamide; and the surface active compound (B) is a polyoxyethylated fatty alcohol.

4. A mixture as claimed in claim **3** wherein the surface active compound B is said polyoxyalkylated fatty alcohol together with the sodium salt of paraffinsulfonic acid.

5. An emulsifier composition for creaseproofing a cellulosic textile material in an aqueous liquor which optionally may contain an organic solvent and which contains a methylolated amino resin-forming substance and optionally an amino resinforming substance which has been etherified at the methylol group, comprising

A. from 5 to 70 parts by weight of the composition of a copolymer containing polymerized units of the following monomers:
   a. from 1 to 10% by weight of the copolymer of an alpha, beta-ethylenically unsaturated monocarboxylic acid which contains from 3 to 10 carbon atoms or a mixture of said acids,
   b. from 99–70% by weight of the copolymer of an ester of said acids defined under (a) above with C_{1-8} alcohols of the aliphatic series, or a mixture of said esters and
   c. from 0 to 20% by weight of the copolymer of a monomer selected from the group consisting of acrylamide, methacrylamide, N-methylolacrylamide and N-methlolmethacrylamide, or a mixture of said monomers,

B. from 30 to 80 parts by weight of the composition of a surfactant selected from the group consisting of a polyoxyethylated fatty alcohol and the sodium salt of paraffinsulfonic acid and a polyoxyethylated fatty alcohol and

C. from 30 to 70 parts by weight of the composition of water.

6. An emulsifier composition as claimed in claim **5** wherein the polyoxyethylated fatty alcohol used with the sodium salt of paraffin-sulfonic acid has a melting point of 35°–40°C, a drop-forming temperature of 46°–49°C, and a turbidity point (1% aqueous solution) of ca. 100°C or (2% solution in 10% aqueous NaCl solution) of 73°–78°C.

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