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(54) Title: PROCESS FOR PRODUCING WATER-SOLUBLE CONTAINERS FOR DOSING DETERGENT

(57) Abstract: The present invention relates to a process for producing a water-soluble container comprising the steps of a) forming an open pouch from a first water-soluble film;b) filling at least part of the pouch with a composition;c) covering the filled pouch with a second water-soluble film d) sealing the first water-soluble film of the filled pouch with the second water-soluble film,wherein at least one of the first or second water-soluble films is a multi-layered film comprising at least two film layers L1 and/or L2 in any order or a washing- and cleaning-active polymer film, and wherein before sealing step d) the second water-soluble film covering the filled pouch is contacted with water, a water-soluble container obtainable by said process, the use of said process for the production of a detergent pod or dishwashing pod, and the use of said water-soluble container for dosing detergent into a laundry machine or a dishwashing machine.

Process for producing water-soluble containers for dosing detergent

The present invention relates to a process for producing water-soluble containers for dosing detergent, a water-soluble container obtainable by said process, the use of said process for producing detergent pods or dishwashing pods, and the use of said water-soluble containers for dosing detergent into a laundry machine or a dishwashing machine.

Background of the invention

It is known to use water-soluble films of polyvinyl alcohol for portion-wise packaging of liquid, gel and solid detergents and cleaners. The polyvinyl alcohol film dissolves at the beginning of the washing and cleaning process and releases the detergents and cleaning agents, so that they can develop their effect. The advantages of the portion-wise packaged detergents and cleaners (so-called single-dose units or mono-dose units) for the consumer are manifold. These include the avoidance of incorrect dosages, the ease of handling, and that the consumer does not physically come into contact with the ingredients of the detergents and cleaners. This also includes aesthetic aspects that lead to the preference of the portion-wise packed detergents and cleaners. Current dosage forms may contain a variety of separately formulated active ingredients and auxiliaries, which are released individually during the cleaning process. Such multi-chamber systems allow, for example, the separation of incompatible ingredients and thus the design of new formulation concepts. The proportion of the polyvinyl alcohol film in the total weight of the washing or cleaning agent portion in the total weight of the single dose unit is between 2 and 20% by weight, depending on the application.

A lot of patent applications from different applicant are known which disclose processes for producing portion-wise packaging of liquid, gel and solid detergents and cleaners based on water-soluble films such as e.g. EP 1 161 369 A1, WO 02/16206 A1, EP 1 678 037 A1, EP 2 504 242 A1 or EP 3 126 483 A1 which, however, all have the drawback that for the production of the water soluble containers water-soluble films are used which only serve as packaging material but do not add to the wash or cleaning performance. Thus, there is a need for a process for producing water-soluble containers for dosing detergent which are based on water-soluble films including active washing and cleaning substances.

The present invention is based on the surprising findings that it is possible to produce water-soluble containers using a water-soluble multi-layered film which comprises at least one layer which comprises a wash active surfactant polymer composition or which comprises a polymer composition which by means of radical polymerization of a monomer composition which includes at least one monomer which is selected from α,β-ethylenically unsaturated mono- or dicarbon acids, salts of α,β-ethylenically unsaturated mono- or dicarbon acids, anhydrides of α,β-ethylenically unsaturated mono- or dicarbon acids, or mixtures thereof, whereby the radical polymerization is conducted in the presence of at least one polyether component.

A multi-layered film comprising at least one of such layers has different properties compared to the polyvinyl alcohol films used in the art for the production of water-soluble containers so that a production process for water soluble container based on such multi-layered films needs to be

developed. Such a process has been developed in the present invention which produced water-soluble containers based on said multi-layered films with an appropriate seal strength.

Summary of the invention

The present invention relates to a process for producing a water-soluble container comprising the steps of

a) forming an open pouch from a first water-soluble film;
b) filling at least part of the pouch with a composition;
c) covering the filled pouch with a second water-soluble film
d) sealing the first water-soluble film of the filled pouch with the second water-soluble film,

wherein

at least one of the first or second water-soluble films is a multi-layered film comprising at least two film layers L1 and/or L2 in any order,

wherein at least one film layer L1 comprises a polymer composition P1 obtainable by radical polymerization of a monomer composition M1 in the presence of at least one polyether component PE,

whereby M1 comprises at least one monomer A,

whereby A is selected from α,β-ethylenically unsaturated mono- or dicarbon acids, salts of α,β-ethylenically unsaturated mono- or dicarbon acids or mixtures thereof,

and

whereby PE is selected from polyether alcohols with a number average molecular weight Mn of at least 200 g/mol, mono and di-(C1 to C6-alkyl)ethers of such polyether alcohols, polyether groups-containing tensides or mixtures thereof,

and

at least one film layer L2 comprises at least one polymer P2 which is different from polymer composition P1 and is selected from

- natural or modified polysaccharides;
- homo- or copolymers comprising monomer units derivable from vinyl alcohol, vinylesters, alkoxylated vinyl alcohols, or mixtures thereof;
- homo-or copolymers comprising at least one monomer selected from N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, 2-vinylpyridine, 4-vinyl-pyridine, salts of N-vinylimidazole, salts of 2-vinylpyridine, salts of 4-vinyl-pyridine, vinylpyridine-N-oxide, N-carboxymethyl-4-vinylpyridine halogenides or mixtures thereof;
- homo- or copolymers of acrylic acid and /or methacrylic acid, preferably copolymers comprising at least one acrylic acid monomer selected from acrylic acid, salts of acrylic acid or mixtures thereof and at least one maleic acid monomer selected from maleic acid, maleic acid anhydride, salts of maleic acid or mixtures thereof;
- copolymer comprising at least a (meth)acrylic acid monomer selected from acrylic acid, methacrylic acid, salts of acrylic acid, salts of methacrylic acid or mixtures thereof and at least one hydrophobic monomer selected from C1-C8 alkylesters of (meth) acrylic acid, C2-C10 olefins, styrene or α-methyl-styrene;
- homo- or copolymers of acrylamide and or methacrylamide;
- polyaminoacids;

- water-soluble or water-dispersible polyamides;
- polyalkyleneglycols, mono-or diethers of polyalkyleneglycols;
- polyalkyleneoxide such as polyethyleneoxide; and
- mixtures thereof;

or at least one of the first or second water-soluble films is a washing- and cleaning-active polymer film, comprising or consisting of at least one layer obtainable by

i) providing an aqueous composition by mixing
   - a polymer P1') that comprises polymerized units of at least one monomer A'), selected from α,β-ethylenically unsaturated carboxylic acids, salts of α,β-ethylenically unsaturated carboxylic acids and mixtures thereof,
   - a polyoxyalkylene ether PE') having at least one C_8-C_{18}-alkyl group that is unsubstituted or substituted by at least one hydroxyl group, and an average of 3 to 25 alkylene oxide units per molecule, and
   - water,

   wherein at the most 30 mol% of the carboxy groups of the polymer P1') are in the deprotonated form,
   the weight ratio of the polymer P1') to the polyoxyalkylene ether PE') is in a range from 0.9 : 1 to 5 : 1, and
   the aqueous composition has a water content of at least 10% by weight and at most 50% by weight, based on the total weight of the aqueous composition,
ii) converting the aqueous composition to a polymer film;

and wherein before sealing step d) the second water-soluble film covering the filled pouch is contacted with water.

Further, the present invention relates to a water soluble container obtainable by the process as described above or below.

Still further, the present invention relates to the use of the process as described above or below for the production of a detergent pod or dishwashing pod.

Additionally, the present invention relates to the use of the water-soluble container as described above or below for dosing detergent into a laundry machine and/or a dishwashing machine.

Definitions

In the context of the present invention, the terms "detergent portion" and "cleaning agent portion" are understood to mean a quantity of a detergent or a cleaning agent which is sufficient for a washing or cleaning operation taking place in an aqueous phase. This can be, for example, a laundry washing process, as is carried out with commercially available laundry machines or a dish washing process which is carried out with commercially available dish washing machines. According to the invention, this term is also understood to mean an active ingredient portion for a handwash cycle or a manual cleaning process (as is carried out, for example, in a handwash basin or in a bowl). The washing and cleaning-active multi-layered

films according to the invention are preferably used for the production of active ingredient portions for mechanical washing or cleaning operations.

In the context of the present invention, the term “polymer film” refers to a flat structure which has an essentially two-dimensional extension. The thickness of the films according to the invention is preferably 0.5 µm to 20 mm, particularly preferably 1 µm to 10 mm. The thickness of the polymer films of the invention is small in relation to the length and width. Preferably, the thickness of the polymer films is smaller by a factor of at least 2, more preferably of at least 5 and especially of at least 10 than the length of the greatest longitudinal axis. In a specific embodiment, the thickness of the polymer films is smaller by a factor of at least 20, more specifically at least 50, even more specifically at least 100 and very specifically at least 500 than the length of the greatest longitudinal axis. In principle, the upper value for the greatest longitudinal extent of the polymer films of the invention is uncritical. The polymer films of the invention can be produced, for example, in the form of film rolls, where the greatest length may even be in the region of 100 m or higher.
The polymer films of the invention can be in form of single layer films or multilayer films.
The term “multi-layered film” in connection with the present invention defines a self-supporting planar construction which comprises at least two film layers. A multi-layered film according to the present invention is a film composite which comprises at least two films which are permanently connected with a substantial part of their surface over its entire surface. Thereby, it is understood that at least two films are permanently connected with at least 50% of their surface over its entire surface. If two films of different sizes are connected to each other, at least the film with the smaller surface is permanently connected over its entire surface to at least 50% of its surface. Thus the multi-layered films used in the process of the present invention differ from films used for the production of water-soluble container known in the art in which a single film or two or more films are connected by means of a seal seam. Those films known in the art are only connected over their entire surfaces to not more than 50% of their surfaces.

Detailed description of the invention

Multi-layered film

In one embodiment of the present invention at least one of the first or second water-soluble films is a multi-layered film.

The multi-layered film used in the process according to the present invention comprises at least two film layers L1 and/or L2 in any order, preferably at least two film layers L1 and L2 in any order, wherein at least one film layer L1 comprises a polymer composition P1 obtainable by radical polymerization of a monomer composition M1 in the presence of at least one polyether component PE, whereby M1 comprises at least one monomer A, whereby A is selected from α,β-ethylenically unsaturated mono- or dicarbon acids, salts of α,β-ethylenically unsaturated mono- or dicarbon acids or mixtures thereof, and whereby PE is selected from polyether alcohols with a number average molecular weight Mn of at least 200 g/mol, mono and di-(C_1 to C_6-alkyl)ethers of such polyether alcohols, polyether groups-containing surfactants or mixtures

thereof, and at least one film layer L2 comprises at least one polymer P2 which is different from polymer composition P1 and is selected from

- natural or modified polysaccharides;
- homo- or copolymers comprising monomer units derivable from vinyl alcohol, vinylesters, alkoxylated vinyl alcohols, or mixtures thereof;
- homo-or copolymers comprising at least one monomer selected from N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, 2-vinylpyridine, 4-vinyl-pyridine, salts of N-vinylimidazole, salts of 2-vinylpyridine, salts of 4-vinyl-pyridine, vinylpyridine-N-oxide, N-carboxymethyl-4-vinylpyridine halogenides or mixtures thereof;
- homo- or copolymers of acrylic acid and /or methacrylic acid, preferably copolymers comprising at least one acrylic acid monomer selected from acrylic acid, salts of acrylic acid or mixtures thereof and at least one maleic acid monomer selected from maleic acid, maleic acid anhydride, salts of maleic acid or mixtures thereof;
- copolymer comprising at least a (meth)acrylic acid monomer selected from acrylic acid, methacrylic acid, salts of acrylic acid, salts of methacrylic acid or mixtures thereof and at least one hydrophobic monomer selected from C1-C8 alkylesters of (meth) acrylic acid, C2-C10 olefins, styrene or α-methyl-styrene;
- homo- or copolymers of acrylamide and or methacrylamide;
- polyaminoacids;
- water-soluble or water-dispersible polyamides;
- polyalkyleneglycols, mono-or diethers of polyalkyleneglycols;
- polyalkyleneoxide such as polyethyleneoxide; and
- mixtures thereof.

Monomer composition M1:

Monomer A:
In a specific embodiment, the monomer composition M1 consists only of α, β-ethylenically unsaturated carboxylic acids, salts of α,β-ethylenically unsaturated carboxylic acids and mixtures thereof.

The α,β-ethylenically unsaturated carboxylic acid is preferably selected from acrylic acid, methacrylic acid, ethacrylic acid maleic acid, fumaric acid, itaconic acid, α-chloroacrylic acid, crotonic acid, citraconic acid, mesaconic acid, glutaconic acid and aconitic acid. Suitable salts of the abovementioned acids are, in particular, the sodium, potassium and ammonium salts and the salts with amines or aminoalcohols. The monomers A can be used as such or as mixtures with one another. The stated proportions by weight are all based on the acid form.

The at least one α, β-ethylenically unsaturated carboxylic acid is preferably used in unneutralized form for the polymerization. If the α, β-ethylenically unsaturated carboxylic acids are used in partially neutralized form for the polymerization, the acid groups are preferably neutralized to at most 50 mol%, more preferably to at most 30 mol%.

The monomer A is particularly preferably selected from acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, salts of the abovementioned carboxylic acids and mixtures thereof.

In particular, the monomer A is selected from acrylic acid, methacrylic acid, salts of acrylic acid, salts of methacrylic acid and mixtures thereof.

In a specific embodiment, only acrylic acid is used as monomer A.

The monomer A is preferably used in an amount of 50 to 100 wt .-%, particularly preferably 60 to 100 wt .-%, based on the total weight of the monomer composition M1.

In a preferred embodiment, the monomer composition M1 comprises at least 50% by weight, preferably at least 80% by weight, in particular at least 90% by weight, based on the total weight of the monomer composition M1, of acrylic acid and / or acrylic acid salts.

Monomer B:
The monomer composition M1 may comprise, in addition to the monomers A, at least one monomer B selected from unsaturated sulfonic acids, salts of unsaturated sulfonic acids, unsaturated phosphonic acid, salts of unsaturated phosphonic acids and mixtures thereof.

The monomer B is preferably selected from 2-acrylamido-2-methylpropane-sulfonic acid, vinylsulfonic acid, allylsulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-acryloxypropylsulfonic acid, 2-hydroxy-3-methacryloxypropylsulfonic acid, styrenesulfonic acid, vinylphosphonic acid, allylphosphonic acid, salts of the aforementioned acids and mixtures thereof.

Preferred monomer B is 2-acrylamido-2-methylpropanesulfonic acid.

Suitable salts of the abovementioned acids are in particular the sodium, potassium and ammonium salts and the salts with amines. The monomers B can be used as such or as mixtures with one another. The stated proportions by weight are all based on the acid form.

Preferably, the monomer composition M1 is then at least 50% by weight, particularly preferably at least 80% by weight, in particular at least 90% by weight, based on the total weight of the monomer composition M1, of monomers A and B. If the monomer composition M1 comprises at least one monomer B, this is preferably used in an amount of 0.1 to 50% by weight, particularly preferably 1 to 25% by weight, based on the total weight of the monomer composition M1.

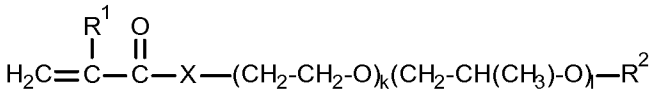
Monomers C:
The monomer composition M1 may additionally comprise at least one other of the acid group-containing monomers and their salts different monomer (= monomer C).

The monomer composition M1) can thus have the following monomer compositions: A or A + B or A + C or A + B + C.

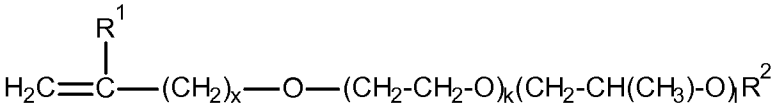
Preferably, the monomer composition M1 additionally comprises at least one monomer C, selected from

C1) nitrogen heterocycles having a radically polymerizable α, β-ethylenically unsaturated double bond,

C2) Compounds of the general formulas (I.a) and (I.b)



(I.a)



(I.b)

wherein
the order of the alkylene oxide units is arbitrary,
x is 0, 1 or 2,
k and l independently of one another are an integer from 0 to 100, the sum of k and l being at least 2, preferably at least 5,
R^1 is hydrogen or C_1-C_8-alkyl,
R^2 is hydrogen, C_1-C_{30} alkyl, C_2-C_{30} alkenyl or C_5-C_8 cycloalkyl, and
X is O or a group of the formula NR^3, in which R^3 is H, alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl;

C3) vinyl aromatics,

C4) unsaturated hydrocarbons selected from C_2-C_{10} monoolefins and nonaromatic hydrocarbons having at least two conjugated double bonds,

C5) esters of α, β-ethylenically unsaturated mono- and dicarboxylic acids with C_1-C_{30}-alkanols,

C6) compounds having a radically polymerizable α, β-ethylenically unsaturated double bond and at least one cationogenic and/or cationic group per molecule,

C7) esters of vinyl alcohol or allyl alcohol with C_1-C_{30} monocarboxylic acids,

C8) esters of α, β-ethylenically unsaturated mono- and dicarboxylic acids with C_2-C_{30}-alkanediols, amides of α, β-ethylenically unsaturated mono- and dicarboxylic acids with C_2-C_{30}-aminoalcohols having a primary or secondary amino group,

C9) amide group-containing monomers other than I.a), C6 and C8;

C10) α, β-ethylenically unsaturated nitriles,

C11) vinyl halides, vinylidene halides,

C12) ethylenically unsaturated monomers with urea groups,

and mixtures of two or more than two of the aforementioned monomers C1) to C12).

Monomer C1:
Preferred nitrogen heterocycles having a radically polymerizable α, β-ethylenically unsaturated double bond C1 are selected from 1-vinylimidazole (N-vinylimidazole), various vinyl- and allyl-substituted nitrogen heterocycles other than 1-vinylimidazole and mixtures thereof.

From the amine nitrogens of the aforementioned compounds can be generated either by protonation with acids or by quaternization with alkylating cationic groups charged. Suitable monomers C1 are also the compounds obtained by protonation or quaternization of 1-vinylimidazole and various vinyl- and allyl-substituted nitrogen heterocycles thereof. For protonation suitable acids are e.g. carboxylic acids such as lactic acid, or mineral acids such as phosphoric acid, sulfuric acid and hydrochloric acid. Alkylating agents suitable for quaternization are C_1 -C_4 -alkyl halides or di- (C_1-C_4-alkyl) sulfates such as ethyl chloride, ethyl bromide, methyl chloride, methyl bromide, dimethyl sulfate and diethyl sulfate. Protonation or quaternization can generally be carried out both before and after the polymerization. Preferably, protonation or quaternization takes place after the polymerization. Examples of such charged monomers C1 are quaternized vinylimidazoles, in particular 3-methyl-1-vinylimidazolium chloride, methosulfate and ethosulfate.

Preferred monomers C1 are also vinyl- and allyl-substituted nitrogen heterocycles, other than vinylimidazoles, selected from 2-vinylpyridine, 4-vinylpyridine, 2-allylpyridine, 4-allylpyridine, 2-vinylpiperidine, 4-vinylpiperidine and the salts thereof obtained by protonation or by quaternization.

In particular, the monomer composition M1 comprises at least one comonomer C1 selected from 1-vinylimidazole, 2-vinylpyridine, 4-vinylpyridine, 2-allylpyridine, 4-allylpyridine and the salts thereof obtained by protonation or by quaternization. Specifically, the monomer composition M1 comprises as comonomer C1 1-vinylimidazole.

Monomer C2:

The monomer composition M1 may additionally comprise at least one monomer C2 selected from compounds of the general formulas (I.a) and (I.b) as defined above.

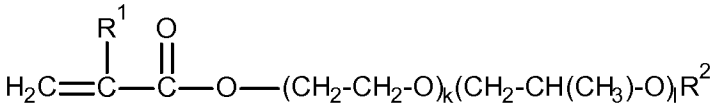
In the formulas I.a) and I.b), k is preferably an integer from 1 to 500, particularly preferably 2 to 400, in particular 3 to 250. Preferably, l is an integer from 0 to 100.

R^1 in the formula I.a) is preferably hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl or n-hexyl, in particular hydrogen, methyl or ethyl.

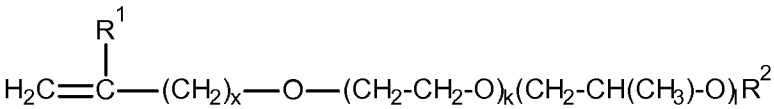
Preferably, R^2 in the formulas I.a) and I.b) is n-octyl, 1,1,3,3-tetramethylbutyl, ethylhexyl, n-nonyl, n-decyl, n-undecyl, tridecyl, myristyl, pentadecyl, palmityl, heptadecyl, octadecyl, nonadecyl, arrachinyl, behenyl, lignocerenyl, cerotinyl, melissinyl, palmitoleinyl, oleyl, linolyl, linolenyl, stearyl, lauryl.

Preferably, X in the formula I.a) is O or NH, in particular O.

The monomer composition M1 particularly preferably comprises at least one monomer C2 selected from compounds of the general formulas (I.a1) and (I.b1)



(I.a1)



(I.b1)

wherein
the order of the alkylene oxide units is arbitrary,
x is 0, 1 or 2,
k and l independently of one another are an integer from 0 to 100, the sum of k and l being at least 2, preferably at least 5,
R^1 is hydrogen or methyl,
R^2 is hydrogen, C1-C4-alkyl.
In the formulas I.a1) and I.b1), k is preferably an integer from 1 to 100, more preferably 2 to 50, in particular 3 to 30. Preferably, l is an integer from 0 to 50.

Preferably, R^2 in the formulas I.a1) and I.b1) is hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl or tert-butyl.

In formula I.b1), x is preferably 1 or 2.

Suitable polyether acrylates I.a) or I.a1) are e.g. the polycondensation products of the aforementioned α, β-ethylenically unsaturated mono- and/or dicarboxylic acids and their acid chlorides, amides and anhydrides with polyetherols. Suitable polyetherols can be readily prepared by reacting ethylene oxide, 1,2-propylene oxide and / or epichlorohydrin with a starter molecule such as water or a short-chain alcohol R2-OH. The alkylene oxides can be used individually, alternately in succession or as a mixture. The polyether acrylates I.a1) can be used alone or in mixtures for the preparation of the polymers used according to the invention.

Suitable allyl alcohol alkoxylates I.b) or I.b1) are e.g. the etherification of allyl chloride with corresponding polyetherols. Suitable polyetherols can be readily prepared by reacting ethylene oxide, 1,2-propylene oxide and/or epichlorohydrin with a starting alcohol R^2-OH. The alkylene oxides can be used individually, alternately in succession or as a mixture. The allyl alcohol alkoxylates I.b) can be used alone or in mixtures for the preparation of the polymers used according to the invention.

In particular, the monomer C2 used is methyl diglycol acrylate, methyl diglycol methacrylate, ethyl diglycol acrylate or ethyl diglycol methacrylate. Preferred is ethyl diglycol acrylate.

Monomer C3:
The monomer composition M1 may additionally comprise at least one monomer C3 selected from vinylaromatics. Preferred vinylaromatics C3 are styrene, 2-methylstyrene, 4-methylstyrene, 2-(n-butyl)styrene, 4-(n-butyl)styrene, 4-(n-decyl)styrene and mixtures thereof. Particularly preferred are styrene and 2-methylstyrene, especially styrene.

Monomer C4:
The monomer composition M1 may additionally comprise at least one unsaturated hydrocarbon C4 selected from C_2-C_{10} monoolefins and non-aromatic hydrocarbons having at least two conjugated double bonds.

Examples of C_2 -C_{10} monoolefins are ethene, propene, but-1-ene, but-2-ene, isobutene, pent-1-ene, pent-2-ene, 2-methyl-but-1-ene, 2 methyl-but-2-ene, 3-methylbut-1-ene, 3-methyl-but-2-ene, 2,2-dimethylprop-1-ene, hex-1-ene, hex-2-ene, hex-3-ene, hept-1-ene, hept-2-ene, hept-3-ene, oct-1-ene, oct-2-ene, oct-3-ene, oct-4-ene, non-1-ene, non-2-ene, non-3-ene, non-4-ene, dec-1-ene, dec-2-ene, dec-3-ene, dec-4-ene, dec-5-ene and their position isomers and unsaturated terminated oligomers and polymers of the above olefins, in particular α-olefins (ethene, propene, but-1-ene, pent-1-ene, hex-1-ene, hept-1-ene, oct-1-ene, non-1-ene, dec-1-ene).

Non-aromatic hydrocarbons having at least two conjugated double bonds denote both aliphatic and cycloaliphatic unsaturated hydrocarbons having at least two conjugated double bonds. The cycloaliphatic unsaturated hydrocarbons having at least two conjugated double bonds are either

those which do not comprise the maximum number of conjugated carbon-carbon double bonds predetermined by the ring size or those which, although they have the maximum number of conjugated carbon-carbon double bonds carbon atoms given by the ring size, do not conform to the Hückel rule; be it because they are homoaromatic, antiaromatic or a non-aromatic polyene.

Aliphatic hydrocarbons having at least two conjugated double bonds usually contain from 4 to 20 carbon atoms. Examples of aliphatic hydrocarbons having at least two conjugated double bonds are 1,3-butadiene, 1,3-pentadiene, isoprene, 1,3-hexadiene, 2,4-hexadiene, 1,3,5-hexatriene, 1,3-heptadiene, 2,4-heptadiene, 1,3,4-heptatriene, 1,3-octadiene, 2,4-octadiene, 3,5-octadiene, 1,3,5-octatriene, 2,4,6-octatriene, 1, 3,5,7-octatetraene and the like.

Cycloaliphatic hydrocarbons having at least two conjugated double bonds usually contain 4 to 20 carbon atoms as ring members. Examples are 1,3-cyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,3,5-cycloheptatriene, 1,3-cyclootadiene, 1,3,5-cyclootatriene, 1,3,5,7-cyclooctatetraene and the like.

Preferred monomers C4 are ethene, propene, butene, isobutene, diisobutene, isoprene, 1,3-butadiene and mixtures thereof.

Monomer C5:
The monomer composition M1 may additionally comprise at least one monomer C5 selected from esters of α, β-ethylenically unsaturated mono- and dicarboxylic acids with C_1-C_{30}-alkanols.

Suitable esters of α, β-ethylenically unsaturated mono- and dicarboxylic acids with C_1-C_{30}-alkanols are e.g. methyl(meth)acrylate, methyl(meth)acrylate, ethyl(meth)acrylate, ethyl(eth)acrylate, n-propyl(meth)acrylate, isopropyl(meth)acrylate, n-butyl(meth)acrylate, tert-butyl(meth)acrylate tert-butyl(eth)acrylate, n-pentyl(meth)acrylate, n-hexyl(meth)acrylate, n-heptyl(meth)acrylate, n-octyl(meth)acrylate, 1,1,3,3-tetramethylbutyl(meth)acrylate, ethylhexyl(meth)acrylate, n-nonyl(meth)acrylate, n-decyl(meth)acrylate, n-undecyl(meth)acrylate, tridecyl(meth)acrylate, myristyl(meth)acrylate, pentadecyl(meth)acrylate, palmityl(meth)acrylate, heptadecyl(meth)acrylate, nonadecyl(meth)acrylate, arrachinyl(meth)acrylate, behenyl(meth)acrylate, lignocerenyl(meth)acrylate, cerotinyl(meth)acrylate, melissinyl(meth)acrylate, palmitoleinyl(meth)acrylate, oleyl(meth)acrylate, linolyl(meth)acrylate, linolenyl(meth)acrylate, stearyl(meth)acrylate, lauryl(meth)acrylate and mixtures thereof.

Monomer C6:
The monomer composition M1 may additionally comprise at least one monomer C6 selected from compounds having a radically polymerizable α, β-ethylenically unsaturated double bond and at least one cationogenic and / or cationic group per molecule.

The cationogenic and/or cationic groups of the monomers C6 are preferably nitrogen-containing groups, such as primary, secondary and tertiary amino groups, and quaternary ammonium

groups. Preferably, the nitrogen-containing groups are tertiary amino groups or quaternary ammonium groups. Charged cationic groups can be generated from the amine nitrogens either by protonation or by quaternization with acids or alkylating agents. These include e.g. carboxylic acids such as lactic acid, or mineral acids such as phosphoric acid, sulfuric acid and hydrochloric acid, or as alkylating C_1-C_4 alkyl halides or sulfates such as ethyl chloride, ethyl bromide, methyl chloride, methyl bromide, dimethyl sulfate and diethyl sulfate. Protonation or quaternization can generally be carried out both before and after the polymerization.

Preferably, the monomers C6 are selected from esters of α, β-ethylenically unsaturated mono- and dicarboxylic acids with aminoalcohols which may be mono- or dialkylated on the amine nitrogen, amides of α, β-ethylenically unsaturated mono- and dicarboxylic acids with diamines which comprise at least one primary or secondary amino group, N, N-diallylamine, N, N-diallyl-N-alkylamines and their derivatives and mixtures thereof.

The esters of α, β-ethylenically unsaturated mono- and dicarboxylic acids with aminoalcohols, which may be mono- or dialkylated on the amine nitrogen, are preferably derived from C_2 -C_{12} -aminoalcohols which are mono- or -dialkylated on the amino nitrogen C1 -C8 -monoalkyl. As the acid component of these esters are e.g. acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid, crotonic acid, maleic anhydride, monobutyl maleate and mixtures thereof. Acrylic acid, methacrylic acid and mixtures thereof are preferably used as the acid component.

Preferred monomers C6 are N-methylaminoethyl(meth)acrylate, N-ethylaminoethyl(meth)acrylate, N-(n-propyl)aminoethyl(meth)acrylate, N-(tert-butyl)aminoethyl(meth)acrylate, N,N-dimethylaminomethyl(meth)acrylate, N,N-dimethylaminoethyl(meth)acrylate, N,N-diethylaminomethyl(meth)acrylate, N,N-diethylaminoethyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate, N,N-diethylaminopropyl(meth)acrylate and N,N-dimethylaminocyclohexyl(meth)acrylate.

Suitable monomers C6 are furthermore the amides of the abovementioned α, β-ethylenically unsaturated mono- and dicarboxylic acids with diamines which have at least one primary or secondary amino group. Preferred are diamines having a tertiary and a primary or secondary amino group.

Preferred as monomers C6 are e.g. N-[tert-butylaminoethyl] (meth)acrylamide, N-[2-(dimethylamino)ethyl] acrylamide, N-[2-(dimethylamino)ethyl] methacrylamide, N-[3-(dimethylamino)propyl] acrylamide, N-[3-(dimethylamino)propyl] methacrylamide, N-[4-(dimethylamino)butyl] acrylamide, N-[4-(dimethylamino)butyl] methacrylamide, N-[2-(diethylamino)ethyl] acrylamide, N-[4-(dimethylamino)cyclohexyl] acrylamide and N-[4-(dimethylamino)cyclohexyl] methacrylamide.

Monomer C7:

The monomer composition M1 may additionally comprise at least one monomer C7 selected from compounds of esters of vinyl alcohol or allyl alcohol with C_1-C_{30}-monocarboxylic acids.

Suitable esters of vinyl alcohol with C_1-C_{30} monocarboxylic acids are e.g. methyl vinylester, ethyl vinylester, n-propyl vinylester, isopropyl vinylester, n-butyl vinylester, tert-butyl vinylester, n-pentyl vinylester, n-hexyl vinylester, n-heptyl vinylester, n-octyl vinylester, 1,1,3,3-tetramethylbutyl vinylester, ethylhexyl vinylester, n-nonyl vinylester, n-decyl vinylester, n-undecyl vinylester, tridecyl vinylester, myristyl vinylester, pentadecyl vinylester, palmityl vinylesters, heptadecyl vinylesters, octadecyl vinylesters, nonadecyl vinylesters, arrachinyl vinylesters, behenyl vinylesters, lignocerenyl vinylesters, cerotinyl vinylesters, melissinyl vinylesters, palmitoleinyl vinylesters, oleyl vinylesters, linolyl vinylesters, linolenyl vinylesters, stearyl vinylesters, lauryl vinylesters and mixtures thereof.

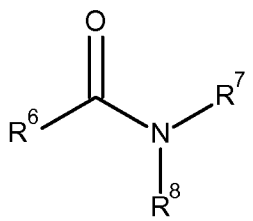
Monomer C8:
The monomer composition M1 may additionally comprise at least one monomer C8 selected from esters of α, β-ethylenically unsaturated mono- and dicarboxylic acids with C_2-C_{30}-alkanediols and amides of α, β-ethylenically unsaturated mono- and dicarboxylic acids with C_2-C_{30}-aminoalcohols with a primary or secondary amino group.

Suitable esters of α, β-ethylenically unsaturated mono- and dicarboxylic acids with C_2-C_{30} alkanediols are 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, 3-hydroxybutyl acrylate, 3-hydroxybutyl methacrylate, 4-hydroxybutyl acrylate, 4-hydroxybutyl methacrylate, 6-hydroxyhexyl acrylate, 6-hydroxyhexyl methacrylate, 3-hydroxy-2-ethylhexyl acrylate, 3-hydroxy-2-ethylhexyl methacrylate, etc.

Suitable amides of α, β-ethylenically unsaturated mono- and dicarboxylic acids with C_2-C_{30} aminoalcohols having a primary or secondary amino group 2-hydroxyethylacrylamide, 2-hydroxyethylmethacrylamide, 2-hydroxyethylethacrylamide, 2-hydroxypropylacrylamide, 2-hydroxypropylmethacrylamide, 3-hydroxypropylacrylamide, 3-hydroxypropylmethacrylamide, 3-hydroxybutylacrylamide, 3-hydroxybutylmethacrylamide, 4-hydroxybutylacrylamide, 4-hydroxybutylmethacrylamide, 6-hydroxyhexylacrylamide, 6- hydroxyhexylmethacrylamide, 3-hydroxy-2-ethylhexylacrylamide and 3-hydroxy-2-ethylhexylmethacrylamide.

Monomer C9:
The monomer composition M1 may additionally comprise at least one monomer C9 selected from amide group-containing monomers other than I.a), C6 and C8.

Suitable amide group-containing monomers C9 are compounds of the general formula (V)



(V)

wherein

one of the radicals R6 to R8 is a group of the formula $CH_2 = CR^9$ - with R^9 = H or C1 -C4-alkyl and the remaining radicals R^6 to R^8 independently of one another are H, alkyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl,
whereby R^6 and R^7 together with the amide group to which they are attached may also stand for a lactam having 5 to 8 ring atoms,
whereby R^7 and R^8, together with the nitrogen atom to which they are attached, may also stand for a five- to seven-membered heterocycle.

The monomers C9 are preferably selected from primary amides of α, β-ethylenically unsaturated monocarboxylic acids, N-vinylamides of saturated monocarboxylic acids, N-vinyllactams, N-alkyl and N, N-dialkylamides of α, β-ethylenically unsaturated monocarboxylic acids and mixtures thereof.

Preferred monomers C9 are N-vinyl lactams and their derivatives, which include e.g. one or more C_1-C_6-alkyl substituents such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl. These include e.g. N-vinylpyrrolidone, N-vinylpiperidone, N-vinylcaprolactam, N-vinyl-5-methyl-2-pyrrolidone, N-vinyl-5-ethyl-2-pyrrolidone, N-vinyl-6-methyl-2-piperidone, N-vinyl-6-ethyl-2-piperidone, N-vinyl-7-methyl-2-caprolactam, N-vinyl-7-ethyl-2-caprolactam, etc.

Particular preference is given to using N-vinylpyrrolidone and/or N-vinylcaprolactam.

Suitable monomers C9 are furthermore acrylamide and methacrylamide.

Suitable N-alkyl and N, N-dialkylamides of α, β-ethylenically unsaturated monocarboxylic acids are e.g. methyl(meth)acrylamide, methylethacrylamide, ethyl(meth)acrylamide, ethylethacrylamide, n-propyl(meth)acrylamide, isopropyl(meth)acrylamide, n-butyl(meth)acrylamide, tert-butyl(meth)acrylamide, tert-butylethacrylamide, n-pentyl(meth)acrylamide, n-hexyl(meth)acrylamide, n-heptyl(meth)acrylamide, n-octyl(meth)acrylamide, 1,1,3,3-tetramethylbutyl(meth)acrylamide, ethylhexyl(meth)acrylamide, n-nonyl(meth)acrylamide, n-decyl(meth)acrylamide, n-undecyl(meth)acrylamide, tridecyl(meth)acrylamide, myristyl(meth)acrylamide, pentadecyl(meth)acrylamide, palmityl(meth)acrylamide, heptadecyl(meth)acrylamide, nonadecyl(meth)acrylamide, arrachinyl(meth)acrylamide, behenyl(meth)acrylamide, lignocerenyl(meth)acrylamide, cerotinyl(meth)acrylamide, melissinyl(meth)acrylamide, palmitoleinyl(meth)acrylamide, oleyl(meth)acrylamide, linolyl(meth)acrylamide, linolenyl(meth)acrylamide, stearyl(meth)acrylamide, lauryl(meth)acrylamide, N-methyl-N-(n-octyl)(meth)acrylamide, N, N-di(n-octyl)(meth)acrylamide and mixtures thereof.

Examples of suitable open-chain N-vinylamide compounds as monomers C9 are N-vinylformamide, N-vinyl-N-methylformamide, N-vinylacetamide, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, N-vinylpropionamide, N-vinyl N-methylpropionamide, N-vinyl-butyramide and mixtures thereof. Preferably N-vinylformamide is used.

Monomer C10:
The monomer composition M1 may additionally comprise at least one monomer C10 selected from α, β-ethylenically unsaturated nitriles.

Suitable α, β-ethylenically unsaturated nitriles are acrylonitrile or methacrylonitrile.

Monomer C11:
The monomer composition M1 may additionally comprise at least one monomer C11 selected from vinyl halides and vinylidene halides.

Suitable vinyl halides and vinylidene halides are vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride and mixtures thereof.

Monomer C12:
The monomer composition M1 may additionally comprise at least one monomer C12 selected from ethylenically unsaturated monomers having urea groups.

Suitable monomers C12 with urea groups are N-vinylurea, N-allylurea or derivatives of imidazolidin-2-one. These include N-vinyl and N-allylimidazolidin-2-one, N-vinyloxyethylimidazolidin-2-one, N-(2-(meth)acrylamidoethyl)imidazolidin-2-one, N-(2-(meth)acryloxyethyl)imidazolidine-2-one (i.e. 2-ureido(meth)acrylate), N-[2-((meth)acryloxyacetamido)ethyl] imidazolidin-2-one, etc.

In a particular embodiment, the monomer composition M1 comprises acrylic acid and optionally at least one comonomer selected from α, β-ethylenically unsaturated mono- (e.g. methacrylic acid) or dicarboxylic acids, salts, anhydrides, esters and amides other than acrylic acid α, β-ethylenically unsaturated mono- or dicarboxylic acids, olefinically unsaturated sulfonic acids (e.g. 2-acrylamido-2-methylpropanesulfonic acid AMPS), salts of olefinically unsaturated sulfonic acids, C2 -C10-monoolefins, non-aromatic hydrocarbons having at least two conjugated double bonds, vinylaromatics, N-vinyllactams and mixtures thereof.

In a specific embodiment, the monomer composition M1 comprises acrylic acid and optionally at least one comonomer selected from ethene, propene, isobutene, diisobutene, isoprene, 1,3-butadiene, methacrylic acid, 2-acrylamido-2-methylpropane-sulphonic acid, maleic acid, maleic anhydride, itaconic acid, N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, styrene and mixtures thereof.

In a very specific embodiment, the monomer composition M1 comprises acrylic acid and optionally at least one comonomer selected from methacrylic acid, 2-acrylamido-2-methylpropanesulfonic acid mixtures thereof.

In particular, the monomer composition M1 consists of at least 80% by weight, preferably at least 90% by weight, in particular at least 95% by weight, based on the total weight of the monomer composition M1, of acrylic acid.

The monomer composition M1 may preferably comprise the further monomers C1 to C12 in an amount of from 0 to 30% by weight, particularly preferably 0 to 20% by weight, in particular 0 to 10% by weight, based on the total weight the monomer composition M1. If the monomer composition M1 comprises at least one monomer selected from C1 to C12, then in each case preferably in an amount of 0.1 to 30% by weight, particularly preferably 1 to 20% by weight, in particular 1.5 to 10 % by weight, based on the total weight of the monomer composition M1.

In a specific embodiment, the monomer composition M1 comprises no further comonomers apart from the monomers A and B.

More specifically, the monomer composition comprises no further comonomers other than acrylic acid.

The polymer composition P1 substantially comprises uncrosslinked polymers. The monomer composition M1 used to prepare the polymer composition P1 thus comprises in particular no added crosslinking monomers. Crosslinking monomers in the context of the invention are compounds having two or more than two polymerizable ethylenically unsaturated double bonds per molecule.

Preferably, the monomer composition M1 based on the total weight less than 0.1 % by weight, more preferably less than 0.05 % by weight, in particular less than 0.001 % by weight of crosslinking monomers containing two or more than two radically have polymerizable α, β-ethylenically unsaturated double bonds per molecule.

In a specific embodiment, the monomer composition M1 comprises no crosslinking monomers which have two or more than two polymerizable α, β-ethylenically unsaturated double bonds per molecule.

Polyether component PE:
Suitable as polyether component PE are polyetherols having a number average molecular weight of at least 200 g/mol and their mono- and di-(C_1-C_6-alkyl ethers).

Suitable polyetherols and their mono- and di-(C_1-C_6-alkyl ethers) may be linear or branched, preferably linear. Suitable polyetherols and their mono- and di-(C1-C6-alkyl ethers) generally have a number-average molecular weight in the range from about 200 to 100,000, preferably from 300 to 50,000, particularly preferably from 500 to 40,000. Suitable polyetherols are, for example, water-soluble or water-dispersible nonionic polymers which comprise alkylene oxide repeat units. Preferably, the proportion of alkylene oxide repeating units is at least 30 % by weight, based on the total weight of the compound. Suitable polyetherols are polyalkylene

glycols, such as polyethylene glycols, polypropylene glycols, polytetrahydrofurans and alkylene oxide copolymers. Suitable alkylene oxides for the preparation of alkylene oxide copolymers are e.g. ethylene oxide, propylene oxide, epichlorohydrine, 1,2- and 2,3-butylene oxide. Suitable examples are copolymers of ethylene oxide and propylene oxide, copolymers of ethylene oxide and butylene oxide and copolymers of ethylene oxide, propylene oxide and at least one butylene oxide. The alkylene oxide copolymers may comprise randomly distributed alkylene oxide units or in copolymerized form in the form of blocks. Preferably, in the ethylene oxide / propylene oxide copolymers, the proportion of repeating units derived from ethylene oxide is 40 to 99% by weight. Particularly preferred as the polyether component PE are ethylene oxide homopolymers and ethylene oxide / propylene oxide copolymers.

Also suitable as polyether component PE are the mono- and di-(C_1-C_6-alkyl ethers) of the polyetherols described above. Preference is given to polyalkylene glycol monomethyl ether and polyalkylene glycol dimethyl ether.

Also suitable as polyether component PE are polyether-containing surfactants. Generally suitable are nonionic and ionic surfactants which have at least one nonpolar and at least one polar group and which comprise a polyether group.

The polyether groups-containing surfactants PE are preferably selected from alkylpolyoxyalkylenether, arylpolyoxyalkylenether, alkylarylpolyoxyalkylenether, alkoxylated animal and/or vegetable fats and/or oils, fatty amine alkoxylates, fatty acid amide alkoxylates, fatty acid diethanolamide alkoxylates, polyoxyethylenesorbitan fatty acid esters, alkylpolyethersulfates, arylpolyethersulfates, alkylarylpolyethersulfates, alkylpolyethersulfonates, arylpolyethersulfonates, alkylarylpolyethersulfonates, alkylpolyether phosphateates, aryl polyether phosphates, alkylaryl polyether phosphates, glycerol ether sulfonates, glycerol ether sulfates, monoglyceride (ether) sulfates, fatty acid amide ether sulfates, polyoxyalkylene sorbitan fatty acid esters, and mixtures thereof.

The preferred nonionic polyether group-containing surfactants PE include, for example:

Alkyl polyoxyalkylene ethers derived from C_3-C_6 low molecular weight alcohols or C_7-C_{30} fatty alcohols. Here, the ether component may be derived from ethylene oxide units, propylene oxide units, 1,2-butylene oxide units, 1,4-butylene oxide units, and random copolymers and block copolymers thereof. Suitable nonionic surfactants include, inter alia, surfactants of the general formula (VI)

$$R^{10}\text{-O-}(CH_2CH_2O)_x\text{-}(CHR^{11}CH_2O)_y\text{-}R^{12} \quad \text{(VI)},$$

wherein

R^{10} is a linear or branched alkyl radical having 6 to 22 C atoms,

R^{11} and R^{12} independently of one another are hydrogen or a linear or branched alkyl radical having 1 to 10 C atoms or H, wherein R^{12} is preferably methyl, and
x and y are independently 0 to 300. Preferably, x = 1 to 100 and y = 0 to 30.

These include, in particular, fatty alcohol alkoxylates and oxo alcohol alkoxylates, such as isotridecyl alcohol and oleyl alcohol polyoxyethylene ethers.

Hydroxyl-containing surfactants of the general formula (VII)

$$R^{13}\text{-O-}(CH_2CH_2O)_s\text{-}(CH_2CH_2CH_2O)_t\text{-}(CH_2CH_2CH_2CH_2O)_u\text{-}(CH_2CHR^{14}O)_v\text{-}CH_2CH(OH)R^{15}$$

(VII)

wherein
in the compounds of the formula (VII) the sequence of the alkylene oxide units is arbitrary,
s, t, u and v independently represent an integer from 0 to 500, the sum of s, t, u and v being > 0,
R^{13} and R^{15} independently of one another represent a linear or branched, saturated C_1-C_{40}-alkyl radical or a mono- or polyunsaturated C_2-C_{40}-alkenyl radical, and
R^{14} is selected from methyl, ethyl, n-propyl, isopropyl or n-butyl.

In the compounds of the general formula (VII), the sum of s, t, u and v is preferably from 10 to 300, particularly preferably from 15 to 200 and in particular from 20 to 150.

Preferably, t and u are 0. Then the sum of s and v is preferably from 10 to 300, particularly preferably from 15 to 200 and in particular from 20 to 150.

In the compounds of the general formula (VII), R^{13} and R^{15} are preferably, independently of one another, a linear or branched, saturated C_2-C_{30}-alkyl radical. R^{13} and R^{15} may also be mixtures of different alkyl radicals.

In the compounds of the general formula (VII), R^{14} is preferably methyl or ethyl, in particular methyl.

A preferred embodiment are hydroxyl-containing surfactants of the general formula

$$R^{13}\text{-O-}(CH_2CH_2O)_s\text{-}(CH_2CH(CH_3)O)_v\text{-}CH_2CH(OH)R^{15}$$

(VII.1)

wherein
the order of the -(CH_2CH_2O)- and the $(CH_2CH(CH_3)O)$ units is arbitrary,
s and v are independently an integer from 0 to 500, the sum of s and v being > 0, and
R^{13} and R^{15} independently of one another represent a linear, saturated C_1-C_{30}-alkyl radical or a branched, saturated C_3-C_{30}-alkyl radical or mono- or polyunsaturated C_2-C_{30}-alkenyl radical.

In the compounds of the general formula (VII.1), the sum of s and v is preferably from 10 to 300, particularly preferably from 15 to 200 and in particular from 20 to 150.

The group of these nonionic surfactants include e.g. hydroxy mixed ethers of the general formula (C_{6-22}-alkyl)-CH(OH)CH_2O-$(EO)_{20-120}$-(C_{2-26}-alkyl).

Alcohol polyoxyalkylene esters of the general formula (VIII)

$$R^{16}\text{-O-}(CH_2CH_2O)_p\text{-}(CH_2CHR^{17}O)_q\text{-C(=O)}R^{18}$$

(VIII)

wherein
in the compounds of the formula (VIII) the sequence of the alkylene oxide units is arbitrary,
p and q independently of one another represent an integer from 0 to 500, the sum of p and q being > 0,
R^{16} and R^{18} independently of one another represent a linear or branched, saturated C_1-C_{40}-alkyl radical or a mono- or polyunsaturated C_2-C_{40}-alkenyl radical, and
R^{17} is selected from methyl, ethyl, n-propyl, isopropyl or n-butyl.

In the compounds of the general formula (VIII), the sum of p and q is preferably from 10 to 300, particularly preferably from 15 to 200 and in particular from 20 to 150.

In the compounds of the general formula (VIII), preferably R^{16} and R^{18} independently of one another represent a linear or branched, saturated C_4-C_{30}-alkyl radical. R^{16} and R^{18} may also be mixtures of different alkyl radicals.

In the compounds of the general formula (VIII), R^{17} is preferably methyl or ethyl, in particular methyl.

These include e.g. lauryl alcohol polyoxyethylene acetate.
- alkylarylalkoholpolyoxyethylenether, e.g. Octylphenol polyoxyethylene ether,
- alkoxylated animal and/or vegetable fats and/or oils, e.g. corn oil ethoxylates, castor oil ethoxylates, tallow fat ethoxylates,
- alkyl phenol alkoxylates, such as ethoxylated isooctyl-, octyl- or nonylphenol, tributylphenol polyoxyethylene ethers,
- fatty amine alkoxylates, fatty acid amide- and fatty acid diethanolamide alkoxylates, especially their ethoxylates,
- polyoxyalkylenesorbitan fatty acid esters.

An example of an alkylpolyethersulfate is sodium dodecylpoly (oxyethylene) sulfate (sodium lauryl ether sulfate, SLES). A preferred commercially available modified fatty alcohol polyglycol ether is a double ending C_xH_{2x+1}/C_yH_{2y+1}-terminated polyethylene oxide having a free OH group and x, y = 6-14.

Polymer composition P1:
Preferably, polymer composition P1 is prepared by

A) providing a monomer composition M1 which comprises at least one monomer A which is selected from α, β-ethylenically unsaturated mono- and dicarboxylic acids, salts of α, β-ethylenically unsaturated mono- and dicarboxylic acids, anhydrides α, β-ethylenically unsaturated mono- and dicarboxylic acids and mixtures thereof,

B) subjecting the monomer composition M1 provided in step A) to a free radical polymerization in the presence of at least one polyether component PE which is selected from polyetherols having a number average molecular weight of at least 200 g/mol, mono- and di- (C_1-C_6-alkyl) ethers such polyethers, polyether- groups containing surfactants and mixtures thereof, and optionally in the presence of at least one additive.

With respect to the monomer composition M1 provided in step A), the aforementioned suitable and preferred monomers A as well as the optional comonomers B and C are referred to in their entirety.

The radical polymerization of the monomer composition M1 in step B) is preferably carried out in the feed process. In general, at least the monomers in liquid form can be fed to the reaction batch. Liquid monomers can be fed to the reaction mixture without the addition of a solvent LM1, otherwise the monomers are used as a solution in a suitable solvent LM1. It is also possible to use monomers present in solid form.

The radical polymerization for the preparation of the polymer composition P1 can be carried out in the presence of a solvent LM1 which is selected from water, C_1-C_6-alkanols, polyols other than PE, their mono- and dialkyl ethers and mixtures thereof. Suitable polyols and their mono- and di-alkyl ethers also include alkylene glycol mono (C_1-C_4-alkyl) ethers, alkylene glycol di (C_1-C_4-alkyl) ethers, oligoalkylene glycols and their mono (C_1-C_4-alkyl) ethers and di (C_1-C_4-alkyl) ethers.

The solvent LM1 is preferably selected from water, methanol, ethanol, n-propanol, isopropanol, n-butanol, ethylene glycol, ethylene glycol mono (C_1-C_4-alkyl) ethers, ethylene glycol di (C_1-C_4-alkyl) ethers, 1,2-propylene glycol, 1,2-propylene glycol mono (C_1-C_4-alkyl) ethers, 1,2-propylene glycol di (C_1-C_4-alkyl) ethers, glycerol, polyglycerols, oligoalkylene glycols having a number average molecular weight of less than 1000 g/mol, and mixtures thereof.

Suitable oligoethylene glycols are among the CTFA designations PEG-6, PEG-8, PEG-12, PEG-6-32, PEG-20, PEG-150, PEG-200, PEG-400, PEG-7M, PEG-12M and PEG-115M commercially available. These include in particular the Pluriol E ® brands of BASF SE. Suitable alkylpolyalkylene glycols are the corresponding Pluriol A... E® brands from BASF SE.

The solvent LM1 is particularly preferably selected from water, ethanol, n-propanol, isopropanol, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,2-dipropylene glycol and mixtures thereof.

In a specific embodiment, the solvent used as LM1 is water or a mixture of water and at least one solvent LM1 other than water selected from ethanol, n-propanol, isopropanol, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1, 2-dipropylene glycol and mixtures thereof.

In a specific embodiment, the radical polymerization in step B) is conducted in the presence of a solvent LM1 which comprises water in an amount of at least 50% by weight, preferably at least 75% by weight, especially at least 90% by weight, based on the total weight the solvent LM1. In particular, the radical polymerization in step B) takes place in the presence of a solvent LM1, which consists of water.

Preferably, the radical polymerization in step B) is conducted in feed mode, whereby feeds, which comprise at least one α, β-ethylenically unsaturated carboxylic acid, do not comprise a solvent LM1.

The feed rates of the monomer feed / the monomer feeds and any further feeds (initiator, regulator, etc.) are preferably selected as such that the polymerization is maintained at the desired polymerization rate. The addition of the individual feeds can be carried out continuously, periodically, with a constant or alternating feed rate, substantially simultaneously or with a time lag. Preferably, the addition of all feeds to the reaction mixture is carried out continuously.

The monomer composition M1 and the polyether component PE are preferably used in the radical polymerization in a weight ratio of from 0.5:1 to 5:1, particularly preferably from 0.7:1 to 3:1.

If a solvent LM1 is used to prepare the polymer composition, the weight ratio of the polyether component PE to the component LM1 is preferably in the range from 0.1:1 to 5:1, particularly preferably from 0.5:1 to 3:1.

The radical polymerization in step B) preferably is conducted at a temperature in the range from 20 to 95°C, more preferably from 30 to 90°C, in particular from 40 to 80°C.

The radical polymerization in step B) can be carried out in the presence of at least one additive. Suitable additives are e.g. corrosion inhibitors, defoamers, dyes, fragrances, thickeners, solubilizers, organic solvents, electrolytes, antimicrobial agents, antioxidants, UV absorbers and mixtures thereof.

The radical polymerization in step B) of the process preferably comprises the steps of

B1) providing a template which comprises at least part of the polyether component PE, optionally at least part of the regulator R and, if the polymerization is carried out in the presence of a solvent LM1, optionally at least part of LM1;

B2) adding the monomer composition M1 in one or more feeds and adding a feed containing the radical initiator S dissolved in a part of the at least one polyether component PE and/or the solvent LM1 and optionally adding an feed which comprises the amount of regulator R that is not used in the template,

B3) optionally post-polymerizing the reaction mixture obtained in step B2).

Usually, the template is heated to the polymerization temperature with stirring prior to adding the feeds.

Preferably, the individual reactants are added simultaneously in separate feeds, wherein the flow rates of the feeds are usually kept as constant as possible over the period of addition.

The amount of polyether component PE in the initial charge (step B1) is preferably from 30 to 100% by weight, more preferably from 65 to 100% by weight and in particular from 80 to 100% by weight, based on the total weight of the polyether component PE used in the polymerization.

Preferably, the amount of solvent LM1 in the template is not more than 70 % by weight, based on the total weight of the components of the template. Preferably, the amount of solvent in the template is not more than 40 % by weight, in particular not more than 35 % by weight, based on the total weight of the components of the template. The amount of solvent changes over the entire course of the process usually only a few percent by weight. Typically, solvents LM1 are used which have a boiling point at atmospheric pressure (1 bar) of less than 240 °C.

In a special variant, the template contains no solvent. This is added only in step B2) via at least one of the feeds. In a very special variant, no solvent is introduced and no solvent is added over the entire course of the process.

In a further special variant, the solvent is completely added in the template.

In another special variant, the template contains no regulator. If a regulator is used, it is added only in step B2) via at least one of the feeds.

The addition of the feeds in step B2) is conducted over a period of time which is advantageously chosen as such that the heat of reaction formed in the exothermic polymerization reaction can be withdrawn without major technical effort, e.g. without the use of a reflux condenser. Usually, the feeds are added over a period of 1 to 10 hours. Preferably, the feeds are added over a period of 2 to 8 hours, more preferably over 2 to 6 hours.

In an alternative embodiment, the free-radical polymerization in step B) of the process is conducted continuously. Then the monomer composition M1, the polyether component PE, at least one initiator, optionally at least one regulator R and optionally at least one solvent LM1 are added to the reactor in the form of a liquid stream or preferably at least two liquid streams. In general, the stream containing the initiator generally does not also include the regulator. If at least two liquid streams are used, they are mixed in a customary manner to obtain the reaction mixture. The polymerization may be conducted in one stage or in two or more than two, i.e. in 2, 3, 4, 5 or more stages. In a suitable embodiment, in the case of a multistage polymerization, at least one additional stream is added between at least two of the polymerization stages. It may be a monomer-containing stream, initiator-containing stream, solvent-containing stream, regulator-containing stream, a mixture thereof and/or any other material stream.

During the radical polymerization, the optional solvent and/or any resulting condensation products are generally not withdrawn. I.e. during the polymerization, there is usually no or only a very small, within the scope of the technical possibilities, mass transfer with the environment.

The polymerization can usually be carried out at ambient pressure or reduced or elevated pressure. Preferably, the polymerization is carried out at ambient pressure.

The polymerization is usually carried out at a constant temperature, but can also be varied as needed during the polymerization. Preferably, the polymerization temperature is kept as constant as possible over the entire reaction period, i.e. the steps B2) and B3). Depending on the starting materials, the polymerization temperature usually ranges from 20 to 95°C. Preferably, the polymerization temperature is in the range of 30 to 90°C, and more preferably in the range of 40 to 80°C. If the polymerization is not carried out under elevated pressure and at least one optional solvent LM1 was added to the reaction mixture, the solvent or solvent mixture determines the maximum reaction temperature by their corresponding boiling temperatures.

The polymerization can be carried out in the absence or in the presence of an inert gas. Usually, the polymerization is carried out in the presence of an inert gas. An inert gas is usually understood to be a gas which, under the given reaction conditions, does not react with the educts, reagents, solvents or the resulting products involved in the reaction.

If the polymerization is carried out in the presence of a solvent, the solvent is selected from the solvents LM1 described above.

To prepare the polymers, the monomers can be polymerized with the aid of radical-forming initiators, hereinafter also referred to as radical initiators or starters. Radical initiators (initiators) for radical polymerization are in principle all radical initiators which are substantially soluble in the reaction medium, as prevails at the time of their addition, and have sufficient activity at the given reaction temperatures to initiate the polymerization. In the process according to the invention, a single radical starter or a combination of at least two radical initiators can be used.

In the latter case, the at least two radical initiators can be added in a mixture or preferably separately, simultaneously or sequentially, e.g. at different times in the course of the reaction.

Radical initiators which can be used for radical polymerization are the customary peroxo and/or azo compounds, for example hydrogen peroxide, alkali metal or ammonium peroxodisulfates (such as, for example, sodium peroxodisulfate), diacetyl peroxide, dibenzoyl peroxide, succinyl peroxide, di-tert-butyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxypivalate, tert-butyl peroxyneodecanoate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxymaleinate, cumene hydroperoxide, diisopropyl peroxydicarbamate, bis-(o-toluoyl) peroxide, didecanoyl peroxide, dioctanoyl peroxide, tert-butyl peroctoate, dilauroyl peroxide, tert-butyl perisobutyrate, tert-butyl peracetate, di-tert-amyl peroxide, tert-butyl hydroperoxide, 2,2'-azo-bis-isobutyronitrile, 2,2'-azo-bis (2-amidinopropane) dihydrochloride (= azo-bis (2-methylpropionamidine) dihydrochloride), azo-bis (2,4-dimethylvaleronitrile) or 2,2'-azo-bis (2-methylbutyronitrile).

Also suitable are initiator mixtures or redox initiator systems, such as
ascorbic acid / iron (II) sulfate / sodium peroxodisulfate,
tert-butyl hydroperoxide / sodium disulfite,
tert-butyl hydroperoxide / sodium hydroxymethanesulfinate,
H_2O_2 / Cu^I.

In the polymerization process, the amount of initiator system (initiator) ranges from 0.01 to 10 pphm, preferably from 0.1 to 5 pphm, more preferably from 0.2 to 2 pphm and especially in the range of from 0.3 to 1.5 pphm (parts per hundred monomer = parts by weight per hundred parts by weight of monomer).

In the polymerization process, the radical initiator is generally provided as a solution in a solvent which comprises at least one of the abovementioned solvents LM1 and optionally additionally at least one polyether of the polyether component PE.

The polymerization can be carried out without the use of a regulator (polymerization regulator) or in the presence of at least one regulator. Regulators generally refer to compounds having high transfer constants which accelerate chain transfer reactions and thus cause a reduction in the degree of polymerization of the resulting polymers. In the case of the regulators, one can distinguish between mono-, bi- or polyfunctional regulators depending on the number of functional groups in the molecule which can lead to one or more chain transfer reactions. Suitable regulators are described in detail, for example, by K.C. Berger and G. Brandrup in J. Brandrup, E.H. Immergut, Polymer Handbook, 3rd ed., John Wiley & Sons, New York, 1989, p. II / 81 - II / 141.

Suitable regulators are, for example, aldehydes, such as formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde.

Also suitable as regulators are formic acid, its salts or esters, such as ammonium formate, 2,5-diphenyl-1-hexene, hydroxylammonium sulfate and hydroxylammonium phosphate.

Other suitable regulators are allyl compounds, such as allyl alcohol, functionalized allyl ethers such as allyl ethoxylates, alkyl allyl ethers, or glycerol monoallyl ethers.

Preference is given to using compounds, which comprise sulfur as regulators. Compounds of this type are, for example, inorganic hydrogen sulfites, disulfites and dithionites or organic sulfides, disulfides, polysulfides, sulfoxides and sulfones. These include di-n-butylsulfide, di-n-octylsulfide, diphenylsulfide, thiodiglycol, ethylthioethanol, diisopropyl disulfide, di-n-butyl disulfide, di-n-hexyl disulfide, diacetyl disulfide, diethanol sulfide, di-t-butyl trisulfide, dimethyl sulfoxide, dialkyl sulfide, dialkyl disulfide and/or diaryl sulfide. Also suitable as polymerization regulators are thiols (compounds which comprise sulfur in the form of SH groups, also referred to as mercaptans). Preferred regulators are mono-, bi- and polyfunctional mercaptans, mercaptoalcohols and/or mercaptocarboxylic acids. Examples of these compounds are allyl thioglycolates, ethyl thioglycolate, cysteine, 2-mercaptoethanol, 1,3-mercaptopropanol, 3-mercaptopropane-1,2-diol, 1,4-mercaptobutanol, mercaptoacetic acid, 3-mercaptopropionic acid, mercaptosuccinic acid, thioglycerol, thioacetic acid, thiourea and alkylmercaptans such as n-butylmercaptan, n-hexylmercaptan or n-dodecylmercaptan. Examples of bifunctional regulators containing two sulfur atoms in bonded form are bifunctional thiols, such as dimercaptopropanesulfonic acid (sodium salt), dimercaptosuccinic acid, dimercapto-1-propanol, dimercaptoethane, dimercaptopropane, dimercaptobutane, dimercaptopentane, dimercaptohexane, ethylene glycol bis-thioglycolate and butanediol-bis-thioglycolate. Examples of polyfunctional regulators are compounds containing more than two sulfur in bound form. Examples of these are trifunctional and/or tetrafunctional mercaptans.

The regulator is particularly preferably selected from mercaptoethanol, mercaptoacetic acid, mercaptopropionic acid, ethylhexyl thioglycolate and sodium hydrogensulfite.

Also preferred as regulators are hypophosphorous acid (phosphinic acid) and salts of hypophosphorous acid. A preferred salt of the hypophosphorous acid is the sodium salt.

When a regulator is used in the polymerization process, the amount is usually 1 to 40 pphm (parts per hundred monomer, i.e. parts by weight based on one hundred parts by weight of the monomer composition). The amount of regulator used in the polymerization process is preferably in the range from 3 to 30 pphm, more preferably in the range from 5 to 25 pphm. It is also possible to carry out the polymerization without addition of a regulator.

Usually, the regulator is added continuously to the polymerization mixture in step B2) completely via one of the feeds. However, it is also possible to either fully add the regulator to the template, i.e. before the actual polymerization, or to add only a part of the regulator to the template and the remainder is added continuously in step B2) to the polymerization mixture via

one of the feeds. The addition of the regulator can be carried out in each case without or with solvent LM1.

The amount of regulator and the way it is added to the reaction mixture have a strong influence on the average molecular weight of the polymer composition. If no regulator or only a small amount of regulator is used and/or if the addition is conducted predominantly before the polymerization, usually higher average molecular weights of the polymer are obtained. On the other hand, if larger amounts of regulators are used and/or if the addition of the regulator is conducted largely during the polymerization (step B2), usually a lower average molecular weight is obtained.

Preferably, the polymer composition obtained after completion of the polymerization (step B3) is transferred to a suitable vessel and optionally cooled directly to ambient temperature (20°C).

The polymer compositions P1 obtained as such are advantageously suitable for the production of multi-layered films, e.g. for use as a coating of a liquid detergent or cleaning agent.

The weight-average molecular weight Mw of the polymer composition can be determined, for example, by means of gel permeation chromatography (GPC) in aqueous solution using neutralized polyacrylic acid as polymer standard, as is generally known to the person skilled in the art. In this type of molecular weight determination, the components of the polymer composition are detected, which comprise the monomers M1 in polymerized form. The polymer composition P1 preferably has a weight-average molecular weight of from 2,000 to 100,000 g/mol, preferably from 3,000 to 80,000 g/mol.

The polymer composition P1 has a sufficiently low glass transition temperature Tg suitable for film formation. The polymer compositions P1 preferably have a glass transition temperature Tg in the range from 0 to 80°C., more preferably from 0 to 60°C., in particular from 0 to 30°C.

The polymer composition P1 preferably has a content of acid groups of more than 1 mmol/g, particularly preferably more than 1.3 mmol/g, before it is used for film production (i.e. before it is dried). The polymer composition P1 preferably has a content of acid groups of at most 15 mmol/g before it is used for film production. The polymer composition P1 in particular has a content of acid groups of 1.5 mmol/g to 10 mmol/g before it is used for film production.

In a preferred embodiment, the acid groups of the polymer composition according to the invention are present in unneutralized form.

Polymer P2:

As already discussed above the multi-layered film further comprises at least one other layer L2 which comprises at least one polymer P2 which is different from polymer composition P1 and is selected from

- natural or modified polysaccharides;

- homo- or copolymers comprising monomer units derivable from vinyl alcohol, vinylesters, alkoxylated vinyl alcohols, or mixtures thereof;
- homo-or copolymers comprising at least one monomer selected from N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, 2-vinylpyridine, 4-vinyl-pyridine, salts of N-vinylimidazole, salts of 2-vinylpyridine, salts of 4-vinyl-pyridine, vinylpyridine-N-oxide, N-carboxymethyl-4-vinylpyridine halogenides or mixtures thereof;
- homo- or copolymers of acrylic acid and /or methacrylic acid, preferably copolymers comprising at least one acrylic acid monomer selected from acrylic acid, salts of acrylic acid or mixtures thereof and at least one maleic acid monomer selected from maleic acid, maleic acid anhydride, salts of maleic acid or mixtures thereof;
- copolymer comprising at least a (meth)acrylic acid monomer selected from acrylic acid, methacrylic acid, salts of acrylic acid, salts of methacrylic acid or mixtures thereof and at least one hydrophobic monomer selected from C_1-C_8 alkylesters of (meth) acrylic acid, C_2-C_{10} olefins, styrene or α-methyl-styrene;
- homo- or copolymers of acrylamide and or methacrylamide;
- polyaminoacids;
- water-soluble or water-dispersible polyamides;
- polyalkyleneglycols, mono-or diethers of polyalkyleneglycols;
- polyalkyleneoxide such as polyethyleneoxide; and
- mixtures thereof.

The multi-layered film particularly preferably comprises at least one further layer which comprises at least one polymer P2 or consists of at least one polymer P2 which is selected from Cellulose ethers and cellulose esters,
Homo- and copolymers containing repeating units derived from vinyl alcohol, vinyl esters, alkoxylated vinyl alcohols or mixtures thereof,
Polymers selected from polyvinylpyrrolidone homopolymers, polyvinylimidazole homopolymers, copolymers compriseing copolymerized vinylpyrrolidone and vinylimidazole, polyvinylpyridine-N-oxide, poly-N-carboxymethyl-4-vinylpyridium halides,
mixtures thereof.

The multi-layered film comprises in particular at least one further layer which comprises at least one polymer P2 or consists of at least one polymer P2 selected from cellulose derivatives, preferably carboxyalkylcelluloses and salts thereof, sulfoalkylcelluloses and salts thereof, acidic sulfuric ester salts of cellulose, alkylcelluloses, hydroxyalkylcelluloses, (hydroxyalkyl) alkylcelluloses and mixtures of two or more of these cellulose derivatives.

Polysaccharides suitable as polymers P2 are natural polysaccharides, e.g. cellulose, hemicellulose, glycogen, starch (amylose and amylopectin), dextran, pectins, inulin, xanthan, chitin, callose, thermally, hydrolytically or enzymatically degraded starch, e.g. maltodextrin etc.

Preferred modified polysaccharides are e.g. cellulose ethers, cellulose esters, cellulose amides, etc.

Cellulose ethers are derivatives of cellulose that result from partial or total substitution of the hydrogen atoms in the hydroxy groups of the cellulose. Cellulose ethers from the reaction of cellulose with more than one etherifying agent are also referred to as cellulose mixed ethers.

Preferred cellulose ethers are selected from alkylcelluloses, hydroxyalkylcelluloses, (hydroxyalkyl) alkylcelluloses, carboxyalkylcelluloses and salts thereof, (carboxyalkyl) alkylcelluloses and salts thereof, (carboxyalkyl) (hydroxyalkyl) celluloses and salts thereof, (carboxyalkyl) (hydroxyalkyl) alkylcelluloses and salts thereof, sulfoalkylcelluloses and salts thereof.

Preferred carboxyalkyl radicals are the carboxymethyl radical and the carboxyethyl radical. Particularly preferred as carboxyalkyl radical is the carboxymethyl radical. Preferred as sulfoalkyl radical are the sulfomethyl radical and the sulfoethyl radical. Particularly preferred as sulfoalkyl radical is the sulfomethyl radical. Preferred salts are the sodium, potassium, calcium and ammonium salts.

Particularly preferred cellulose ethers are selected from carboxymethylcellulose, carboxyethylcellulose, methylcellulose, ethylcellulose, n-propylcellulose, ethylmethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxybutylcellulose, hydroxyethylmethylcellulose, hydroxypropylmethylcellulose, hydroxyethylethylcellulose, hydroxypropylethylcellulose, carboxymethylmethylcellulose, carboxymethylethylcellulose, carboxymethylhydroxyethylcellulose, carboxymethylhydroxyethylmethylcellulose, carboxymethylhydroxyethylethylcellulose, sulfomethylcellulose and sulfoethylcellulose. The carboxyalkyl radicals and the sulfoalkyl radicals may also be present as salts.

Cellulose esters are derivatives of cellulose which are formed by esterification of the hydroxy groups with acids. Preferred are the sulfuric acid esters of cellulose. In a specific embodiment, the sulfuric acid is only subjected to a partial esterification, so that the resulting sulfuric acid esters still have free acid groups or their salts. Particular preferred are sulfuric ester salts of cellulose. These are distinguished by their graying-inhibiting effect.

Preferred modified polysaccharides are selected from methyl cellulose, ethyl cellulose, propyl cellulose, methyl/ethyl cellulose, ethyl/propyl cellulose, carboxymethyl cellulose, salts of carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyethylmethyl cellulose, hydroxyethylethyl cellulose, hydroxypropylmethyl cellulose, hydroxypropylethyl cellulose, etc.

In a further preferred embodiment, the polymers P2 are selected from homo- and copolymers comprising repeating units derived from vinyl alcohol, vinyl esters, alkoxylated vinyl alcohols or mixtures thereof.

Suitable vinyl esters (vinyl acylates) are generally the esters of vinyl alcohol with C_1-C_{15}-carboxylic acids, preferably C_1-C8-carboxylic acids, more preferably C_1-C_4-carboxylic acids.

Preferred vinyl acylates are vinyl acetate, vinyl n-propionate, vinyl n-butyrate, vinyl 2-ethylhexanoate, vinyl laurate, etc. Particularly preferred is vinyl acetate.

Partially or completely saponified (hydrolyzed) polyvinyl acetates (PVA) are generally referred to as "polyvinyl alcohol (PVOH)". Partially hydrolysed polyvinyl acetates are obtained by incomplete hydrolysis of polyvinyl acetates, i.e. the partially hydrolyzed polymer has both ester groups and hydroxyl groups. The saponification of the polyvinyl acetates can be carried out in a manner known per se in alkaline or acidic, i.e. with the addition of acid or base.

The performance properties of polyvinyl alcohols are determined inter alia by the degree of polymerization and the degree of hydrolysis (degree of saponification). As the degree of saponification increases, the solubility in water decreases. Polyvinyl alcohols with degrees of hydrolysis of up to about 90 mol% are generally soluble in cold water. Polyvinyl alcohols with degrees of hydrolysis of about 90 to about 99.9 mol% are generally no longer soluble in cold water, but are soluble in hot water.

Polyvinyl alcohols suitable as polymers P2 preferably have a saponification degree of from 50 to 99.9 mol%, particularly preferably from 70 to 99 mol%, in particular from 80 to 98 mol%.

The properties of polyvinyl alcohols can further be modified by the incorporation of additional monomers such as the sodium salts of 2-acrylamido-2-methylpropane sulfonic acid, vinylsulfonic acid or allylsulfonic acid.

Polyvinyl alcohols suitable as polymers P2 preferably have a weight-average molecular weight of from 10,000 to 300,000 g/mol, more preferably from 15,000 to 250,000 g/mol.

Polyvinylalcohol that can typically be used as polymers P2 are known under the tradename Poval™ from Kuraray company. Non limited examples are Poval™ 8-88, Poval™ 18-88, Poval™ 26-88, Poval™ 30-92, Poval™ 10-98, Poval™ 20-98 or Poval™ 28-99.

To tune the performance properties according to the specific need of the application blends comprising polyvinylalcohols of different molecular weight and degree of hydrolysis can be used. Non limited examples are a blend of Poval™ 26-88 (three parts) and Poval™ 20-98 (one part) or a blend of Poval™ 30-92 (two parts) and Poval™ 10-98 (one part).

Polyvinyl alcohols suitable as polymers P2 preferably have a viscosity of 2 to 120 mPa s, more preferably of 7 to 70 mPa s and in particular of 15 to 60 mPa s, measured according to DIN 53015 on a 4% solution in water.

In a further preferred embodiment, the polymers P2 are selected from homopolymers and copolymers which comprise at least one monomer in copolymerized form, which is selected from N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, 2-vinylpyridine, 4-vinylpyridine,

salts thereof three latter monomers, vinylpyridine-N-oxide, N-carboxymethyl-4-vinylpyridium halides and mixtures thereof.

N-vinylimidazole, 2-vinylpyridine and 4-vinylpyridine can be converted by protonation or quaternization into the corresponding salts. Suitable acids are e.g. mineral acids such as sulfuric acid, hydrochloric acid and phosphoric acid, and carboxylic acids. Alkylating agents suitable for quaternization are C_1-C_4 alkyl halides or C1-C4 alkyl sulfates such as ethyl chloride, ethyl bromide, methyl chloride, methyl bromide, dimethyl sulfate and diethyl sulfate.

Preferred are polyvinylpyrrolidone homopolymers and copolymers which comprise copolymerized N-vinylpyrrolidone and another ethylenically unsaturated monomer different therefrom. Suitable N-vinylpyrrolidone copolymers are generally neutral, anionic, cationic and amphoteric polymers.

Particularly preferred N-vinylpyrrolidone copolymers are selected from
Copolymers of N-vinylpyrrolidone and vinyl acetate,
Copolymers of N-vinylpyrrolidone and vinyl propionate,
Copolymers of N-vinylpyrrolidone, vinyl acetate and vinyl propionate,
Copolymers of N-vinylpyrrolidone and vinyl acrylate,
Copolymers of N-vinylpyrrolidone, ethyl methacrylate and methacrylic acid,
Copolymers of N-vinylpyrrolidone and N-vinylimidazole and their derivatives obtained by protonation and/or quaternization,
Copolymers of N-vinylpyrrolidone and dimethylaminoethyl methacrylate and their derivatives obtained by protonation and/or quaternization,
Copolymers of N-vinylpyrrolidone, N-vinylcaprolactam and N-vinylimidazole and their derivatives obtained by protonation and/or quaternization.

In a further preferred embodiment, the polymers P2 are selected from homopolymers and copolymers of acrylic acid and/or methacrylic acid.

In a first specific embodiment of the homopolymers and copolymers of acrylic acid and/or methacrylic acid, the polymer P2 used is an acrylic acid homopolymer. Acrylic acid homopolymers P2 preferably have a number-average molecular weight in the range from 800 to 70,000 g/mol, more preferably from 900 to 50,000 g/mol, in particular from 1000 to 20,000 g/mol, especially from 1000 to 10,000 g/mol. The term acrylic acid homopolymer also encompasses polymers in which the carboxylic acid groups are partially or completely neutralized. These include acrylic acid homopolymers in which the carboxylic acid groups are present partially or completely in the form of alkali metal salts or ammonium salts. Preference is given to acrylic acid homopolymers in which the carboxylic acid groups are protonated or in which the carboxylic acid groups are present partially or completely in the form of sodium salts. Homopolymers of acrylic acid which are particularly suitable as polymers P2 are the Sokalan® PA grades from BASF SE.

In a second specific embodiment of the homo- and copolymers of acrylic acid and/or methacrylic acid, the polymer P2 used is a copolymer comprising at least one acrylic acid monomer selected from acrylic acid, acrylic acid salts and mixtures thereof and at least one maleic acid monomer selected from maleic acid, maleic anhydride, maleic acid salts and mixtures thereof, in copolymerized form. These preferably have a number-average molecular weight in the range from 2500 to 150,000 g/mol, more preferably from 2800 to 70,000 g/mol, in particular from 2900 to 50,000 g/mol, more particularly from 3000 to 30,000 g/mol. Included here are also copolymers in which the carboxylic acid groups are partially or completely neutralized. For this purpose, it is possible to use monomers in salt form either for the polymerization or the resulting copolymer is subjected to a partial or complete neutralization. Preferred are copolymers in which the carboxylic acid groups are protonated or partially or completely present in the form of alkali metal salts or ammonium salts. Preferred alkali metal salts are the sodium or potassium salts, especially the sodium salts.

Preferred polymers P2 are copolymers of maleic acid (or maleic acid monomers) and acrylic acid (or acrylic acid monomers) in a weight ratio of 10:90 to 95: 5, particularly preferably in a weight ratio of 30:70 to 90:10.

Preferred polymers P2 are also terpolymers of maleic acid (or maleic acid monomers), acrylic acid (or acrylic acid monomers) and a vinyl ester of a C_1-C_3 carboxylic acid in a weight ratio of 10 (maleic acid) : 90 (acrylic acid + vinyl ester) to 95 (maleic acid) : 10 (acrylic acid + vinyl ester). The weight ratio of acrylic acid to vinyl ester is preferably in a range of 30:70 to 70:30.

Particularly suitable polymers P2 based on acrylic acid monomers and maleic acid monomers are the corresponding Sokalan® CP grades from BASF SE.

In a third specific embodiment of the homo- and copolymers of acrylic acid and/or methacrylic acid, the polymer P2 is a copolymer, which comprises at least one (meth) acrylic acid monomer selected from (meth) acrylic acid, (meth) acrylic acid salts and mixtures thereof and at least one hydrophobic monomer. The hydrophobic monomer is especially selected from C_1-C_8 alkyl esters of (meth) acrylic acid such as e.g. the methyl, ethyl, n- and iso-propyl, n-butyl and 2-ethylhexyl esters of (meth) acrylic acid and C_2-C_{10}-olefins, e.g. ethene, propene, 1,2-butene, isobutene, diisobutene, styrene and α-methylstyrene.

In a further preferred embodiment, the polymer P2 used is a copolymer of at least one maleic acid monomer selected from maleic acid, maleic anhydride, maleic acid salts and mixtures thereof with at least one C_2-C_8-olefin. Also suitable are copolymers which comprise at least one maleic acid monomer selected from maleic acid, maleic anhydride, maleic acid salts and mixtures thereof, in copolymerized form at least one C_2-C_8-olefin and at least one other comonomer which is different therefrom.

Particularly preferred are copolymers, which comprise at least one maleic acid monomer selected from maleic acid, maleic anhydride, maleic acid salts and mixtures thereof and at least

one C_2-C_8-olefin copolymerized as sole monomers. These preferably have a number average molecular weight in the range from 3000 to 150,000 g/mol, particularly preferably from 5000 to 70,000 g/mol, in particular from 8000 to 50,000 g/mol, more particularly from 10,000 to 30,000 g/mol. Included therein are also copolymers in which the carboxylic acid groups are partially or completely neutralized. For this purpose, either maleic acid salts can be used for the polymerization or the resulting copolymer is subjected to a partial or complete neutralization. Preferred are copolymers in which the carboxylic acid groups are protonated or partially or completely present in the form of alkali metal salts or ammonium salts. Preferred alkali metal salts are the sodium or potassium salts, especially the sodium salts.

A specific embodiment are copolymers of maleic acid with C_2-C_8 olefins in a molar ratio of 40:60 to 80:20, whereby copolymers of maleic acid with ethylene, propylene, isobutene, diisobutene or styrene are particularly preferred. Particularly suitable polymeric carboxylic acid group-containing compounds based on olefins and maleic acid are likewise the corresponding Sokalan® CP grades from BASF SE.

Another preferred embodiment is copolymers comprising at least one maleic acid monomer selected from maleic acid, maleic anhydride, maleic acid salts and mixtures thereof, at least one C_2-C_8 olefin and at least one acrylic acid monomer selected from acrylic acid, acrylic acid salts and mixtures thereof, in copolymerized form.

A further preferred embodiment is copolymers which comprise at least one maleic acid monomer selected from maleic acid, maleic anhydride, maleic acid salts and mixtures thereof, at least one C_2-C_8 olefin and at least one ester of (meth) acrylic acid in copolymerized form. The ester of (meth) acrylic acid is then in particular selected from C_2-C_8-alkyl esters of (meth) acrylic acid, e.g. the methyl, ethyl, n- and iso-propyl, n-butyl and 2-ethylhexyl esters of (meth) acrylic acid.

In a further preferred embodiment, the polymers P2 are selected from homopolymers and copolymers which comprise, in polymerized form, at least one monomer selected from acrylamide, methacrylamide and mixtures thereof. These polymers P2 are preferably water-soluble or water-dispersible. In particular, these polymers P2 are water-soluble.

In a specific embodiment, the polymers P2 are selected from homopolymers of acrylamide or methacrylamide.

In a further specific embodiment, the polymers P2 are selected from copolymers of acrylamide and/or methacrylamide. These comprise at least one comonomer in copolymerized form, which is selected from acrylamide and methacrylamide different hydrophilic monomers (A1), monoethylenically unsaturated, amphiphilic monomers (A2) and other ethylenically unsaturated monomers (A3).

Suitable hydrophilic, monoethylenically unsaturated monomers (A1) are neutral monomers, such as N-methyl (meth) acrylamide, N, N'-dimethyl (meth) acrylamide or N-methylol (meth) acrylamide, monomers comprising hydroxyl and/or ether groups, such as e.g. hydroxyethyl (meth) acrylate, hydroxypropyl (meth) acrylate, allyl alcohol, hydroxyvinylethyl ether, hydroxyvinylpropyl ether, hydroxyvinylbutyl ether, polyethylene glycol (meth) acrylate, N-vinylformamide, N-vinylacetamide, N-vinylpyrrolidone or N-vinylcaprolactam and vinyl esters, such as vinyl formate or vinyl acetate. N-vinyl derivatives can be hydrolyzed after polymerization to vinylamine units, vinyl esters to vinyl alcohol units. Suitable hydrophilic, monoethylenically unsaturated monomers (A1) are furthermore monomers which comprise at least one acidic group or salts thereof. These include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, vinylsulfonic acid, allylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, 2-methacrylamido-2-methylpropanesulfonic acid, 2-acrylamidobutanesulfonic acid, 3-acrylamido-3-methylbutanesulfonic acid, 2-acrylamido-2,4,4-trimethylpentanesulfonic acid, vinylphosphonic acid, allylphosphonic acid, N-(meth) acrylamidoalkylphosphonic acids, (meth) acryloyloxyalkylphosphonic acids and salts and mixtures thereof. The other monoethylenically unsaturated hydrophilic monomers may be hydrophilic cationic monomers. Suitable cationic monomers (A1c) include, in particular, ammonium-group containing monomers, in particular ammonium derivatives of N-(ω-aminoalkyl) (meth) acrylamides or ω-aminoalkyl (meth) acrylic esters.

The amphiphilic monomers (A2) are preferably monoethylenically unsaturated monomers which have at least one hydrophilic group and at least one, preferably terminal, hydrophobic group.

The monomers (A3) may be e.g. monoethylenically unsaturated monomers which have a more hydrophobic character than the hydrophilic monomers (A1) and which accordingly are only slightly water-soluble. Examples of such monomers include N-alkyl and N, N'-dialkyl (meth) acrylamides wherein the number of carbon atoms in the alkyl groups together is at least 3, preferably at least 4. Examples of such monomers include N-butyl (meth) acrylamide, N-cyclohexyl (meth) acrylamide or N-benzyl (meth) acrylamide.

In a further preferred embodiment, the polymers P2 are selected from polyamino acids. Suitable polyamino acids are in principle compounds, which comprise at least one amino acid, such as aspartic acid, glutamic acid, lysine, glycine, etc. in copolymerized form. The polyamino acids also include the derivatives obtainable by polymer-analogous reaction, such as esterification, amidation, etc. Preferred polyamino acids are polyaspartic acid, polyaspartic acid derivatives, polyglutamic acid, polyglutamic acid derivatives and mixtures thereof.

Polyaspartic acid may e.g. by alkaline hydrolysis of polysuccinimide (PSI, anhydropolyaspartic acid). Polysuccinimide can be prepared by thermal condensation of aspartic acid or from ammonia and maleic acid. Polyaspartic acid may e.g. be used as a biodegradable complexing agent and cobuilder in detergents and cleaners.

Polyamino acids having surfactant properties can be obtained by at least partially converting the free carboxylic acid groups of polyaspartic acid or polyglutamic acid into N-alkylamides and/or into esters. Polyaspartic acid amides can also be prepared by reacting polysuccinimide with amines. For the preparation of hydroxyethylaspartamides the ring opening of polysuccinimide can be carried out with ethanolamine. DE 37 00 128 A and EP 0 458 079 A describe the subsequent esterification of such hydroxyethyl derivatives with carboxylic acid derivatives. Copolymers of polyaspartic ester are, as described in DE 195 45 678 A, obtainable by condensation of monoalkyl esters of maleic or fumaric acid with addition of ammonia. In DE 195 45 678 A is further described that copolymeric polyaspartic esters are accessible by reaction of polysuccinimide with alcohols and optionally subsequent hydrolysis. Depending on the degree of esterification and hydrophobicity of the alcohol component, polyaspartic esters, in addition to their biodegradability, are distinguished by excellent properties as stabilizers for O / W and W / O emulsions, foam-stabilizing and foam-enhancing cosurfactants in detergents and cleaners and as complexing agents for metal cations.

In a further preferred embodiment, the polymers P2 are selected from polyalkylene glycols and mono- or diethers of polyalkylene glycols. Preferred polyalkylene glycols have a number average molecular weight in the range from 1000 to 4,000,000 g/mol, particularly preferably from 1,500 to 1,000,000 g/mol

Suitable polyalkylene glycols and their mono- or diethers may be linear or branched, preferably linear. Suitable polyalkylene glycols are e.g. water-soluble or water-dispersible nonionic polymers, which comprise alkylene oxide repeat units. The proportion of alkylene oxide repeating units is preferably at least 30% by weight, preferably at least 50% by weight, in particular at least 75% by weight, based on the total weight of the compound. Suitable polyalkylene glycols are polyethylene glycols, polypropylene glycols, polytetrahydrofurans and alkylene oxide copolymers. Suitable alkylene oxides for the preparation of alkylene oxide copolymers are, for. For example, ethylene oxide, propylene oxide, epichlorohydrin, 1,2- and 2,3-butylene oxide. Suitable examples are copolymers of ethylene oxide and propylene oxide, copolymers of ethylene oxide and butylene oxide and copolymers of ethylene oxide, propylene oxide and at least one butylene oxide. The alkylene oxide copolymers may comprise randomly distributed alkylene oxide units or in copolymerized form in the form of blocks. Preferably, in the ethylene oxide / propylene oxide copolymers, the proportion of repeating units derived from ethylene oxide is 40 to 99% by weight. Particularly preferred are ethylene oxide homopolymers and ethylene oxide / propylene oxide copolymers.

Suitable mono- and diethers of polyalkylene glycols are the mono (C_1-C_{18} alkyl ethers) and di (C_1-C_{18} alkyl ethers). Preferred mono- and diethers of polyalkylene glycols are the mono (C_1-C_6 alkyl ethers) and di (C_1-C_6 alkyl ethers). Especially preferred are the mono (C_1-C_2 alkyl ethers) and di (C_1-C_2 alkyl ethers). Particularly preferred are polyalkylene glycol monomethyl ether and polyalkylene glycol dimethyl ether.

Polymer blends are suitable e.g. for adjusting the mechanical properties and/or the dissolution properties of the multi-layered films used in the present invention. In this case, the polymers used in the polymer mixture may differ in terms of their chemical composition and/or in terms of their physico-chemical properties.

In a specific embodiment, the multi-layered film used in the invention comprises at least one layer which comprises a mixture of two or more polymers. Suitable mixtures may comprise 2 or more different polymer compositions P1 or at least one polymer composition P1 and at least one polymer P2 or 2 or more different polymers P2.

In a first embodiment, a polymer mixture is used which comprises 2 or more polymers which differ in their chemical composition. In a second embodiment, a polymer mixture is used which comprises two or more polymers which differ in their molecular weight. According to this second embodiment, for example, a polymer mixture is used which comprises at least two polymers P2 which comprise repeating units derived from vinyl alcohol.
As described, the films to be produced according to the invention have at least one layer L1 which comprises a polymer composition P1 or consists of a polymer composition P1.

The process for preparing the multi-layered film preferably comprises the steps of
(a) preparing an aqueous solution of the polymer composition P1 as described above, wherein the aqueous solution may, in addition to or instead of water, inter alia also include alcohol, such as 2-propanol,
(b) casting the aqueous polymer composition P1 from (a) as a film onto a support material to obtain layer L1,
(c) optionally drying the film after the application of layer L1 to the substrate,
(d) applying a layer L2,
wherein the layer L2 comprises at least one polymer P2 or consists of at least one polymer P2 as described above
(e) optionally drying the film after the application of L2 to the substrate,
(f) optionally applying one or more further layers L1 and/or L2,
(g) optionally drying the film after applying one or more further layers L1 and/or L2 to the support material according to (f),
drying the film after the application of all layers L1 and L2 to the support material,
wherein the layers L1 and/or L2 can be applied in a freely chosen order or also simultaneously and in each case optionally can be dried after each application of one or more layers.

In a specific embodiment said multi-layered film, after drying the film after the application of L2 to the carrier material in step e), the layer L2 is combined with a second two-layered film in the sense of a lamination.
The second two-layered film can be produced simultaneously in steps (a) to (d) previously or in a parallel-connected installation. If the same composition was used for the contacting layers of the two films, the multilayer film produced in this way by lamination consists of three chemically different layers.

In another embodiment, the two-layered film prepared in steps (a) to (d) is cut in the center in the machine direction; Subsequently, the two obtained film halves are laminated.
In this embodiment, it is also possible to laminate the chemically identical interface to each other to effectively obtain layers of which two are chemically different.

The advantage of the two abovementioned embodiments of the present invention is a markedly accelerated drying due to the reduced layer thickness, which is directly related to an increased production speed. Without being limited to theory, the mass transfer of the solvent through the film at a constant diffusion coefficient is proportional to 1 / film thickness.

Preferably, the multi-layered film comprises at least two film layers L1 and/or L2 in any order.

It is more preferred that the multi-layered film comprises at least one layer L1 and at least one layer L2 and that the multi-layered film comprises at least three layers.

Especially preferred the multi-layered film comprises at least three layers with the sequence of L2-L1-L2. Mostly preferred the multi-layered film consists of three layers with the sequence of L2-L1-L2.

Preferably, the production process of the multi-layered film comprises a lamination step in which at least two parts of the multi-layered film are joined to form a multi- layered composite. Thereby, the each of two parts of the multi-layered film preferably comprises at least one layer L1 and/or L2.

The multi-layered film preferably has an overall thickness of at least 10 µm, more preferably of at least 25 µm, still more preferably of at least 50 µm and most preferably of at least 75 µm. The upper limit of the thickness of the multi-layered film preferably does not exceed 500 µm, more preferably 400 µm, still more preferably 300 µm and most preferably 200 µm.

Thereby, layer L1 preferably has a thickness of at least 5 µm, more preferably of at least 15 µm, still more preferably of at least 30 µm and most preferably of at least 50 µm.

The upper limit of the thickness of layer L1 preferably does not exceed 400 µm, more preferably 300 µm, still more preferably 200 µm and most preferably 100 µm.

Washing- and cleaning-active polymer film

In another embodiment of the present invention at least one of the first or second water-soluble films is a washing- and cleaning-active polymer film.

For preparing said washing- and cleaning-active polymer film at least one polymer P1'), at least one polyoxyalkylene ether PE') and water are subjected to a blending operation by common methods known to a person skilled in the art. It is of critical importance that in the mixing step no α,β-ethylenically unsaturated monomers are subjected to a free-radical polymerization in the

presence of the polyoxyalkylene ether PE'). It is already known to prepare film-forming polymer compositions by free-radical polymerization of a monomer composition comprising α,β-ethylenically unsaturated carboxylic acids in the presence of polyoxyalkylene ethers, e.g. from WO 2015/000969, WO 2015/000970 and WO 2015/000971. Physically mixing at least one polymer P1') and at least one polyoxyalkylene ether PE') on the one hand and polymerization of α,β-ethylenically unsaturated monomers capable of forming a polymer P1') in the presence of at least one polyoxyalkylene ether PE') on the other hand are two alternatives for the formation of washing- and cleaning-active polymer compositions, each process having its own characeristic properties. For instance, compared to the free radical polymerization process mentioned above the process of physically mixing of at least one polymer P1') and at least one polyoxyalkylene ether PE') avoids any side reactions leading to undesirable by-products that might negatively affect the properties of the film. Further, in the mixing process no exothermic reaction occurs that might lead to the necessity to remove heat from the reaction zone or to take further safety measures.

Polymer P1'):
The polymer P1') can be prepared by free-radical polymerization of a monomer composition M') that comprises

- at least one monomer A') which is selected from α,β-ethylenically unsaturated carboxylic acids, salts of α,β-ethylenically unsaturated carboxylic acids and mixtures thereof,
- optionally at least one monomer B') which is selected from unsaturated sulfonic acids, salts of unsaturated sulfonic acids, unsaturated phosphonic acid, salts of unsaturated phosphonic acids and mixtures thereof, and
- optionally at least one monomer C'), different from A') and B').

Monomer composition M'):

Monomer A'):
The monomer composition M') used for producing the polymer P1') comprises at least one monomer A') which is selected from α,β-ethylenically unsaturated carboxylic acids, salts of α,β-ethylenically unsaturated carboxylic acids and mixtures thereof.

In a specific embodiment, the monomer composition M') consists only of α,β-ethylenically unsaturated carboxylic acids, salts of α,β-ethylenically unsaturated carboxylic acids and mixtures thereof.

The α,β-ethylenically unsaturated carboxylic acid is preferably selected from acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, fumaric acid, itaconic acid, α-chloroacrylic acid, crotonic acid, citraconic acid, mesaconic acid, glutaconic acid and aconitic acid. Suitable salts of the aforementioned acids are, in particular, the sodium, potassium and ammonium salts, and the salts with amines. The monomers A') can be used as such or as mixtures with one another. The stated weight fractions all refer to the acid form.

Preferably, the at least one α,β-ethylenically unsaturated carboxylic acid is used for the polymerization in non-neutralized form. If the α,β-ethylenically unsaturated carboxylic acids are used for the polymerization in partially neutralized form, then the acid groups are neutralized preferably to at most 50 mol%, particularly preferably to at most 30 mol%.

Particularly preferably, the monomer A') is selected from acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, salts of the aforementioned carboxylic acids and mixtures thereof.

In particular, the monomer A') is selected from acrylic acid, methacrylic acid, salts of acrylic acid, salts of methacrylic acid and mixtures thereof.

In a specific embodiment, exclusively acrylic acid is used as monomer A').

The monomer A') is used preferably in an amount of from 50 to 100% by weight, particularly preferably 60 to 100% by weight, based on the total weight of the monomer composition M').

In a preferred embodiment, the monomer composition M') consists to at least 50% by weight, preferably to at least 80% by weight, in particular to at least 90% by weight, based on the total weight of the monomer composition M'), of acrylic acid and/or acrylic acid salts.

Monomer B'):
The monomer composition M') can comprise, in addition to the monomers A'), at least one monomer B') which is selected from unsaturated sulfonic acids, salts of unsaturated sulfonic acids, unsaturated phosphonic acid, salts of unsaturated phosphonic acids and mixtures thereof.

The monomer B') is preferably selected from 2-acrylamido-2-methylpropanesulfonic acid, vinylsulfonic acid, allylsulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-acryloxypropylsulfonic acid, 2-hydroxy-3-methacryloxypropylsulfonic acid, styrenesulfonic acid, vinylphosphonic acid, allylphosphonic acid, salts of the aforementioned acids, and mixtures thereof.

2-Acrylamido-2-methylpropanesulfonic acid is preferred as monomer B').

Suitable salts of the aforementioned acids are in particular the sodium, potassium and ammonium salts, and the salts with amines. The monomers B') can be used as such or as mixtures with one another. The stated weight fractions all refer to the acid form.

Preferably, the monomer composition M') then consists to at least 50% by weight, particularly preferably to at least 80% by weight, in particular to at least 90% by weight, based on the total weight of the monomer composition M'), of monomers A') and B'). If the monomer composition M') comprises at least one monomer B'), then this is used preferably in an amount of from 0.1 to

50% by weight, particularly preferably 1 to 25% by weight, based on the total weight of the monomer composition M').

Further monomers C'):

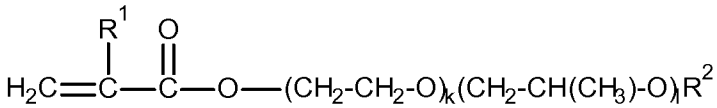
The monomer composition M') can additionally comprise at least one further monomer different from the monomers containing acid groups and salts thereof.

Preferably, the monomer composition M') additionally comprises at least one comonomer C') selected from

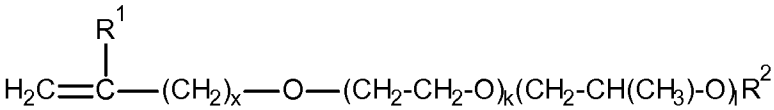
C1') nitrogen heterocycles with a free-radically polymerizable α,β-ethylenically unsaturated double bond,

C2') monomers containing amide groups,

C3') compounds of the general formulae (I.a) and (I.b)



(I.a)



(I.b)

in which

the order of the alkylene oxide units is arbitrary,

x is 0, 1 or 2,

k and l, independently of one another, are an integer from 0 to 100, where the sum of k and l is at least 2, preferably at least 5,

R^1 is hydrogen or methyl,

R^2 is hydrogen, C1-C4-alkyl,

and mixtures of two or more than two of the aforementioned monomers C1') to C3').

The monomer composition M') can comprise the further monomers C1') to C3') in each case preferably in an amount of from 0 to 30% by weight, particularly preferably 0 to 20% by weight, in particular 0 to 10% by weight, based on the total weight of the monomer composition M'). If the monomer composition M') comprises at least one monomer selected from C1') to C3'), then in each case preferably in an amount of from 0.1 to 30% by weight, particularly preferably 1 to 20% by weight, in particular 1.5 to 10% by weight, based on the total weight of the monomer composition M'). In a specific embodiment, the monomer composition M') comprises no further comonomers apart from the monomers A').

Monomer C1'):

Preferred nitrogen heterocycles with a free-radically polymerizable α,β-ethylenically unsaturated double bond C1') are selected from 1-vinylimidazole (N-vinylimidazole), vinyl- and allyl-substituted nitrogen heterocycles different from 1-vinylimidazole, and mixtures thereof.

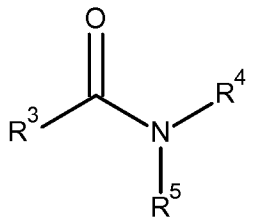
From the amine nitrogens of the aforementioned compounds it is possible to generate charged cationic groups either by protonation with acids or by quaternization with alkylating agents. Suitable monomers C1') are also the compounds obtained by protonation or quaternization of 1-vinylimidazole and vinyl- and allyl-substituted nitrogen heterocycles different therefrom. Acids suitable for the protonation are e.g. carboxylic acids, such as lactic acid, or mineral acids, such as phosphoric acid, sulfuric acid and hydrochloric acid. Alkylating agents suitable for the quaternization are C_1-C_4-alkyl halides or di(C_1-C_4-alkyl) sulfates, such as ethyl chloride, ethyl bromide, methyl chloride, methyl bromide, dimethyl sulfate and diethyl sulfate. A protonation or quaternization can generally take place either before or after the polymerization. Preferably, a protonation or quaternization takes place after the polymerization. Examples of such charged monomers C1') are quaternized vinylimidazoles, in particular 3-methyl-1-vinylimidazolium chloride, methosulfate and ethosulfate.

Preferred monomers C1') are furthermore vinyl- and allyl-substituted nitrogen heterocycles different from vinylimidazoles selected from 2-vinylpyridine, 4-vinylpyridine, 2-allylpyridine, 4-allylpyridine and the salts thereof obtained by protonation or by quaternization.

In particular, the monomer composition M') comprises at least one comonomer C1') selected from 1-vinylimidazole, 2-vinylpyridine, 4-vinylpyridine, 2-allylpyridine, 4-allylpyridine and the salts thereof obtained by protonation or by quaternization. Specifically, the monomer composition M') comprises 1-vinylimidazole as comonomer C1').

Monomer C2'):

Suitable amide-group-containing monomers C2') are compounds of the general formula (II)



(II)

in which

one of the radicals R^3 to R^5 is a group of the formula $CH_2=CR^6$- where R^6 = H or C_1-C_4-alkyl and the other radicals R^6 to R^8, independently of one another, are H or C_1-C_7-alkyl,

where R^3 and R^4, together with the amide group to which they are bonded, can also be a lactam having 5 to 8 ring atoms,

where R^4 and R^5, together with the nitrogen atom to which they are bonded, can also be a five- to seven-membered heterocycle.

Preferably, the monomers C2') are selected from primary amides of α,β-ethylenically unsaturated monocarboxylic acids, N-vinylamides of saturated monocarboxylic acids, N-vinyllactams, N-alkyl- and N,N-dialkylamides, α,β-ethylenically unsaturated monocarboxylic acids and mixtures thereof.

Preferred monomers C2') are N-vinyllactams and derivatives thereof, which can have, e.g., one or more C1-C6-alkyl substituents, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, etc. These include, e.g., N-vinylpyrrolidone, N-vinylpiperidone, N-vinylcaprolactam, N-vinyl-5-methyl-2-pyrrolidone, N-vinyl-5-ethyl-2-pyrrolidone, N-vinyl-6-methyl-2-piperidone, N-vinyl-6-ethyl-2-piperidone, N-vinyl-7-methyl-2-caprolactam and N-vinyl-7-ethyl-2-caprolactam.

Particular preference is given to using N-vinylpyrrolidone and/or N-vinylcaprolactam.

Suitable monomers C2') are furthermore acrylamide and methacrylamide.

N-Alkyl- and N,N-dialkylamides of α,β-ethylenically unsaturated monocarboxylic acids suitable as monomers C2') are, for example, methyl(meth)acrylamide, methylethacrylamide, ethyl(meth)acrylamide, ethylethacrylamide, n-propyl(meth)acrylamide, isopropyl(meth)acrylamide, n-butyl(meth)acrylamide, tert-butyl(meth)acrylamide, tert-butylethacrylamide, and mixtures thereof.

Open-chain N-vinylamide compounds suitable as monomers C2') are, for example, N-vinylformamide, N-vinyl-N-methylformamide, N-vinylacetamide, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, N-vinylpropionamide, N-vinyl-N-methylpropionamide, N-vinylbutyramide and mixtures thereof. Preference is given to using N-vinylformamide.

Ether-group-containing monomer C3'):
The monomer composition M') can additionally comprise at least one monomer C3') selected from compounds of the general formulae (I.a) and (I.b), as defined above.

In the formulae I.a) and I.b), k is preferably an integer from 1 to 100, particularly preferably 2 to 50, in particular 3 to 30. Preferably, l is an integer from 0 to 50.

Preferably, R^2 in the formulae I.a) and I.b) is hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl or tert-butyl.

In the formula I.b), x is preferably 1 or 2.

Preferably, the polymer P1') comprises less than 15% by weight, preferably less than 10% by weight, polymerized units of monomers different from monomers A').

The polymer P1') is essentially uncrosslinked. The monomer composition M') used for producing the polymer P1') thus comprises in particular no added crosslinking monomers. In the

context of the invention, crosslinking monomers are compounds with two or more than two polymerizable ethylenically unsaturated double bonds per molecule.

Specifically, the monomer composition M') comprises, based on the total weight, less than 0.5% by weight, even more specifically less than 0.1% by weight, of crosslinking monomers which have two or more than two free-radically polymerizable α,β-ethylenically unsaturated double bonds per molecule.

In a preferred embodiment, the monomer composition M') comprises no crosslinking monomers having two or more than two polymerizable α,β-ethylenically unsaturated double bonds per molecule.

The polymer P1') can be prepared by free-radical polymerization of a monomer composition M'). It is possible to work by any known free-radical polymerization process. In addition to polymerization in bulk, mention should be made especially of the processes of solution polymerization and emulsion polymerization, preference being given to solution polymerization.

As regards the monomer composition M') used for the preparation of P1'), reference is made to the aforementioned suitable and preferred monomers in their entirety.

The polymerization is preferably performed in water as a solvent. However, it can also be undertaken in alcoholic solvents, especially C_1-C_4-alcohols, such as methanol, ethanol and isopropanol, or mixtures of these solvents with water.

The free-radical polymerization of the monomer composition M') is preferably carried out in the feed procedure. Here, in general at least the monomers are metered into the reaction mixture in liquid form. Monomers that are liquid under the addition conditions can be introduced into the reaction mixture without adding a solvent. Otherwise the monomers are used as solution in a suitable solvent.

Suitable polymerization initiators are compounds which decompose thermally, by a redox mechanism or photochemically (photo initiators) to form free radicals.

Among the polymerization initiators that can be thermally activated, preference is given to initiators having a decomposition temperature in the range from 20 to 180°C, especially from 50 to 90°C. Examples of suitable thermal initiators are inorganic peroxo compounds such as peroxodisulfates (ammonium peroxodisulfate and preferably sodium peroxodisulfate), peroxosulfates, percarbonates and hydrogen peroxide; organic peroxo compounds such as diacetyl peroxide, di-tert-butyl peroxide, diamyl peroxide, 5-dioctanoyl peroxide, didecanoyl peroxide, dilauroyl peroxide, dibenzoyl peroxide, tert-butyl perneodecanoate, tert-butyl perbenzoate, tert-butyl perisobutyrate, tert-butyl perpivalate, tert-butyl peroctoate, tert-butyl peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, tert-butylperoxy-2-ethylhexanoate

and 10-diisopropyl peroxydicarbamate; azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile) and azobis(2-amidopropane) dihydrochloride.

These initiators can be used in combination with reducing compounds as initiator/regulator systems. Examples of such reducing compounds include phosphorus compounds such as phosphorous acid, hypophosphites and phosphinates, sulfur compounds such as sodium hydrogensulfite, sodium sulfite and sodium formaldehyde- sulfoxylate, and hydrazine.

Also frequently used are redox initiator systems which consist of a peroxo compound, a metal salt and a reducing agent. Examples of suitable peroxo compounds are hydrogen peroxide, peroxodisulfate (as the ammonium, sodium or potassium salt), peroxosulfates, and organic peroxo compounds such as tert-butyl hydroperoxide, cumene hydroperoxide or dibenzoyl peroxide. Suitable metal salts are in particular iron(II) salts such as iron(II) sulfate heptahydrate. Suitable reducing agents are sodium sulfite, the disodium salt of 2-hydroxy-2-sulfinatoacetic acid, the disodium salt of 2-hydroxy-2-sulfonatoacetic acid, sodium hydroxymethanesulfinate, ascorbic acid, isoascorbic acid or mixtures thereof.

Examples of suitable photoinitiators are benzophenone, acetophenone, benzyl dialkyl ketones and derivatives thereof.

Preference is given to using thermal initiators, preferably inorganic peroxo compounds, especially sodium peroxodisulfate. The peroxo compounds are advantageously used in combination with sulfur-containing reducing agents, especially sodium hydrogensulfite, as the redox initiator system. In the case of use of this initiator/regulator system, copolymers comprising sulfonate and/or sulfate as end groups are obtained, which are notable for exceptional cleaning power and scale- inhibiting action.

Alternatively, it is also possible to use phosphorus-containing regulator systems, for example sodium hypophosphite and phosphinates.

The amounts of initiator/regulator system should be matched to the substances used in each case. If, for example, the peroxodisulfate/ hydrogensulfite system is used, typically 1 to 7% by weight, preferably 2 to 6% by weight, of peroxodisulfate and generally 3 to 25% by weight, preferably 4 to 15% by weight, of hydrogensulfite are used, based in each case on monomer composition M').

If desired, it is also possible to use organic polymerization regulators. Suitable examples are sulfur compounds such as mercaptoethanol, 2-ethylhexyl thioglycolate, thioglycolic acid and dodecyl mercaptan. When polymerization regulators are used, the amount thereof is generally 0.1 to 25% by weight, preferably 0.5 to 20% by weight and more preferably 1.0 to 15% by weight, based in each case on monomer composition M').

The polymerization temperature is generally 20 to 200°C, preferably 20 to 150°C and more preferably 20 to 120°C.

The polymerization can be performed under atmospheric pressure, but is preferably undertaken in a closed system under the autogenous pressure which evolves.

The polymerization can take place in the absence or in the presence of an inert gas. Usually, the polymerization is carried out in the presence of an inert gas, e.g. nitrogen.

The weight-average molecular weight Mw of the polymer P1') can be determined by means of gel permeation chromatography (GPC) in aqueous solution using neutralized polyacrylic acid as polymer standard. The polymer P1') preferably has a weight-average molecular weight of from 1000 to 100 000 g/mol, more preferably 1500 to 50 000 g/mol, in particular 2000 to 20 000 g /mol.

Preferably, polymer P1') has a polydispersity index (PDI) of from 1.2 to 6.0, more preferably 1.4 to 4.0, in particular 1.6 to 3.5.

The polymer P1') can be obtained in the acidic state, but it can also, if desired be partly neutralized by addition of bases. Suitable bases are alkali metal hydroxides , like NaOH and KOH, alkaline earth metal hydroxides, like $Ca(OH)_2$ and $Mg(OH)_2$, ammonia and amine bases, like monoethanol amine. Especially preferred is sodium hydroxide. Neutralization can be performed as early as during the polymerization or after the polymerization has ended.

Prior to its use in step i) for providing the aqueous composition, at the most 30 mol% of the carboxy groups of the polymer P1') are in the deprotonated form. Preferably, at the most 25 mol%, more preferably at the most 15 mol%, of the carboxy groups of the polymer P1') are in the deprotonated form. In a special embodiment, the acid groups of the polymer composition according to the invention are present in non-neutralized form.

The polymer P1') used in accordance with the invention can be used directly in the form of the aqueous solutions obtained in the course of preparation by means of solvent polymerization, or in dried form (obtained, for example, by spray drying, spray granulation such as fluid bed spray granulation or spouted bed spray granulation, roller drying or freeze drying).

Suitable polymers P1') are commercially available or are intermediates of commercially available products. In a preferred embodiment, a commercially available polyacrylic acid is employed that is not crosslinked and not neutralized or only to a low extend neutralized. Suitable products are Sokalan® CP 10 S, Sokalan® CP 12 S, Sokalan® CP 13 S, Sokalan® PA 25 XS, Sokalan® PA 80 S and Sokalan® NR 2530 from BASF SE.

Ethers of polyoxyalkylene glycols PE'):
Suitable components PE') are selected from monoalkyl ethers, dialkyl ethers, mono-(hydroxyalkyl) ethers and di(hydroxyalkyl) ethers of polyoxyalkylene glycols.

Suitable ethers of polyoxyalkylene glycols PE') have a number-average molecular weight in the range from about 200 to 2000, preferably 250 to 1500.

The stated degrees of alkoxylation, specifically degrees of ethoxylation, are statistical averages (number-average, Mn) which can be an integer or a fraction for a specific product. Preferred alcohol ethoxylates have a narrowed homolog distribution (narrow range ethoxylates, NRE).

Suitable alkylene oxides for producing the ethers of polyoxyalkylene glycols PE') are e.g. ethylene oxide, propylene oxide, epichlorohydrin, 1,2- and 2,3-butylene oxide.

Suitable polyoxyalkylene ether groups are, for example, homopolymers of ethylene oxide, homopolymers of propylene oxide, copolymers of ethylene oxide and propylene oxide, copolymers of ethylene oxide and butylene oxide, and copolymers of ethylene oxide, propylene oxide and at least one butylene oxide. The polyoxyalkylene ether groups which comprise various alkylene oxides in copolymerized form can comprise the alkylene oxide units in random distribution or in the form of blocks. A specific embodiment is a polyoxyalkylene ether group which comprises ethylene oxide and propylene oxide in copolymerized form. Preferably, in the ethylene oxide/propylene oxide copolymers, the fraction of repeat units derived from ethylene oxide is 40 to 99% by weight. Particular preference is given to ethers of polyoxyalkylene glycols PE') whose polyoxyalkylene ether group comprises exclusively ethylene oxide repeat units.

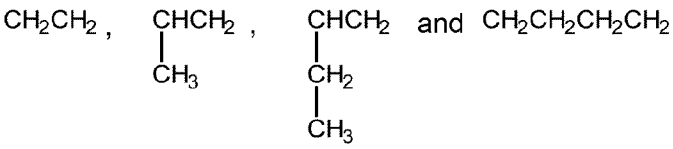
In a first preferred embodiment, the polyoxyalkylene ethers PE') are compounds of the general formula (III.1)

$$R^7O\text{-}(R^8O)_sR^9 \qquad \text{(III.1)}$$

in which

R^7 is C_8-C_{18}-alkyl,

R^8 is selected in the repeat units (R^8O) in each case independently of one another from



R^9 is hydrogen or C_1-C_4-alkyl, and

s is an integer from 3 to 25.

In the following, the compounds of the formula (III.1) are also denoted as (C_8-C_{18}-alkyl)polyoxyalkylene ethers.

The C_8-C_{18}-alkyl radicals of the (C_8-C_{18}-alkyl)polyoxyalkylene ethers PE') can be derived from the corresponding alcohols, specifically alcohols of the general formula R^7-OH by formal elimination of the OH group. The C_8-C_{18}-alkyl radicals of the (C_8-C_{18}-alkyl)polyoxyalkylene ethers PE') can be derived from pure alcohols or from alcohol mixtures. Preferably, they are industrially available alcohols or alcohol mixtures.

The C_8-C_{18}-alkyl radicals of the (C_8-C_{18}-alkyl)polyoxyalkylene ethers (PE') or the alcohols R^7-OH used for their production can also originate from a renewable, natural and/or sustainable source. In the context of the invention, renewable sources are understood as meaning natural (biogenic) and/or sustainable sources and not fossil sources, such as petroleum, natural gas or coal.

Preferred (C_8-C_{18}-alkyl)polyoxyalkylene ethers generally have a number-average molecular weight in the range from about 260 to 1000, preferably 300 to 800.

Suitable (C_8-C_{18}-alkyl)polyoxyalkylene ethers are water-soluble nonionic polymers which have alkylene oxide repeat units.

The C_8-C_{18}-alkyl radicals of the (C_8-C_{18}-alkyl)polyoxyalkylene ethers (PE') used according to the invention or the radicals R^7 can be derived from alcohols and alcohol mixtures of native or petrochemical origin having 8 to 18 carbon atoms. The (C_8-C_{18}-alkyl) radicals or the radicals R^7 can be derived from primary, secondary, tertiary or quaternary alcohols. Preferably, the (C_8-C_{18}-alkyl) radicals and/or the radicals R^7 are derived from primary alcohols. The (C_8-C_{18}-alkyl) radicals of the (C_8-C_{18}-alkyl)polyoxyalkylene ethers or the radicals R^7 can furthermore be straight-chain or branched. Preferably, the (C_8-C_{18}-alkyl) radicals or the radicals R^7 are linear or predominantly linear alkyl radicals. Predominantly linear alkyl radicals are understood as meaning those which have essentially methyl group branches and essentially no longer-chain branches. In a first preferred embodiment, the (C_8-C_{18}-alkyl) radicals are linear alkyl radicals. In a second preferred embodiment, the (C_8-C_{18}-alkyl) radicals are predominantly linear alkyl radicals, as also occur in natural or synthetic fatty acids and fatty alcohols, and oxo alcohols. Specifically, the (C_8-C_{18}-alkyl) radicals can be linear or preferably 2-methyl-branched and/or comprise linear and methyl-branched radicals in a mixture, as are customarily present in oxo alcohol radicals. In a further preferred embodiment, the (C_8-C_{18}-alkyl) radicals are branched alkyl radicals as they have longer-chain alcohols which are obtained by Guerbet condensation. During the Guerbet condensation, primary or secondary alcohols are condensed at high temperatures and high pressure in the presence of alkali metal hydroxides or alkoxides to give longer-chain alcohols, which are also called Guerbet alcohols. A suitable Guerbet alcohol is a C_{16}-C_{20}-alcohol that is n-butyl-terminated and alkoxylated with 7 to 8 ethylene oxide groups per molecule.

The C_8-C_{18}-alkyl radicals of the (C_8-C_{18}-alkyl)polyoxyalkylene ethers (PE') are preferably C_{12}-C_{18}-alkyl radicals, for example C_9-C_{16}-alkyl radicals or C_{10}-C_{14}-alkyl radicals. In the compounds of the general formula (III), R^7 is preferably C_{12}-C_{18}-alkyl, such as C_9-C_{16}-alkyl or C_{10}-C_{14}-alkyl.

Suitable are (C_8-C_{18}-alkyl)polyoxyalkylene ethers which are derived from a single alcohol having 12 to 18 carbon atoms, for example having 9 to 16 carbon atoms or having 10 to 14 carbon atoms. These include, for example, coconut, palm, tallow fatty or oleyl alcohol.

Suitable are also (C_8-C_{18}-alkyl)polyoxyalkylene ethers which are derived from alcohol mixtures, e.g. selected from $C_{12}C_{14}$-alcohols, C_9C_{11}-alcohols, $C_{13}C_{15}$-alcohols, $C_{12}C_{18}$-alcohols and $C_{12}C_{14}$-alcohols.

The (C_8-C_{18}-alkyl)polyoxyalkylene ethers comprise in the polyoxyalkylene ether group preferably on average 3 to 12, more preferably 3 to 10, particularly preferably 5 to 9, alkylene oxide units, per mole of alcohol. In the compounds of the general formula (III.1), s is preferably 3 to 12, more preferably 3 to 10, in particular 5 to 9.

Suitable alkylene oxides for producing the (C_8-C_{18}-alkyl)polyoxyalkylene ethers are e.g. ethylene oxide, propylene oxide, epichlorohydrin, 1,2- and 2,3-butylene oxide. Preferred polyoxyalkylene ether groups of the compound (III.1) are, for example, homopolymers of ethylene oxide, homopolymers of propylene oxide and copolymers of ethylene oxide and propylene oxide. As mentioned before, the polyoxyalkylene ether groups which comprise various alkylene oxides in copolymerized form can comprise the alkylene oxide units in random distribution or in the form of blocks. Particular preference is given to (C_8-C_{18}-alkyl)polyoxyalkylene ethers whose polyoxyalkylene ether group comprises exclusively ethylene oxide repeat units.

Preferably, the polyether groups of the (C_8-C_{18}-alkyl)polyoxyalkylene ethers PE') carry a hydrogen atom at the non-C_8-C_{18}-alkyl-terminated ends or are terminated with a C_1-C_4-alkyl group (i.e. terminally capped). In the compounds of the general formula (III.1), R^9 is accordingly H or C_1-C_4-alkyl. Preferably, R^9 is H or methyl. In a particularly preferred embodiment, the polyether groups on the non-C_8-C_{18}-alkyl-terminated ends carry a hydrogen atom, i.e. R^9 is particularly preferably H.

The (C_8-C_{18}-alkyl)polyoxyalkylene ethers PE') are preferably alkoxylated, advantageously ethoxylated, primary alcohols having preferably 8 to 18 carbon atoms and on average 3 to 12, preferably 3 to 10, particularly preferably 5 to 9, mole of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical can be linear or preferably 2-methyl-branched and/or can comprise linear and methyl-branched radicals in a mixture, as are customarily present in oxo alcohol radicals.

The (C_8-C_{18}-alkyl)polyoxyalkylene ethers PE') are preferably selected from:

- $C_{12}C_{14}$-fatty alcohols with 3 EO, 5 EO, 7 EO or 9 EO,
- C_9C_{11}-oxo alcohols with 7 EO,
- C_{13}-oxo alcohol with 3 EO, 5 EO, 7 EO or 9 EO,
- $C_{13}C_{15}$-oxo alcohols with 3 EO, 5 EO, 7 EO or 9 EO,
- $C_{12}C_{18}$-fatty alcohols with 3 EO, 5 EO, 7 EO or 9 EO and mixtures thereof,

- 2-propylheptanol with 3 EO, 4 EO, 5 EO, 6 EO, 7 EO, 8 EO and 9 EO

and mixtures of two or more than two of the aforementioned ethoxylated alcohols.

Preferred mixtures of ethoxylated alcohols are mixtures of $C_{12}C_{14}$-alcohol with 3 EO and $C_{12}C_{18}$-alcohol with 7 EO. Preferred mixtures of ethoxylated alcohols are also mixtures of short-chain alcohol ethoxylates (e.g. 2-propylheptanol with 7 EO) and long-chain alcohol ethoxylates (e.g. $C_{16}C_{18}$-alcohols with 7 EO).

Suitable components PE') are also mono(hydroxyalkyl) ethers and di(hydroxyalkyl) ethers of polyoxyalkylene glycols.

Depending on the length of the alkyl chain, each hydroxyalkyl group may bear 1, 2, 3 or more than 3 OH groups. Preferably, the components PE') are selected from mono(hydroxyalkyl) ethers of polyoxyalkylene glycols, and di(hydroxyalkyl) ethers of polyoxyalkylene glycols, wherein both hydroxyalkyl groups bears only 1 OH.

In a second preferred embodiment, the polyoxyalkylene ethers PE') are compounds of the general formula (III.2)

$$R^7O\text{-}(R^8O)_sR^9 \qquad \text{(III.2)}$$

in which

R^7 is C_8-C_{18}-alkyl,

R^8 is selected in the repeat units (R8O) in each case independently of one another from

CH_2CH_2 and CH_2CH_2 with CH_3 on the second carbon

R^9 is C_8-C_{18}-hydroxyalkyl, and

s is an integer from 3 to 25.

In the compounds of the general formula (III.2), s is preferably an integer of 3 to 12.

Preferred are compounds of the formula:

$$(C_{8\text{-}18}\text{-alkyl})\text{-}CH(OH)CH_2O\text{-}(EO)_{2\text{-}24}\text{-}(C_{8\text{-}18}\text{-alkyl})$$

Production of the polymer films:

The washing- and cleaning-active polymer film is preferably produced in a process comprising the steps of:

i) providing an aqueous composition by mixing

- a polymer P1') that comprises polymerized units of at least one monomer A'), selected from α,β-ethylenically unsaturated carboxylic acids, salts of α,β-ethylenically unsaturated carboxylic acids and mixtures thereof,

- an polyoxyalkylene ether PE') having at least one C_8-C_{18}-alkyl group that is unsubstituted or substituted by at least one hydroxyl group, and an average of 3 to 25 alkylene oxide units per molecule, and
- water,

wherein at the most 30 mol% of the carboxy groups of the polymer P1') are in the deprotonated form,
the weight ratio of the polymer P1') to the polyoxyalkylene ether PE') is in a range from 0.9 : 1 to 5 : 1, and
the aqueous composition has a water content of at least 10% by weight and at most 50% by weight, based on the total weight of the aqueous composition, and

ii) converting the aqueous composition to a polymer film.

Preferably, the weight ratio of the polymer P1') to the polyoxyalkylene ether PE') is in a range from 0.9 : 1 to 4 : 1, more preferably 1 : 1 to 3 : 1.

Preferably, the aqueous composition has a water content of at least 15% by weight, more preferably at least 20% by weight, based on the total weight of the aqueous composition. Preferably, the aqueous composition has a water content of at most 50% by weight, based on the total weight of the aqueous composition.

Step i):
In step i) of the process one or more mixers may be used to provide the aqueous composition. If more than one mixer is used, these may be mixers of identical or different design, which are used in any desired sequence, arrangement and combination, for example an arrangement of all mixers in series, a combination of a parallel and series arrangement or a parallel arrangement of all mixers. If a plurality of mixers is used, the series arrangement is preferred.

Suitable mixers are in particular dynamic mixers whose mixing elements contain movable parts and static mixers, i.e. mixing elements without moving parts in the interior.

Mixers can be applied in a continuous manner as continuous mixers, whereby all components are continuously fed to the mixer and the obtained mixture or partial mixture is continuously discharged, in a discontinuous (batch wise) manner, whereby all components are added to the mixer in advance and the obtained mixture is discharged at least partially after the mixing operation is at least partially finished, or in a semibatch manner, whereby optionally at least one of the components is at least partially added in advance, while at least one of the components is at least partially dosed to the mixer and the obtained mixture is discharged at least partially, when the missing operation is at least partially finished.

Suitable mixers are in particular dispersing machines, stirred tanks, kneaders, extruders, dynamic mixers, static mixers, rotating mixers, and mills.

Suitable dispersing machines are machines of the rotor stator type, the rotating dispersion disc type, the dual asymmetric centrifuge type (Speedmixer), and all other common dispersing machines.

Suitable stirred tank reactors are equipped with at least one moving mixing element, such as a stirrer. Common stirrer types comprise, for example, propeller stirrers, impeller stirrers, disk stirrers, paddle stirrers, anchor stirrers, oblique blade stirrers, crossbeam stirrers, helical ribbon impellers, screw-type stirrers, etc.

Kneaders are available in various designs. The general shape of the kneader can preferably be conical or cylindrical or a combination of both geometries. Common kneaders comprise single shaft and twin shaft designs, but also the utilization of three or more shafts is possible. Usually, conveying elements or mixing elements, or preferably a combination of both are aligned along the shafts. The shafts can be rotated continuously, oscillated or moved in a combination of rotation and oscillation. In case of multiple shafts, these can be aligned in parallel or in a defined angle. Kneaders for continuous service may comprise special zones for physical operations, such as cooling, heating, degassing, evaporation of volatiles etc.
Suitable rotating mixers are e.g. planetary mixers and double planetary mixers.

Mixers can next to mixing also be used to fulfill other purposes, such as cooling, heating, degassing, evaporation of water and optionally other components.

Preferably, in step i) the mixing is performed at temperature in the range from 0 to 100°C, more preferably 20 to 95°C, in particular 30 to 90°C.

Usually, the mixing in step i) takes place over a period of 1 minutes to 48 hours, preferably 1,5 minutes to 24 hours.

In a suitable embodiment, mixing is performed batch-wise in a kettle as mixing apparatus. In a first variant of this embodiment the components to be mixed for providing the aqueous composition, i.e. the polymer P1'), the polyoxyalkylene ether PE') and water are initially completely fed to the kettle and then subjected to the mixing operation. In a further variant of this embodiment at least one of the components is added to the kettle in one or more than one portion to the mixing operation. Preferably, the initial feed comprises at least a part of the water used for providing the aqueous composition. More preferably, the initial feed comprises the complete amount of the water used for providing the aqueous composition.

In another suitable embodiment, mixing is performed batch-wise in a dual asymmetric centrifuge (Hauschild™ Speedmixer). Then, the temperature is preferably in a range of from 0 to 100 °C, more preferably 20 to 70 °C, especially 40 to 75 °C. The rotation speed is preferably in a range of from 100 to 3500 rpm, more preferably 1000 to 2500 rpm. Preferably mixing takes place over a period of 0.2 to 10 minutes, more preferably 1 to 5 minutes.

In another suitable embodiment, mixing is performed batch-wise or semibatch-wise in a kneader. In a special embodiment a Duplex kneader is employed. The rotation speed is preferably in a range of from 10 to 500 rpm, more preferably 20 to 100 rpm. The temperature is preferably in a range of from 0 to 100 °C, more preferably 20 to 70 °C, especially 40 to 75 °C. Preferably mixing takes place over a period of 2 min to 5 hours, more preferably 10 min to 120 min.

It is possible to add additives to the aqueous composition prior to and/or during and/or after mixing step i).Suitable additives are those used for the formation of polymer films, like plasticizers, scavengers, agents for modification of gas permeability and water vapor permeability, antistats, glidants, slip agents, UV absorbers, etc. Suitable additives are also those mentioned in the following for the detergent and cleaner formulations. In a special embodiment at least one enzyme is used as additive. Suitable enzymes are those as are customarily used as industrial enzymes. These include both enzymes with optimum activity in the neutral to alkaline pH range, as well as enzymes with optimum activity in the acidic pH range.

Step ii): film formation

In step ii) of the process according to the invention, the aqueous composition obtained in step i) is converted to a polymer film.

The process of the invention allows the formation of single layer films and of multilayer films. In principle, for the formation of a single layer film, the aqueous composition obtained in step i), comprising a polymer P1'), a polyoxyalkylene ether PE'), water and optionally at least one additive, is subjected to a film formation. The film formation preferably takes place by casting, blow molding, thermoforming or calendering.

Multilayer films consist preferably of 2 to 20 layers, more preferably 2 to 15 layers and especially 2 to 10 layers. These specifically include multilayer films consisting of 2, 3, 4, 5, 6, 7 or 8 layers. All these layers may be of different composition, or two or more than two of the layers may have the same composition. The composition of the individual layers depends on the field of use of the multilayer film.

The multilayer film comprises at least one layer comprising or consisting of a mixture of at least one polymer P1') and at least one polyoxyalkylene ether PE'). Preferably, the multilayer film comprises at least one further layer comprising or consisting of at least one polymer P2') other than the polymers P1'). Suitable polymers P2') are defined in detail in the following.

In a preferred embodiment, the individual layers of the multilayer films are water-soluble or water-dispersible. According to the field of use of the multilayer films, it may be advantageous for the individual layers to have a particular solubility in water. For example, it may be desirable for different layers to have different solubility in water. It may also be desirable, for example, for an outer surface layer to have a lesser degree of water solubility in order to prevent blocking

and/or partial dissolution in the event of high air humidity and/or high contact moisture (e.g. hand moisture). Alternatively, it may also be desirable for an outer surface layer to have sufficient water solubility in order to timely release an active ingredient present therein or ensheathed therewith on contact with water.

According to the field of use of the multilayer films, it may also be advantageous for the individual layers to have a temperature-dependent solubility in water.

The multilayer film of the invention preferably comprises at least one further layer comprising or consisting of at least one polymer P2') selected from

- natural and modified polysaccharides,
- homo- and copolymers comprising repeat units which derive from vinyl alcohol, vinyl esters, alkoxylated vinyl alcohols or mixtures thereof,
- homo- and copolymers comprising at least one copolymerized monomer selected from N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, 2-vinylpyridine, 4-vinylpyridine, salts of the three latter monomers, vinylpyridine N-oxide, N-carboxymethyl-4-vinylpyridium halides and mixtures thereof,
- homo- and copolymers of acrylic acid and/or methacrylic acid, especially copolymers comprising at least one copolymerized acrylic monomer selected from acrylic acid, acrylic salts and mixtures thereof, and at least one copolymerized maleic monomer selected from maleic acid, maleic anhydride, maleic salts and mixtures thereof,
- copolymers comprising at least one copolymerized (meth)acrylic monomer selected from acrylic acid, methacrylic acid, salts thereof and mixtures thereof and at least one copolymerized hydrophobic monomer selected from C_1-C_8-alkyl esters of (meth)acrylic acid, C_2-C_{10} olefins, styrene and α-methylstyrene,
- copolymers comprising at least one copolymerized maleic monomer selected from maleic acid, maleic anhydride, maleic salts and mixtures thereof and at least one copolymerized C_2-C_8 olefin,
- homo- and copolymers of acrylamide and/or methacrylamide,
- polyamino acids,
- water-soluble or water-dispersible polyamides,
- polyalkylene glycols, mono- or diethers of polyalkylene glycols, and
- mixtures thereof.

The multilayer film more preferably comprises at least one further layer comprising or consisting of at least one polymer P2') selected from

- cellulose ethers and cellulose esters,
- homo- and copolymers comprising repeat units which derive from vinyl alcohol, vinyl esters, alkoxylated vinyl alcohols or mixtures thereof,
- polymers selected from polyvinylpyrrolidone homopolymers, polyvinylimidazole homopolymers, copolymers comprising copolymerized vinylpyrrolidone and vinylimidazole, polyvinylpyridine N-oxide, poly-N-carboxymethyl-4-vinylpyridium halides,
- mixtures thereof.

The multilayer film especially comprises at least one further layer comprising or consisting of at least one polymer P2') selected from cellulose derivatives, preferably carboxyalkyl celluloses and salts thereof, sulfoalkyl celluloses and salts thereof, acidic sulfuric ester salts of cellulose, alkyl celluloses, hydroxyalkyl celluloses, hydroxyalkyl alkyl celluloses and mixtures of two or more of these cellulose derivatives.

Polysaccharides suitable as polymers P2') are natural polysaccharides, for example cellulose, hemicellulose, glycogen, starch (amylose and amylopectin), dextran, pectins, inulin, xanthan, chitin, callose, etc. and thermally, hydrolytically or enzymatically degraded natural polysaccharides, for example maltodextrin etc.

Preferred modified polysaccharides are, for example, cellulose ethers, cellulose esters, cellulose amides, etc.

Cellulose ethers are derivatives of cellulose which arise through partial or complete substitution of the hydrogen atoms in the hydroxyl groups of the cellulose. Cellulose ethers from the reaction of cellulose with more than one etherifying agent are also referred to as cellulose mixed ethers.

Preferred cellulose ethers are selected from alkyl celluloses, hydroxyalkyl celluloses, hydroxyalkyl alkyl celluloses, carboxyalkyl celluloses and salts thereof, carboxyalkyl alkyl celluloses and salts thereof, carboxyalkyl hydroxyalkyl celluloses and salts thereof, carboxyalkyl hydroxyalkyl alkyl celluloses and salts, sulfoalkyl celluloses and salts thereof.

Preferred carboxyalkyl radicals are the carboxymethyl radical and the carboxyethyl radical. A particularly preferred carboxyalkyl radical is the carboxymethyl radical. Preferred sulfoalkyl radicals are the sulfomethyl radical and the sulfoethyl radical. A particularly preferred sulfoalkyl radical is the sulfomethyl radical. Preferred salts are the sodium, potassium, calcium and ammonium salts.

Particularly preferred cellulose ethers are selected from carboxymethyl cellulose, carboxyethyl cellulose, methyl cellulose, ethyl cellulose, n-propyl cellulose, ethyl methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxybutyl cellulose, hydroxyethyl methyl cellulose, hydroxypropyl methyl cellulose, hydroxyethyl ethyl cellulose, hydroxypropyl ethyl cellulose, carboxymethyl methyl cellulose, carboxymethyl ethyl cellulose, carboxymethyl hydroxyethyl cellulose, carboxymethyl hydroxyethyl methyl cellulose, carboxymethyl hydroxyethyl ethyl cellulose, sulfomethyl cellulose and sulfoethyl cellulose. The carboxyalkyl radicals and the sulfoalkyl radicals may also be in salt form.

Cellulose esters are derivatives of cellulose which form as a result of esterification of the hydroxyl groups with acids. Preference is given to the sulfuric esters of cellulose. In a specific embodiment, the sulfuric acid is subjected only to a partial esterification, such that the resulting sulfuric esters still have free acid groups or salts thereof. Particular preference is given to using acidic sulfuric ester salts of cellulose. These are notable for their graying-inhibiting effect.

Preferred modified polysaccharides are selected from methyl cellulose, ethyl cellulose, propyl cellulose, methyl/ethyl cellulose, ethyl/propyl cellulose, carboxymethyl cellulose, salts of carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyethyl methyl cellulose, hydroxyethyl ethyl cellulose, hydroxypropyl methyl cellulose, hydroxypropyl ethyl cellulose, etc.

In a further preferred embodiment, the polymers P2') are selected from homo- and copolymers comprising repeat units which derive from vinyl alcohol, vinyl esters, alkoxylated vinyl alcohols or mixtures thereof.

Suitable vinyl esters (vinyl acylates) are generally the esters of vinyl alcohol with C_1-C_{15} carboxylic acids, preferably C_1-C_8 carboxylic acids, more preferably C_1-C_4 carboxylic acids. Preferred vinyl acylates are vinyl acetate, vinyl n-propionate, vinyl n-butyrate, vinyl 2-ethylhexanoate, vinyl laurate, etc. Particular preference is given to vinyl acetate.

Partly or fully hydrolyzed polyvinyl acetates (PVAs) are generally referred to as "polyvinyl alcohol (PVOH)". Partly hydrolyzed polyvinyl acetates are obtained by incomplete hydrolysis of polyvinyl acetates, meaning that the partly hydrolyzed polymer has both ester groups and hydroxyl groups. The hydrolysis of the polyvinyl acetates can be effected in a manner known per se under alkaline or acidic conditions, i.e. with addition of acid or base.

The performance properties of polyvinyl alcohols are determined by factors including the polymerization level and the hydrolysis level (level of hydrolysis). With rising hydrolysis level, the water solubility decreases. Polyvinyl alcohols having hydrolysis levels up to about 90 mol% are generally soluble in cold water. Polyvinyl alcohols having hydrolysis levels of about 90 to about 99.9 mol% are generally no longer soluble in cold water but are soluble in hot water.

Polyvinyl alcohols suitable as polymers P2') preferably have a hydrolysis level of 50 to 99.9 mol%, more preferably of 70 to 99 mol%, especially of 80 to 98 mol%.

Polyvinyl alcohols suitable as polymers P2') preferably have a weight-average molecular weight of 10 000 to 300 000 g/mol, more preferably of 15 000 to 250 000 g/mol.

Polyvinyl alcohols suitable as polymers P2') preferably have a viscosity of 2 to 120 mPa s, more preferably of 7 to 70 mPa s and especially of 15 to 60 mPa s, measured to DIN 53015 on a 4% solution in water.

In a further preferred embodiment, the polymers P2') are selected from homo- and copolymers comprising at least one copolymerized monomer selected from N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, 2-vinylpyridine, 4-vinylpyridine, salts of the three latter monomers, vinylpyridine N-oxide, N-carboxymethyl-4-vinylpyridium halides and mixtures thereof.

N-Vinylimidazole, 2-vinylpyridine and 4-vinylpyridine can be converted to the corresponding salts by protonation or quaternization. Suitable acids are, for example, mineral acids such as sulfuric acid, hydrochloric acid and phosphoric acid, and carboxylic acids. Alkylating agents suitable for quaternization are C_1-C_4-alkyl halides or C_1-C_4-alkyl sulfates, such as ethyl chloride, ethyl bromide, methyl chloride, methyl bromide, dimethyl sulfate and diethyl sulfate.

Preference is given to polyvinylpyrrolidone homopolymers and copolymers comprising copolymerized N-vinylpyrrolidone and another different copolymerized ethylenically unsaturated monomer. Suitable N-vinylpyrrolidone copolymers are quite generally uncharged, anionic, cationic and amphoteric polymers.

Particularly preferred N-vinylpyrrolidone copolymers are selected from
copolymers of N-vinylpyrrolidone and vinyl acetate,
copolymers of N-vinylpyrrolidone and vinyl propionate,
copolymers of N-vinylpyrrolidone, vinyl acetate and vinyl propionate,
copolymers of N-vinylpyrrolidone and vinyl acrylate,
copolymers of N-vinylpyrrolidone, ethyl methacrylate and methacrylic acid,
copolymers of N-vinylpyrrolidone and N-vinylimidazole and the derivatives thereof obtained by protonation and/or quaternization,
copolymers of N-vinylpyrrolidone and dimethylaminoethyl methacrylate and the derivatives thereof obtained by protonation and/or quaternization,
copolymers of N-vinylpyrrolidone, N-vinylcaprolactam and N-vinylimidazole and the derivatives thereof obtained by protonation and/or quaternization.

In a further preferred embodiment, the polymers P2') are selected from homo- and copolymers of acrylic acid and/or methacrylic acid.

In a first specific embodiment of the homo- and copolymers of acrylic acid and/or methacrylic acid, the polymer P2') used is an acrylic acid homopolymer. Acrylic acid homopolymers P2') preferably have a number-average molecular weight in the range from 800 to 70 000 g/mol, more preferably 900 to 50 000 g/mol, particularly 1000 to 20 000 g/mol and especially 1000 to 10 000 g/mol. In this context, the term "acrylic acid homopolymer" also encompasses polymers in which the carboxylic acid groups are in partly or fully neutralized form. These include acrylic acid homopolymers in which the carboxylic acid groups are present partly or completely in the form of alkali metal salts or ammonium salts. Preference is given to acrylic acid homopolymers in which the carboxylic acid groups are protonated or are partly or completely in the form of sodium salts. Homopolymers of acrylic acid particularly suitable as polymers P2') are the Sokalan ® PA brands from BASF SE.

Polyvinylalcohol that can typically be used as polymers P2') are known under the tradename Poval™ from Kuraray company. Non limited examples are Poval™ 8-88, Poval™ 18-88, Poval™ 26-88, Poval™ 30-92, Poval™ 10-98, Poval™ 20-98 or Poval™ 28-99.

To tune the performance properties according to the specific need of the application blends comprising polyvinylalcohols of different molecular weight and degree of hydrolysis can be used. Non limited examples are a blend of Poval™ 26-88 (three parts) and Poval™ 20-98 (one part) or a blend of Poval™ 30-92 (two parts) and Poval™ 10-98 (one part).

In a second specific embodiment of the homo- and copolymers of acrylic acid and/or methacrylic acid, polymer P2') used is a copolymer comprising at least one copolymerized acrylic acid monomer selected from acrylic acid, acrylic salts and mixtures thereof and at least one copolymerized maleic monomer selected from maleic acid, maleic anhydride, maleic salts and mixtures thereof. These preferably have a number-average molecular weight in the range from 2500 to 150 000 g/mol, more preferably 2800 to 70 000 g/mol, particularly 2900 to 50 000 g/mol and especially 3000 to 30 000 g/mol. Also included here are copolymers in which the carboxylic acid groups are in partly or fully neutralized form. For this purpose, it is either possible to use monomers in salt form for polymerization or for the resulting copolymer to be subjected to partial or complete neutralization. Preference is given to copolymers in which the carboxylic acid groups are protonated or are partly or completely in the form of alkali metal salts or ammonium salts. Preferred alkali metal salts are sodium or potassium salts, especially the sodium salts.

Preferred polymers P2') are copolymers of maleic acid (or maleic monomers) and acrylic acid (or acrylic monomers) in a weight ratio of 10:90 to 95:5, more preferably those in a weight ratio of 30:70 to 90:10.

Preferred polymers P2') are also terpolymers of maleic acid (or maleic monomers), acrylic acid (or acrylic monomers) and a vinyl ester of a C_1-C_3 carboxylic acid in a weight ratio of 10 (maleic acid):90 (acrylic acid + vinyl ester) to 95 (maleic acid):10 (acrylic acid + vinyl ester). The weight ratio of acrylic acid to vinyl ester is preferably within a range from 30:70 to 70:30.

Particularly suitable polymers P2') based on acrylic monomers and maleic monomers are the corresponding Sokalan® CP brands from BASF SE.

In a third specific embodiment of the homo- and copolymers of acrylic acid and/or methacrylic acid, polymer P2') used is a copolymer comprising at least one (meth)acrylic acid monomer selected from (meth)acrylic acid, (meth)acrylic salts and mixtures thereof and at least one hydrophobic monomer. The hydrophobic monomer is especially selected from C_1-C_8-alkyl esters of (meth)acrylic acid, for example the methyl, ethyl, n- and isopropyl, n-butyl and 2-ethylhexyl esters of (meth)acrylic acid and C_2-C_{10} olefins, for example ethene, propene, 1,2-butene, isobutene, diisobutene, styrene and α-methylstyrene.

In a further preferred embodiment, the polymer P2') used is a copolymer of at least one maleic monomer selected from maleic acid, maleic anhydride, maleic salts and mixtures thereof with at least one C_2-C_8 olefin. Also suitable are copolymers comprising at least one copolymerized maleic monomer selected from maleic acid, maleic anhydride, maleic salts and mixtures thereof,

at least one copolymerized C_2-C_8 olefin and at least one other different copolymerized comonomer.

Particular preference is given to copolymers comprising at least one copolymerized maleic monomer selected from maleic acid, maleic anhydride, maleic salts and mixtures thereof and at least one copolymerized C_2-C_8 olefin as the sole monomers. These preferably have a number-average molecular weight in the range from 3000 to 150 000 g/mol, more preferably 5000 to 70 000 g/mol, particularly 8000 to 50 000 g/mol and especially 10 000 to 30 000 g/mol. Also included here are copolymers in which the carboxylic acid groups are in partly or fully neutralized form. For this purpose, it is either possible to use maleic salts for polymerization or for the resulting copolymer to be subjected to partial or complete neutralization. Preference is given to copolymers in which the carboxylic acid groups are protonated or are partly or completely in the form of alkali metal salts or ammonium salts. Preferred alkali metal salts are sodium or potassium salts, especially the sodium salts.

A specific embodiment is copolymers of maleic acid with C_2-C_8 olefins in a molar ratio of 40:60 to 80:20, particular preference being given to copolymers of maleic acid with ethylene, propylene, isobutene, diisobutene, isoprenol or styrene. Particularly suitable compounds which contain carboxylic acid groups and are based on olefins and maleic acid are likewise the corresponding Sokalan® CP brands from BASF SE.

A further preferred embodiment is that of copolymers comprising at least one copolymerized maleic monomer selected from maleic acid, maleic anhydride, maleic salts and mixtures thereof, at least one copolymerized C_2-C_8 olefin and at least one copolymerized acrylic monomer selected from acrylic acid, acrylic salts and mixtures thereof.

A further preferred embodiment is that of copolymers comprising at least one copolymerized maleic monomer selected from maleic acid, maleic anhydride, maleic salts and mixtures thereof, at least one copolymerized C_2-C_8 olefin and at least one copolymerized ester of (meth)acrylic acid. In that case, the ester of (meth)acrylic acid is especially selected from C_1-C_8-alkyl esters of (meth)acrylic acid, for example the methyl, ethyl, n- and isopropyl, n-butyl and 2-ethylhexyl esters of (meth)acrylic acid.

In a further preferred embodiment, the polymers P2') are selected from homo- and copolymers comprising at least one copolymerized monomer selected from acrylamide, methacrylamide and mixtures thereof. These polymers P2') are preferably water-soluble or water-dispersible. These polymers P2') are especially water-soluble.

In a specific embodiment, the polymers P2') are selected from homopolymers of acrylamide or methacrylamide.

In a further specific embodiment, the polymers P2') are selected from copolymers of acrylamide and/or methacrylamide. These comprise at least one copolymerized comonomer selected from

hydrophilic monomers (A1') other than acrylamide and methacrylamide, monoethylenically unsaturated amphiphilic monomers (A2') and further ethylenically unsaturated monomers (A3').

Suitable hydrophilic monoethylenically unsaturated monomers (A1') are uncharged monomers such as N-methyl(meth)acrylamide, N,N'-dimethyl(meth)acrylamide or N-methylol(meth)acrylamide, monomers comprising hydroxyl and/or ether groups, for example hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, allyl alcohol, hydroxyvinyl ethyl ether, hydroxyvinyl propyl ether, hydroxyvinyl butyl ether, polyethylene glycol (meth)acrylate, N-vinylformamide, N-vinylacetamide, N-vinylpyrrolidone or N-vinylcaprolactam, and vinyl esters, for example vinyl formate or vinyl acetate. After polymerization, N-vinyl derivatives may be hydrolyzed to vinylamine units, and vinyl esters to vinyl alcohol units. Suitable hydrophilic monoethylenically unsaturated monomers (A1') are also monomers comprising at least one acidic group or salts thereof. These include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, vinylsulfonic acid, allylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, 2-methacrylamido-2-methylpropanesulfonic acid, 2-acrylamidobutanesulfonic acid, 3-acrylamido-3-methylbutanesulfonic acid, 2-acrylamido-2,4,4-trimethylpentanesulfonic acid, vinylphosphonic acid, allylphosphonic acid, N-(meth)acrylamidoalkylphosphonic acids, (meth)acryloyloxyalkylphosphonic acids and salts and mixtures thereof. The further monoethylenically unsaturated hydrophilic monomers may be hydrophilic cationic monomers. Suitable cationic monomers (A1c) especially include monomers having ammonium groups, especially ammonium derivatives of N-(ω-aminoalkyl)(meth)acrylamides or ω-aminoalkyl (meth)acrylates.

The amphiphilic monomers (A2') are monoethylenically unsaturated monomers having at least one hydrophilic group and at least one, preferably terminal, hydrophobic group.

The monomers (A3') may, for example, be monoethylenically unsaturated monomers which have a more hydrophobic character than the hydrophilic monomers (A1') and are accordingly water-soluble only to a minor degree. Examples of such monomers include N-alkyl- and N,N'-dialkyl(meth)acrylamides, where the number of carbon atoms in the alkyl radicals together is at least 3, preferably at least 4. Examples of such monomers include N-butyl(meth)acrylamide, N-cyclohexyl(meth)acrylamide or N-benzyl(meth)acrylamide.

In a further preferred embodiment, the polymers P2') are selected from polyamino acids. Suitable polyamino acids are in principle compounds comprising at least one copolymerized amino acid such as aspartic acid, glutamic acid, lysine, glycine, etc. The polyamino acids also include the derivatives obtainable by polymer-analogous reaction, such as esterification, amidation, etc. Preferred polyamino acids are polyaspartic acid, polyaspartic acid derivatives, polyglutamic acid, polyglutamic acid derivatives and mixtures thereof.

Polyaspartic acid can be prepared, for example, by alkaline hydrolysis of polysuccinimide (PSI, anhydropolyaspartic acid). Polysuccinimide can be prepared by thermal condensation of

aspartic acid or from ammonia and maleic acid. Polyaspartic acid can be used, for example, as a biodegradable complexing agent and cobuilder in washing and cleaning compositions.

Polyamino acids having surfactant properties can be obtained by at least partly converting the free carboxylic acid groups of polyaspartic acid or polyglutamic acid to N-alkylamides and/or to esters. Polyaspartamides can also be prepared by reaction of polysuccinimide with amines. For preparation of hydroxylethylaspartamides, the ring opening of polysuccinimide can be conducted with ethanolamine. DE 37 00 128 A and EP 0 458 079 A describe the subsequent esterification of such hydroxyethyl derivatives with carboxylic acid derivatives. Copolymeric polyaspartic esters are obtainable as described in DE 195 45 678 A by condensation of monoalkyl esters of maleic or fumaric acid with addition of ammonia. DE 195 45 678 A further states that copolymeric polyaspartic esters are obtainable by reaction of polysuccinimide with alcohols, optionally followed by hydrolysis. According to the esterification level and hydrophobicity of the alcohol component, polyaspartic esters, aside from their biodegradability, are notable for excellent properties as stabilizers for O/W and W/O emulsions, as a foam-stabilizing and foam-boosting cosurfactant in washing and cleaning compositions, and as a complexing agent for metal cations.

In a further preferred embodiment, the polymers P2') are selected from polyalkylene glycols and mono- or diethers of polyalkylene glycols. Preferred polyalkylene glycols have a number - average molecular weight in the range from 1000 to 4 000 000 g/mol, more preferably from 1500 to 1 000 000 g/mol.

Suitable polyalkylene glycols and the mono- and diethers thereof may be linear or branched, preferably linear. Suitable polyalkylene glycols are, for example, water-soluble or water-dispersible nonionic polymers having repeat alkylene oxide units. Preferably, the proportion of repeat alkylene oxide units is at least 30% by weight, preferably at least 50% by weight and especially at least 75% by weight, based on the total weight of the compound. Suitable polyalkylene glycols are polyethylene glycols, polypropylene glycols, polytetrahydrofurans and alkylene oxide copolymers. Suitable alkylene oxides for preparation of alkylene oxide copolymers are, for example, ethylene oxide, propylene oxide, epichlorohydrin, 1,2- and 2,3-butylene oxide. Suitable examples are copolymers of ethylene oxide and propylene oxide, copolymers of ethylene oxide and butylene oxide, and copolymers of ethylene oxide, propylene oxide and at least one butylene oxide. The alkylene oxide copolymers may comprise the copolymerized alkylene oxide units in randomly distributed form or in the form of blocks. Preferably, the proportion of repeat units derived from ethylene oxide in the ethylene oxide/propylene oxide copolymers is 40% to 99% by weight. Particular preference is given to ethylene oxide homopolymers and ethylene oxide/propylene oxide copolymers.

Suitable mono- and diethers of polyalkylene glycols are the mono-(C_1-C_{18}-alkyl ethers) and di-(C_1-C_{18}-alkyl ethers). Preferred mono- and diethers of polyalkylene glycols are the mono-(C_1-C_6-alkyl ethers) and di-(C_1-C_6-alkyl ethers). Especially preferred are the mono-(C_1-C_2-alkyl ethers)

and di-(C_1-C_2-alkyl ethers). Especially preferred are polyalkylene glycol monomethyl ethers and polyalkylene glycol dimethyl ethers.

Polymer mixtures are suitable, for example, for adjusting the mechanical properties and/or the dissolution properties of the multilayer films of the invention. The polymers used in the polymer mixture may differ in terms of their chemical composition and/or in terms of their physicochemical properties.

In a specific embodiment, the multilayer film of the invention comprises at least one layer comprising 2 or more polymers, selected from polymers P1'), polymers P2') and mixtures thereof. According to this embodiment, at least one layer of the multilayer film may comprise 2 or more different polymers P1') or at least one polymer P1') and at least one polymer P2') or 2 or more different polymers P2').

In a first embodiment, a combination of 2 or more polymers which differ in terms of their chemical composition is used. In a second embodiment, a combination of 2 or more polymers which differ in terms of their molecular weight is used. According to this second embodiment, for example, a polymer mixture comprising at least two polymers P2') comprising repeat units which derive from vinyl alcohol is used.

Production of single and multilayer films

The following description is suitable for the production of both embodiments of the films suitable of in the process of the present invention, the multilayer film of the first embodiment and the washing- and cleaning-active polymer film of the second embodiment.

In principle, the film production process is not subject to any particular limitations and the person skilled in the art can apply any desired production process known to him on account of his specialist knowledge while using the polymer composition P1 as described above or below or an aqueous composition comprising a polymer P1') and a polyoxyalkylene ether PE') as described above or below. The same is true for the production of coverings and coatings based on the obtained films.

Single layer films can be prepared preferably by casting processes and extrusion processes.

Single layer film:

For the production of a single layer film by extrusion, an aqueous composition or melt based on the aqueous composition obtained according to step i) as described above for the production of the washing- and cleaning-active polymer film of the second embodiment is extruded and blown in a blowing process or is extruded and formed in a thermoforming process to give a film. Optionally the film thus obtained is converted to a form suitable for the covering or coating of detergent or cleaner portions.

For the production of a single layer film by casting, an aqueous composition obtained according to step i), optionally after adding at least one additive, is melted or dissolved in a suitable solvent or solvent mixture, the thus obtained flowable polymer composition is cast to give a film and optionally the solvent or solvent mixture is removed by evaporation.

The solvent is preferably selected from water, ethanol, n-propanol, isopropanol, ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,2-dipropylene glycol and mixtures thereof. In a specific embodiment, the solvent used is water or a mixture of water and at least one solvent different from water, selected from ethanol, n-propanol, isopropanol, ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,2-dipropylene glycol and mixtures thereof.

To produce film portions, the film material can be confectioned in a suitable manner, e.g. by cutting into a suitable size and/or folding to form compartments. Then the edges can be sealed by customary sealing processes, such as hot sealing, liquid sealing or pressure sealing.

Multilayer film:

Multilayer films can be produced e.g. by a lamination method. Lamination methods in which two or more film layers are bonded to one another over their area are known to those skilled in the art. Lamination involves pressing two or more than two films together under elevated pressure and/or at elevated temperature. Multilayer films can also be produced by a wet-on-wet application method. In addition, multilayer films can also be produced by using combinations of the aforementioned production methods and the application method described hereinafter.

In a preferred embodiment, the multilayer film is produced by a process in which at least one free-flowing composition capable of film formation is applied to a carrier material, wherein the carrier material and/or the at least one free-flowing composition comprises or consists of the polymer composition P1 as defined above and hereinafter or comprises a polymer P1') and a polyoxyalkylene ether PE') as defined above and hereinafter. In particular, the carrier material and/or the at least one pourable composition are obtained from the polymer composition P1 or from an aqueous aqueous composition by mixing

- a polymer P1') that comprises polymerized units of at least one monomer A'), selected from α,β-ethylenically unsaturated carboxylic acids, salts of α,β-ethylenically unsaturated carboxylic acids and mixtures thereof,
- an polyoxyalkylene ether PE') having at least one C_8-C_{18}-alkyl group that is unsubstituted or substituted by at least one hydroxyl group, and an average of 3 to 25 alkylene oxide units per molecule, and
- water.

Reference is made to the aqueous composition obtained by step i) as defined above and hereinafter for the production of the washing- and cleaning-active polymer film of the second embodiment.

The process for producing a multilayer film preferably comprises the steps of

i1) a first free-flowing or pourable composition capable of film formation is applied to a carrier material to obtain a first layer,
i2) the first layer applied to the carrier material is optionally subjected to an increase in viscosity,
i3) a second free-flowing or pourable composition capable of film formation is applied to the first layer obtained in step i1) or in step i2) to obtain a second layer,
i4) the second layer is optionally subjected to an increase in viscosity,
i5) step i3) is optionally repeated with a further composition capable of film formation to obtain a further layer and step i4) is optionally then repeated, it being possible to repeat steps i3) and i4) once or more than once,
i6) the layers applied to the carrier material are optionally subjected to a further increase in viscosity,
i7) the multilayer film obtained is optionally detached from the carrier material,

with the proviso that the free-flowing or pourable compositions each comprise a component which is capable of film formation and is independently selected from at least one polymer composition P1 or aqueous compositions comprising a polymer P1') and an polyoxyalkylene ether PE'), at least one polymer P2 or polymer P2') or a mixture thereof, and with the proviso that the carrier material and/or the at least one free-flowing or pourable composition comprises or consists of a polymer composition P1 as defined above and hereinafter or comprises a polymer P1') and a polyoxyalkylene ether PE') as defined above and hereinafter.

In a specific embodiment, the application of two or more than two of the pourable compositions can also be applied partly or fully simultaneously. For this purpose, for example, the application of the (n+1)th composition can be commenced before the application of the nth composition has completely ended.

In a further specific embodiment, the production of the multilayer film proceeds from a carrier material which already comprises the first film layer and optionally also already comprises further film layers of the multilayer film. In other words, a carrier material which already comprises the first film layer and optionally further film layers of the multilayer film is used in step i1). In this case, the carrier material forms part of the multilayer film and remains in the multilayer film after the application of all the further layers. This means that the further layers applied to the carrier material are not subsequently detached again from the carrier material. In this embodiment, there is therefore no step i7) of the above-described process.

The viscosity of the free-flowing composition is matched to the technical demands of the production method and is determined by factors including the concentration of the components capable of film formation, the solvent content (water), the additives added and the temperature.

The pourable compositions capable of film formation are applied in steps i1), i3) and i5) generally by means of standard methods, for example by means of pre-metered and self-metered methods selected from airblade coating, knife coating, airknife coating, squeegee coating, impregnation coating, dip coating, reverse roll coating, transfer roll coating, gravure

coating, kiss coating, flow coating, cascade flow coating, slide coating, curtain coating, mono- and multilaminar slot die coating, spray coating, spin coating, or printing methods such as relief printing, intaglio printing, rotogravure printing, flexographic printing, offset printing, inkjet printing, letterpress printing, pad printing, heatseal printing or screenprinting methods. The application can also be continuous or semicontinuous, for example when the carrier material is moving, for example a permanently or intermittently moving belt.

Suitable carrier materials are firstly all materials which enable simple detachment of the finished multilayer film. Examples of these include glass, metals such as galvanized steel sheet or stainless steel, polymers such as silicones or polyethylene terephthalate, polymer-coated paper, such as silicone paper, etc. Suitable carrier materials are secondly monolaminar or multilaminar polymer films which remain as film layers in the multilayer film of the invention. With regard to the composition of these carrier materials, reference is made to the disclosure relating to the the polymer composition P1 or aqueous composition that comprises a polymer P1') and a polyoxyalkylene ether PE') and the disclosure relating to polymers P2 or polymers P2').

The increase in viscosity in layers i2), i4) and i6) can be effected by means of standard methods and generally depends on the form in which pourable compositions capable of film formation have been applied in steps i1), i3) and i5). If they have been applied as a melt, for example, there is generally already an increase in viscosity in the course of cooling. The cooling can be effected by simply leaving the carrier material to stand or by active cooling, such as cooling of the carrier material, jetting with a cool gas (jet), cooling in a cold room/refrigerator and the like. If the free-flowing composition capable of film formation has been applied in the form of a solution or dispersion, it is generally necessary to remove at least some of the solvent, which can be effected, for example, by simply leaving the carrier material to stand, drying with an air jet or hot air jet, drying in drying cabinets, heating of the carrier material, application of a reduced pressure, optionally with simultaneous supply of heat, IR irradiation, microwave radiation, for example in a corresponding oven, and the like. Should the composition be curable, for example because the polymers present therein comprise as yet unconverted polymerizable/condensable groups, the increase in viscosity can alternatively or additionally be effected by curing the polymer. The measures suitable for curing depend on the polymerizable/condensable groups present. For instance, ethylenically unsaturated crosslinkable groups are especially cured by UV radiation; condensable groups, by contrast, generally cure either by being left to stand or with supply of heat. The heat can again be supplied as described above, i.e., for example, by incidence of warm or hot air or other warm or hot gases, drying in drying cabinets, heating of the carrier material, IR irradiation and the like. It is also possible to gel the solution or dispersion applied by cooling, in the sense of forming a physical network extended over macroscopic dimensions, which likewise results in an increase in viscosity.

In a specific embodiment, the pourable compositions capable of film formation for two or more than two of the layers that form the multilayer film are applied by a wet-on-wet application method. The application in i3), i5) etc. can thus be effected wet-on-wet, meaning that the next layer can also be applied to the layer applied in step i1), i3) and/or i5) without an explicit step for

increasing viscosity having been conducted beforehand. This is especially true when the layer to which the next polymer layer is applied is sufficiently thin, such that it solidifies sufficiently even without being explicitly left to stand, dried, heated, cured, etc. before the next layer is applied, and there is no complete mixing with the components of the next layer. This is also true when the two layers, i.e. those to which application is effected, and the layer applied subsequently do not have any strong tendency to mix, for example because one layer is based on an aqueous polymer solution/dispersion and the other on a hydrophobic organic solution/dispersion or a hydrophobic melt.

The polymers applied in steps i1), i3), i5) etc. are film-forming polymers. One or more than one of the layers comprising film-forming polymers may additionally comprise at least one additive.

In a particular embodiment, after steps i1), i2), i3), i4), i5) and/or a6), it is also possible to apply one or more layers that do not comprise any film-forming polymers. These are especially layers comprising components (functional materials) connected to the desired end use of the multilayer film. Should the film serve, for example, in or as a washing composition or as a sheath for washing compositions, these optional further layers may comprise surfactants, builders, cobuilders, bleaches, enzymes, graying inhibitors, optical brighteners, fragrances, dyes, etc. These components may, like the polymer layers too, be applied in solution/dispersion or melt. Suitable application techniques here too are those mentioned above.

The application of these layers may also be followed by a step of increasing the viscosity, or the next layer can be applied wet-on-wet. The statements made above apply analogously.

If the above-described layers that are applied do not comprise any film-forming polymers but do comprise components connected to the desired end use of the multilayer film, it is possible after steps i1), i2), i3), i4), i5) and/or i6), especially after steps i1), i3) and/or i5), to emboss or punch the polymer layer, so as to give rise to recesses in which the functional materials applied at a later stage can be accommodated in relatively large amounts. This can be effected by means of standard embossing, printing, stamping and punching tools.

The process of the invention allows the production of multilayer films without a complex lamination method in which the individual films have to be bonded to one another. It will be appreciated that the multilayer films of the invention can also be produced, as described above, by bonding two or more than two film layers to one another by laminating. For instance, multilaminar polymer films which serve as carrier material for application of further film layers may be provided by bonding two or more than two film layers to one another by laminating.

For provision of the compositions applied in steps i1), i3), i5) etc., for example, a component which is capable of film formation and is selected from polymer compositions P1 or aqueous compositions comprising a polymer P1') and a polyoxyalkylene ether PE'), at least one polymer P2 or at least one polymer P2') or a mixture thereof, optionally after addition of at least one additive, is melted or dissolved in a suitable solvent or solvent mixture, the pourable

composition thus obtained is poured out to form a layer and the solvent or solvent mixture is optionally removed by evaporation.

Suitable solvents and solvent mixtures are those described above as component S), to which reference is made here in its entirety. The solvent is more preferably selected from water, ethanol, n-propanol, isopropanol, ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,2-dipropylene glycol and mixtures thereof. In a specific embodiment, the solvent used is selected from water and a mixture of water and at least one solvent other than water, selected from ethanol, n-propanol, isopropanol, ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,2-dipropylene glycol and mixtures thereof.

The multilayer film can be applied to a steel belt or a heated roller using single or multi-layer casting or coating tools such as slot nozzles, doctor blade, curtain coating, cascade casting, etc. In this case, one or more layers can be applied simultaneously and the other layers optionally on a different position of the steel strip or the roller. In another embodiment, another layer can be applied in a post-drying step on the freestanding film after detaching from the carrier material (steel strip or roller). Roller-based coating processes are particularly suitable for this subsequent coating.

In a further embodiment, it is also possible to combine a plurality of steel strip or roller-dryer installations in such a way that two separately produced single-layer or multilayer films are connected to one another directly in a lamination step. This step can also be carried out with a previously prepared or commercially available film. The laminating step of the films may be carried out before detaching a film, immediately after detaching the film and before drying of the freestanding film, during the drying of the freestanding film or after the drying, but before the winding. A separate lamination of two films is also possible. In all variants of the lamination, lamination is possible solely by means of a targeted adjustment of the residual moisture in the film and correspondingly selected line loads.

A specific embodiment is a process for producing a washing- and cleaning-active single layer or multilayer polymer film, which comprises at least one additive. Additives can be added before or during the film formation in step b). Whether the addition takes place before or during step b) depends on the type and effect of the particular additive. For the film formation in step b) additives can be added to the aqueous composition before and/or during the film production.

In the case of multilayer films, an individual layer or a plurality of but not all the layers or all the layers may each comprise one or more than one additive. Alternatively, or additionally, it is possible that at least one additive is present between at least two layers.

The additives may be auxiliaries for adjustment of the properties of the pourable compositions capable of film formation, typical additives of the washing and cleaning compositions or mixtures thereof.

A special embodiment is a single layer film that comprises at least one additive. A further special embodiment is a multilayer film in which at least one of the layers includes an additive. Particular preference is given to single layer and multilayer films in which at least one of the layers includes an additive which is a constituent customary for washing and cleaning compositions. In that case, the additive is preferably selected from nonionic, anionic, cationic and amphoteric surfactants, builders, complexing agents such as methylglycinediacetic acid, glutaminediacetic acid, glutamic acid diacetic acid and citric acid and the sodium and potassium salts thereof, bleaches, bleach activators, bleach catalysts, enzymes, bases, corrosion inhibitors, foam inhibitors, defoamers, wetting agents, dyes, pigments, fragrances, bitter agents such as Bitrex®, anti-yellowing agents, fillers, tableting aids, disintegrants, thickeners, solubilizers, organic solvents, electrolytes, pH modifiers, perfume carriers, bitter substances, fluorescers, hydrotropes, antiredeposition agents, optical brighteners, graying inhibitors, antishrink agents, anticrease agents, dye transfer inhibitors, antimicrobial active ingredients, antioxidants, anti-yellowing agents, corrosion inhibitors, antistats, ironing aids, hydrophobizing and impregnating agents, antiswell and antislip agents, plasticizers, scavengers, polymers other than the polymers of the polymer composition P1 or the polymers P1') and other than the polymers P2 or the polymers P2'), agents for modification of gas permeability and water vapor permeability, antistats, glidants, slip agents, UV absorbers and mixtures thereof.

Suitable enzymes are those as are customarily used as industrial enzymes. These include both enzymes with optimum activity in the neutral to alkaline pH range, as well as enzymes with optimum activity in the acidic pH range.

Some additives can fulfill several functions, e.g. as solvent S) and as plasticizer.

In order to make the polymer films more flexible, plasticizers can be added to them before or during production. For production of pourable compositions capable of film formation, preferably 0.5% to 30% by weight, more preferably 2% to 20% by weight and especially 3% to 15% by weight of plasticizer is used, based on the total weight of the composition.

Suitable plasticizers are alkyleneamines, alkanolamines, polyols, such as alkylene glycols and oligoalkylene glycols, e.g. 2-methyl-1,3-propanediol, 3-methyl-1,5-pentadiol, hydroxypropylglycerol, neopentyl glycol, alkoxylated glycerol (such as e.g. Voranol® from Dow Chemicals), water-soluble polyesterpolyols (such as e.g. TriRez from Geo Specialty Chemicals) and mixtures thereof. Suitable plasticizers are also polyetherpolyols, which are available under the name Lupranol® from BASF SE. The term "alkyleneamines" refers to condensation products of alkanolamines with ammonia or primary amines, e.g. ethyleneamines are obtained by reaction of monoethanolamine with ammonia in the presence of a catalyst. Here, the following result as main components: ethylenediamine, piperazine, diethylenetriamine and aminoethylethanolamine.

Preferably, the plasticizers are selected from glycerol, diglycerol, propylene glycols with a weight-average molecular weight of up to 400, e.g. dipropylene glycol, ethylene glycol,

diethylene glycol, triethylene glycol, tetraethylene glycol, sorbitol, isopentyldiol, polyethylene glycol, trimethylolpropane, diethylenetriamine, triethylenepentamine, triethanolamine and mixtures thereof.

In order to make the polymer films according to the invention more resistant to aggressive ingredients (such as e.g. chlorine-releasing compounds, as are used in the area of disinfection of water, etc.), so-called “scavengers” (capture molecules) can be added to the film. Suitable scavengers are polyamines, polymeric polyamines, such as polyethyleneimines, poly(amidoamines) and polyamides. Moreover, it is also possible to use ammonium sulfate, primary and secondary amines with a low vapor pressure, such as ethanolamines, amino acid and salts thereof, and also polyamino acid and salts thereof, fatty amines, glucosamines and other aminated sugars. Furthermore, reducing agents, such as sulfites, bisulfites, thiosulfites, thiosulfates, iodides, nitrites and antioxidants such as carbamates, ascorbates and mixtures thereof can be used.

For production of the single layer and multilayer films, it is possible to add further additives in the form of polymers to the polymer composition P1 or the aqueous composition comprising the polymer P1’) and the polyoxyalkylene ether PE’) and/or to the polymers P2 or polymers P2’) before and/or during the film production. Typically, 0.05 to 20% by weight, preferably 0.1 to 15% by weight, particularly preferably 0.2 to 10% by weight, of polymers (based on the total weight of the polymer compounds, i.e. if present the weight of polymer composition P1 or combined weight of polymers P1’) and the polyoxyalkylene ether PE’), the weight of polymers P2 or polymers P2’) and additional polymers) are used. Such additives can simultaneously improve the washing properties of the film, improve the mechanical properties of the film, and increase the resistance of the film to detergent components. Suitable polymers are e.g. oligosaccharides and polysaccharides, starch, degraded starches (maltodextrins), cellulose ethers, specifically hydroxyethylcellulose, hydroxypropylcellulose, methylcellulose, ethylcellulose, hydroxypropylmethylcellulose, hydroxypropylethylcellulose, microcrystalline cellulose, inulin, carboxymethylcellulose, e.g. in the form of the sodium salts, alginic acid and alginates, pectin acid and pectins, polyethyleneimines, alkoxylated, in particular ethoxylated polyethyleneimines, graft polymers of vinyl acetate on polyalkylene glycols, in particular on polyethylene glycols, homopolymers of N-vinylpyrrolidone, copolymers of N-vinylpyrrolidone and N-vinylimidazole, copolymers of N-vinylpyrrolidone with vinyl acetate and with vinylcaprolactam, polyalkylene oxides, polyvinyl alcohol, polyvinyl alcohols with fractions of nonhydrolyzed vinyl acetate, thickeners, such as, for example, xanthan gum, guar gum, gelatin, agar-agar and mixtures thereof.

It is additionally possible to subject at least one surface or both surfaces of the single and multilayer films of the invention to at least partial coating with at least one additive. Such a treatment may serve, for example, to provide the surface with particular properties, such as nonstick action, antistatic action, hydrophilic or hydrophobic properties, etc. It is thus possible to provide the single and multilayer films, for example, with better detachment properties from the carrier material used in the production, better roll-off properties, better glide properties, reduced

tack, better compatibility with particular components ensheathed or coated therewith, etc. According to the nature and formulation of the additive, the application can be effected by standard methods, for example by spraying, dipping, powder application, etc. Suitable additives for coating of the surface of the multilayer films of the invention are, for example, talc, surfactants such as silicone-containing surfactants, waxes, etc.

As stated above, the film production process is not subject to any particular restrictions and the person skilled in the art is able to apply any desired production process of which he is aware on account of his art knowledge. The same applies to the production of multilayer films which are to be used as such for use as a washing composition or as a cleaning composition. The same applies to the production of sheaths and coatings based on a multilayer film of the invention. Particularly suitable methods are coating bar methods, casting methods, roll application methods and extrusion methods.

The multilayer films of the invention are generally thermoplastic and can be subjected to a forming operation by thermoforming (i.e. hot forming, deep drawing or vacuum deep drawing). A process for producing water-soluble film packagings by a thermoforming process which comprises a hot forming or deep drawing step is described in WO 00/55044.

For production of film portions, the multilayer film of the invention can be processed in a suitable manner, for example by cutting to a desired size and/or folding to form compartments. Subsequently, the edges can be sealed by standard sealing methods such as heat sealing, liquid sealing or pressure sealing.

As stated above, the multilayer film of the invention may preferably consist of 2 to 20 layers, more preferably 2 to 15 layers and especially 2 to 10 layers. These specifically include multilayer films consisting of 2, 3, 4, 5, 6, 7 or 8 layers. The sequence of the layers of the multilayer films of the invention is guided by the desired end use.

<u>Process for producing water-soluble containers</u>

The present invention relates to a process for producing a water-soluble container comprising the steps of

a) forming an open pouch from a first water-soluble film;
b) filling at least part of the pouch with a composition;
c) covering the filled pouch with a second water-soluble film
d) sealing the first water-soluble film of the filled pouch with the second water-soluble film,

wherein at least one of the first or second water-soluble films is a multi-layered film comprising at least two film layers L1 and/or L2 in any order as defined above or below or a washing- and cleaning-active polymer film as defined above or below, and

wherein before sealing step d) the second water-soluble film covering the filled pouch is contacted with water.

The present invention provides a process for producing a water-soluble container comprising a water-soluble multi-layered film enclosing a composition which includes at least one layer L1 which may comprise a detergent or cleaning agent, wherein the water-soluble film itself comprises a washing or cleaning active component adding to the washing or cleaning activity of the detergent or cleaning agent. It has been found that the multi-layered film comprising the at least one layer L1 shows specific properties different to water-soluble PVOH films usually used in the art for the production of water-soluble containers which require an adaptation of the production process of the water-soluble containers.

In another embodiment the washing or cleaning active component is provided in the aqueous composition comprising a polymer P1') and a polyoxyalkylene ether PE') of the washing- and cleaning-active polymer film.

In a first step a first water-soluble film is provided for forming an open pouch. Said first water soluble film can be any kind of film suitable for forming a water-soluble film, such as a mono-layered water-soluble film or a multi-layered water-soluble film.

The first water-soluble film can be based on polymers selected from polyvinyl alcohols, polyvinyl pyrrolidone, polyalkylene oxides, copolymers of acrylamide, copolymers of acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids and salts thereof, polyamino acids or peptides, polyamides, polyacrylamide, copolymers of maleic acids/acrylic acids, polysaccharides including starch and gelatin, natural gums such as xanthum and carragum.

It is, however, preferred that as first water-soluble film the multi-layered film as described above and below or the washing- and cleaning-active polymer film as described above or below is used. It is especially preferred that as first water-soluble film the multi-layered film as described above and below is used.

Preferably, the open pouch is formed by deep drawing the first water-soluble film into a cavity.

The deep drawing can be performed by means of vacuum-forming in which the first water-soluble film is placed over and into the cavity and then a vacuum is applied which pulls the first water-soluble film into the cavity. The vacuum-forming typically involves the step of applying a (partial) vacuum or reduced pressure on the cavity which sucks the first water-soluble film into the cavity and ensures that the first water-soluble film adopts the shape of the cavity. The pouch forming process may also be done by first heating the film and then applying reduced pressure, e.g. (partial vacuum).

The first water-soluble film is preferably deep drawn into the cavity at a reduced pressure of from -0.1 bar to -1 bar, more preferably of from -0.2 bar to -1.0 bar and most preferably of from -0.5 bar to -1.0 bar.

In another embodiment the deep drawing can be performed by means of thermo-forming, in which the first water-soluble film is placed over and into the cavity and then pressure is applied on the first water-soluble film which presses the first water-soluble film into the cavity. The thermoforming thereby involves the step of applying heat to the first water-soluble film which softens the film so that the film can be easily pressed into the cavity. The heat can either be applied before placing the film over and into the cavity or after the film is placed over and into the cavity. In practice, especially of a continuous process for producing the water-soluble container, the first water-soluble film usually heated before placing the film over and into the cavity by passing a means of heating such as e.g. a pre-heating roller.

The first water-soluble film is preferably formed into the cavity at a temperature of from 20°C to 160°C, more preferably of from 50°C to 150°C, still more preferably of from 70°C to 140°C and most preferably of from 80°C to 130°C.

The first water-soluble film is preferably deep drawn into the cavity at a pressure of from 60 kPa to 150 kPa, more preferably of from 70 kPa to 140 kPa and most preferably of from 80 kPa to 130 kPa.

Preferably, the first water-soluble film is deep drawn into the cavity with a dwell time of from 2.0 sec to 15 sec, more preferably of from 3.5 sec to 12.5 sec and most preferably of from 5.0 sec to 11 sec.

Preferably after forming the cavity a part of the first water-soluble film is protruding from the cavity which protruding part is suitable from contacting the second water-soluble film at a later stage of the process of the invention.

As soon as the open pouch is formed the open pouch is filled with a composition.
The composition can be solid, liquid, gel-like or any combination thereof.

The composition preferably is a cleaning or washing composition, more preferably a laundry or dishwashing composition, including fabric care compositions, pre-treatment or soaking compositions and rinse additive compositions.

The composition preferably comprises at least one active cleaning ingredient such as chelating agents, builders, bases, enzymes, perfumes, bleaches, bleach activators, bleach catalysts, fabric softeners, fabric conditioners, surfactants, polymeric dispersants, fabric care agents, soil release polymers, soil repellant polymers, dye transfer inhibitors, thickeners, rheology modifier, anti-corrosion agents, antibacterial agents, effervescence sources, brighteners, photo-bleaches or mixtures thereof. Laundry compositions and especially fabric care compositions preferably comprise at least one or more softening agents such as quaternary ammonium compounds and/or softening clays, and preferably additional agents such as anti-wrinkling aids, perfumes and chelating agents.

Cleaning or washing compositions are well known in the art.

Preferably, the filling level of the open pouch with the composition is from 10 to 95 vol%, more preferably of from 25 to 90 vol%, still more preferably of from 50 to 85 vol% and most preferably of from 65 to 80 vol%, based on the total volume of the open pouch.

After filling the open pouch with the composition, the filled pouch is covered with a second water-soluble film.

The second water-soluble film can be based on polymers selected from polyvinyl alcohols, polyvinyl pyrrolidone, polyalkylene oxides, acrylamide, acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids and salts thereof, polyamino acids or peptides, polyamides, polyacrylamide, copolymers of maleic acids/acrylic acids, polysaccharides including starch and gelatin, natural gums such as xanthum and carragum.

It is, however, preferred that as second water-soluble film the multi-layered film as described above and below or the washing- and cleaning-active polymer film as described above or below is used. It is especially preferred that as first water-soluble film the multi-layered film as described above and below is used.

In a preferred embodiment the first and second water soluble film both are selected from the multi-layered film as described above and below and/or the washing- and cleaning-active polymer film as described above or below. It is especially preferred that the first and second water soluble film both are selected from the multi-layered film as described above and below.

Preferably, the second water-soluble film is covering the filled pouch as such that the second water-soluble film is in contact with the protruding parts of the first water-soluble film.

After covering the filled pouch with the second water-soluble film the filled pouch is closed by sealing the first water-soluble film of the filled pouch with the second-water film.

Preferably, the first water-soluble film of the filled pouch is sealed with the second water-soluble film by means of heat sealing, infra-red sealing, radio-frequency sealing, ultrasonic sealing, laser sealing, solvent sealing, vibration sealing, electromagnetic sealing, hot gas sealing, hot plate sealing, insert bonding, fraction sealing or spin welding.
Especially preferred is heat sealing.

It is preferred that the first water-soluble film of the filled pouch is sealed with the second water-soluble film by means of heat sealing at a temperature of from 40°C to 160°C, more preferably of from 80°C to 150°c and most preferably of from 100°C to 140°C.

It is further preferred that the first water-soluble film of the filled pouch is sealed with the second water-soluble film by means of heat sealing at a pressure of from 250 kPa to 800 kPa, more preferably of from 300 kPa to 700 kPa and most preferably of from 400 kPa to 600 kPa.

Thereby, preferably the first water-soluble film of the filled pouch is sealed with the second water-soluble film by means of heat sealing with a dwell time of 0.4 to 2.5 sec, more preferably of from 0.6 sec to 2.0 sec and most preferably of from 0.8 sec to 1.8 sec.

Preferably, the sealing step is conducted by contacting the filled pouched covered with the second water-soluble film with a means for sealing which is heated to the sealing temperature as described above and which applies the pressure onto the second water-soluble film as described above. A suitable means for sealing is a sealing roller.

In the sealing step the first water-soluble film and the second soluble film are preferably sealed in the areas in which the second water-soluble film is in contact with the protruding parts of the first water-soluble film. As a consequence it is preferred that in the sealing step seal seams of the first and second water-soluble films are obtained.

It is preferred that the width of the seal seam of the first water-soluble film of the filled pouch and the second water-soluble film is within the range of from 2 to 8 mm, more preferably within the range of from 3 to 6 mm.

Thereby, it has been found that although the multi-layered film as described above and below usually has a higher thickness of up to 400 µm as described above, seal seams of a rather small thickness can be produced for the water-soluble containers of the present invention. It is believed that the small thicknesses of the seal seams result from the properties polymer composition P1 of layer L1 of the multi-layered film which has a high flowability especially at elevated temperatures. It is believed that at elevated temperatures the flowability of the polymer composition P1 of layer L1 is increased so that under sealing conditions at least part of the polymer of layer L1 is squeezed out of the seal seam, which reduces the thickness of layer L1 in the seal seam.

The thickness of the seal seam of the first water soluble film of the filled pouch and the second water-soluble film is preferably in the range of from 60 µm to 300 µm, more preferably in the range of from 70 µm to 250 µm, and most preferably in the range of from 80 µm to 200 µm.

It has been found that due to the properties of the multi-layered film, especially of the properties of layer L1 it is mandatory to contact the second water-soluble film covering the filled pouch with water before sealing step d).

Due to the differences in properties of the at least two layers L1 and L2 of the multi-layered film the multi-layered film tends to ripple under sealing conditions so that sealing and eventually the seal strength of the resulting water-soluble container is impaired. It has been found that by

contacting the second water-soluble film covering the filled pouch with very small amounts of water per area compared to typical PVOH films the rippling of the multi-layered film can be significantly reduced to allow effective sealing.

Thereby, it is preferred that the second water-soluble film covering the filled pouch is contacted with a liquid comprising water, an aerosol comprising water or a vapour comprising water.

Preferably, the second water-soluble film covering the filled pouch is contacted with a liquid comprising water and the liquid is applied by means of a means for wetting such as a wetting roller.
It has been found that for obtaining the effect of reduced rippling only a minor amount of water applied onto the second water-soluble film is sufficient. It is not necessary to trench the second water-soluble film in water.

Preferably, the water is applied onto the side of the second water-soluble film, which is in contact with the filled pouch after covering the filled pouch in process step c).

It is assumed, not being bound to theory, that the difference in mechanical properties of L1 and L2 requires a very small amount of water that is mostly absorbed by the outer layer, suitably layer L2, which is plasticized by water in order to reduce the difference in mechanical properties, whereas the second layer, suitably L1, is not affected by the water applied on the outer layer, suitably L1. This is a prerequisite to receive a symmetric shaped pod without wrinkling after vacuum is switched off and the pod is released from the deep drawing cylinder. Preventing wrinkling improves optical appearance of the pod and improves seal strength.

The second water-soluble film suitably is contacted with water before covering the filled pouch.

Preferably, the second water-soluble film is contacted with means for wetting and the time for contacting the second water-soluble film with the means for wetting is 0.4 to 2.5 sec, more preferably of from 0.6 sec to 2.0 sec and most preferably of from 0.8 sec to 1.8 sec.

The time from contacting the second water-soluble film with water to sealing the first water-soluble film of the filled pouch with the second water-soluble film is preferably in the range of from 1.5 sec to 10 sec, more preferably in the range of from 2.0 sec to 8 sec and most preferably in the range of from 2.5 sec to 6.0 sec.

The process according to the present invention is suitable for producing water-soluble containers with a single compartment. The water-soluble container with the single compartment is preferably released from the cavity after the sealing step and cut into shape by cutting along the seal seam.

The process according to the present invention is also suitable for producing water-soluble containers with two or more compartments.

If the multiple compartments are in the same plane, the process is carried out as described above or below using a cavity for forming the open pouch, which already includes two or more compartments.

In another embodiment for producing the two or more compartments process steps a) to c) as described above or below are repeated one for producing a water-soluble container with two compartments or more often for producing a water-soluble container with more than two compartments. Afterwards, the water-soluble container with two or more compartments is preferably released from the cavity after the sealing step and cut into shape by cutting along the seal seam.

Both embodiments also can be combined to produce a water-soluble container with three or more compartments such as e.g. two or more compartments are produced using a cavity for forming the open pouch, which already includes two or more compartments and then one or more compartments are added by repeating process steps a) to c).

With the process of the present invention a single water-soluble container can be produced.

However, for the sake of efficiency more than one water-soluble container are preferably produced with the process of the present invention simultaneously. This can be done by providing a template with a multitude of cavities into which the first water-soluble film is deep drawn to produce a multitude of pouches. The multitude of pouches are then filled with the composition and covered with the second water-soluble film.

Water-soluble container

The present invention relates to a water-soluble container obtainable by the process as described above or below.

In one embodiment the water-soluble container comprises one compartment which is filled with one composition. The composition suitably is solid, liquid, gel-like or any combination thereof.

In another embodiment, the water-soluble container comprises two or more compartments, which can be filled with only one composition but preferably are filled with different compositions. The composition or compositions suitably is solid, liquid, gel-like or any combination thereof. In the case that the two or more compartments are filled with different compositions it is preferred that one composition is filled in one compartment.

The composition preferably is a cleaning or washing composition as described above or below.

In principle the water-soluble container can have any kind of dimensions and shapes. Preferably the water-soluble container has a maximum dimension in each direction of not more than 13 cm.

The water-soluble container is suitable for any kind of cleaning or washing application.
It is preferred that the water-soluble container is a detergent pod or dishwashing pod.

The water-soluble container preferably has a seal strength of at least 30 kg, more preferably of at least 50 kg, still more preferably of at least 65 kg, and most preferably of at least 80 kg, determined according to the test method of ASTM F3159, A12.4. The upper limit of the seal strength is usually not higher than 250 kg.

Thereby, it has been found as can be seen from the example section below that the seal strength depends on the temperature of the thermoforming step and the amount of water applied on the second film before sealing. The higher the temperature of the thermoforming step and the higher the amount of water in the investigated range the higher is the seal strength.
The water-soluble containers according to the present invention show a sufficient seal strength which allows normal handling the water-soluble containers without the risk of rupturing the seal seams. The water-soluble containers of the present invention show improved cleaning and washing capacity compared to the cleaning or washing composition encased in the water-soluble container alone as the polymer composition P1 of layer L1 of the multi-layered adds to the washing and/or cleaning capacity of the water-soluble container.

Use

The present invention relates to the use of the process as described above or below for the production of a detergent pod or dishwashing pod.

Additionally, the present invention relates to the use of the water-soluble container as described above or below for dosing detergent into a laundry machine and/or a dishwashing machine.

Examples

Preparation of the multi-layered films:

Multi-layered film 1:

Preparation of application solution PVOH

20 g of solid polyvinyl alcohol Poval® 26-88, commercially available from Kuraray Europe GmbH, Hattersheim (Main), Germany, was stirred and solved in 80 g deionized water at 60°C. 2.0 g glycerol and 0.20 g of a $C_{13}C_{15}$-oxo alcohol with 7 EO were added to the polyvinyl alcohol solution. The solution was heated to 80°C. Afterwards deionized water was added to obtain a polyvinyl alcohol solution with a polyvinyl alcohol concentration of 18.0 wt%. The polyvinyl alcohol solution was well mixed and tempered at 80°C until the stirred-in air had completely escaped.

Preparation of application solution of a wash active polymer composition

Wash active polymer composition:

	Component	Amount [wt%]	Concentration [%]
Initial Charge	$C_{13}C_{15}$-oxo alcohol with 7 EO	24.00	100.00
	deionized water	18.00	100.00
Feed 1	acrylic acid	48.00	100.00
Feed 2	initiatora)	0.34	100.00
	deionized water	3.84	100.00
Feed 3	2-mercaptoethanol	0.96	100.00
	Na-hypophosphite	2.62	55.00
	deionized water	2.25	100.00

2,2'Azobis(2-methylproprionamidine)dihydrochloride (CAS-No 2997-92-4)

Oxo alcohol and water were initially charged and the initial charge was heated to 75 ° C with stirring at 100 rpm. The feeds 1, 2 and 3 were then added in 4 hours and the reaction mixture was polymerized for an additional hour. Then the mixture was allowed to cool to room temperature. The polymer composition was obtained in the form of a transparent and viscous solution.

100 g of the polymer composition was heated to 80°C. After adding 4.2 g of glycerol, the concentration of the polymer composition was diluted to 65% wt% with deionized water. The application solution was well mixed and tempered at 80°C until the stirred-in air had completely escaped.

Preparation of three-layer film: L2-L1-L2 (PVOH- wash active polymer composition-PVOH)

To produce the multi-layered film, an automatic film-applicator and a universal applicator from Zehntner were used. The PVOH application solution was applied to the surface of a galvanized steel sheet metal carrier previously degreased with ethanol. The gap width of the doctor blade was chosen so that the layer after drying at room temperature has a thickness of 30 µm. After drying the PVOH layer, the application solution of the wash active polymer composition heated to 80°C was applied. The gap width of the doctor blade was adjusted so that after drying at room temperature, the total layer thickness of the film is 110 µm. Subsequently, the PVOH application solution was applied again. The gap width of the doctor blade was adjusted so that after drying at room temperature, the total thickness of the film is 120 µm.

Multi-layered film 2:

The process for preparing the multi-layered film 1 was repeated in a continuous process with the gap width of the comma bar chosen such that the first PVOH layer has a total layer thickness of 22 µm, the two-layer structure with the first PVOH layer and the wash active polymer composition layer has a total layer thickness of 82 µm and the three-layer multi-layered film has a total layer thickness of 90 µm.

Example 1:

For the production of unit dose pods made from wash active multilayer films a machine of the type Hydroforma 660 (Cloud Packaging Solutions) was used at 23°C and 50% relative humidity controlled ambient conditions.

As water soluble and wash active multi-layered film comprising a wash active polymer composition multi-layered film 2 as described above was used.

After mounting both film rolls for top and bottom film for producing a single chamber pod design the film is threaded up at slow speed. Afterwards the machine is set to a production speed of 600 pods/min (equivalent to about 4.2m/min) with cavity dimensions of 65mm x 50mm x 15mm.

Before the bottom film undergoes deep drawing the film passes a pre-heating roller which was adjusted to 130°C. The hot film is guided to a rotating drum carrying the deep drawing cavities where vacuum is applied to deep draw the bottom film.

At 12 o'clock position of the rotating drum the liquid detergent is dosed into the deep drawn bottom film having the shape of an open pouch.

Subsequently the pouch is closed by sealing with a top film which is the same multi-layered film as used for the bottom film.

The top film was wetted with a wetting roller before contacting the top film with the pouch. The wetting roller loaded water from a water bath having a water level of 50% at a velocity setting of 4.5% (0.81 rounds per minute).

The temperature of the sealing roller which laminated bottom and top film together was 130°C. The cutting unit was also set to a temperature of 130°C.

Pods produced by these parameters had a seal seam width of 5mm and a seal strength measured according to the compression test method ASTM F3159, A12.4 of larger than 100kg.

Example 2:

The process of example 1 has been repeated with the differences that the pre-heating roller was adjusted to 100°C, the wetting roller was adjusted to a velocity setting of 0.5% (0.09 rounds per minute) and the water bath to a water level of 30%.

Pods produced by these parameters had a seal seam width of 5mm and a seal strength measured according to the compression test method ASTM F3159, A12.4 of 80kg.

Example 3:

The process of example 2 has been repeated with the difference that the pre-heating roller was adjusted to 90°C.

Pods produced by these parameters had a seal seam width of 5mm and a seal strength measured according to the compression test method ASTM F3159, A12.4 of 57kg.

Mono chamber pods have also been manufactured in a lab scale device to illustrate the importance of appropriate amount of water to be applied in the sealing step. All multilayer films have been conditioned at 23°C and 50% relative humidity for at least 3h prior to usage in the pod manufacturing step.

Example 4 (no water):

For the lab scale manufacturing of mono chamber pods a sheet of multilayer film 1 was placed and fixed on top of a mold (bottom film). In a second step a 1mm thin metal plate preheated to 140°C was placed on top of the bottom film facilitating the deep drawing into the mold which was realized by subsequent application of vacuum. After the bottom film has fully deep drawn liquid detergent taken from the large chamber of commercially available Ariel 3 in 1 pods (purchased 07.01.2019) was filled into the mold onto the bottom film. The top film was placed on top in order to enclose the liquid detergent and sealed with the corresponding stamp (preheated to 170°C) of the mono-chamber design with a pneumatic press (Schmidt Technology GmbH, Type 33/40) at 4bar. The finished pod was stored at 23°C and 50% relative humidity for at least 24h prior to compression testing.

Example 5 (low water):

For the lab scale manufacturing of mono chamber pods a sheet of multilayer film 1 was placed and fixed on top of a mold (bottom film). In a second step a 1mm thin metal plate preheated to 140°C was placed on top of the bottom film facilitating the deep drawing into the mold which was realized by subsequent application of vacuum. After the bottom film has fully deep drawn liquid detergent taken from the large chamber of commercially available Ariel 3 in 1 pods (purchased 07.01.2019) was filled into the mold onto the bottom film. For sealing the sealing area of the bottom film was wetted with a cotton swab. The cotton swab was dipped once in deionized water and squeezed before application of water. The top film was placed on top in order to enclose the liquid detergent and sealed with the corresponding stamp (preheated to 170°C) of the mono-chamber design with a pneumatic press (Schmidt Technology GmbH, Type 33/40) at 4bar. The finished pod was stored at 23°C and 50% relative humidity for at least 24h prior to compression testing.

Example 6 (high water):

For the lab scale manufacturing of mono chamber pods a sheet of multilayer film 1 was placed and fixed on top of a mold (bottom film). In a second step a 1mm thin metal plate preheated to 140°C was placed on top of the bottom film facilitating the deep drawing into the mold which is realized by subsequent application of vacuum. After the bottom film has fully deep drawn liquid detergent taken from the large chamber of commercially available Ariel 3 in 1 pods (purchased 07.01.2019) was filled into the mold onto the bottom film. For sealing the sealing area of the bottom film was wetted with a cotton swab. The cotton swab was dipped in deionized water and water was applied without squeezing the cotton swab. For each of the 4 pod edges the cotton swab was dipped in water again. The top film was placed on top in order to enclose the liquid detergent and sealed with the corresponding stamp (preheated to 170°C) of the mono-chamber design with a pneumatic press (Schmidt Technology GmbH, Type 33/40) at 4bar. The finished pod was stored at 23°C and 50% relative humidity for at least 24h prior to compression testing.

Pods produced in examples 4-6 had a seal seam width of 5mm and a seal strength measured according to the compression test method ASTM F3159, A12.4 as shown in the below table.

Compression test results for different amounts of water applied for sealing.

Type of sealing	Failure at
No water (example 4)	1.96 kg
Low amount of water (example 5)	66.3 kg
High amount of water (example 6)	26.5 kg

Claims

1. A process for producing a water-soluble container comprising the steps of
   a) forming an open pouch from a first water-soluble film;
   b) filling at least part of the pouch with a composition;
   c) covering the filled pouch with a second water-soluble film
   d) sealing the first water-soluble film of the filled pouch with the second water-soluble film,
   wherein
   at least one of the first or second water-soluble films is a multi-layered film comprising at least two film layers L1 and/or L2 in any order,
   wherein at least one film layer L1 comprises a polymer composition P1 obtainable by radical polymerization of a monomer composition M1 in the presence of at least one polyether component PE,
   whereby M1 comprises at least one monomer A,
   whereby A is selected from α,β-ethylenically unsaturated mono- or dicarbon acids, salts of α,β-ethylenically unsaturated mono- or dicarbon acids or mixtures thereof,
   and
   whereby PE is selected from polyether alcohols with a number average molecular weight Mn of at least 200 g/mol, mono and di-(C_1 to C_6-alkyl)ethers of such polyether alcohols, polyether groups-containing tensides or mixtures thereof,
   and
   at least one film layer L2 comprises at least one polymer P2 which is different from polymer composition P1 and is selected from
   - natural or modified polysaccharides;
   - homo- or copolymers comprising monomer units derivable from vinyl alcohol, vinylesters, alkoxylated vinyl alcohols, or mixtures thereof;
   - homo-or copolymers comprising at least one monomer selected from N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, 2-vinylpyridine, 4-vinyl-pyridine, salts of N-vinylimidazole, salts of 2-vinylpyridine, salts of 4-vinyl-pyridine, vinylpyridine-N-oxide, N-carboxymethyl-4-vinylpyridine halogenides or mixtures thereof;
   - homo- or copolymers of acrylic acid and /or methacrylic acid, preferably copolymers comprising at least one acrylic acid monomer selected from acrylic acid, salts of acrylic acid or mixtures thereof and at least one maleic acid monomer selected from maleic acid, maleic acid anhydride, salts of maleic acid or mixtures thereof;
   - copolymer comprising at least a (meth)acrylic acid monomer selected from acrylic acid, methacrylic acid, salts of acrylic acid, salts of methacrylic acid or mixtures thereof and at least one hydrophobic monomer selected from C_1-C_8 alkylesters of (meth) acrylic acid, C_2-C_{10} olefins, styrene or α-methyl-styrene;
   - homo- or copolymers of acrylamide and or methacrylamide;
   - polyaminoacids;
   - water-soluble or water-dispersible polyamides;
   - polyalkyleneglycols, mono-or diethers of polyalkyleneglycols;

- polyalkyleneoxide such as polyethyleneoxide; and
- mixtures thereof;

or at least one of the first or second water-soluble films is a washing- and cleaning-active polymer film, comprising or consisting of at least one layer obtainable by

i) providing an aqueous composition by mixing
   - a polymer P1') that comprises polymerized units of at least one monomer A), selected from α,β-ethylenically unsaturated carboxylic acids, salts of α,β-ethylenically unsaturated carboxylic acids and mixtures thereof,
   - a polyoxyalkylene ether PE') having at least one C_8-C_{18}-alkyl group that is unsubstituted or substituted by at least one hydroxyl group, and an average of 3 to 25 alkylene oxide units per molecule, and
   - water,

   wherein at the most 30 mol% of the carboxy groups of the polymer P1') are in the deprotonated form,
   the weight ratio of the polymer P1') to the polyoxyalkylene ether PE') is in a range from 0.9 : 1 to 5 : 1, and
   the aqueous composition has a water content of at least 10% by weight and at most 50% by weight, based on the total weight of the aqueous composition,
ii) converting the aqueous composition to a polymer film;

and wherein before sealing step d) the second water-soluble film covering the filled pouch is contacted with water.

2. The process according to claim 1, wherein the first and second water-soluble film is a multi-layered film comprising at least two film layers L1 and L2 in any order.

3. The process according to any one of the preceding claims, wherein the multi-layered film comprises at least three layers with the sequence of L2-L1-L2.

4. The process according to any one of the preceding claims, wherein the second water water-soluble film covering the filled pouch is contacted with means for wetting and the time for contacting the second water-soluble film covering the filled pouch with the means for wetting is 0.4 to 2.5 sec.

5. The process according to any one of the preceding claims, wherein the open pouch is formed in process step a) by deep drawing the first water soluble film into a cavity.

6. The process according to claim 5, wherein the first water soluble film is deep drawn into the cavity at a temperature of from 20 to 160°C, preferred 70 to 150°C and most preferred 80 to 130°C.

7. The process according to any one of the preceding claims, wherein the composition is solid, liquid, gel-like or any combination thereof.

8. The process according to any one of the preceding claims, wherein the composition comprises at least one active cleaning ingredient such as chelating agents, builders, bases, enzymes, perfumes, bleaches, bleach activators, bleach catalysts, fabric softeners, fabric conditioners, surfactants, polymeric dispersants, fabric care agents, soil release polymers, soil repellant polymers, dye transfer inhibitors, thickeners, rheology modifier, anti-corrosion agents, antibacterial agents, effervescence sources, brighteners, photo-bleaches or mixtures thereof.

9. The process according to any one of the preceding claims, wherein the filling level of the pouch with the composition is 10 to 95 vol% of the total volume of the pouch.

10. The process according to any one of the preceding claims, wherein the first water-soluble film of the filled pouch is sealed with the second water-soluble film by means of heat sealing at a temperature of 40-160°C.

11. The process according to any one of the preceding claims, wherein the process steps a) to c) are repeated at least once to form a water-soluble container with two or more compartments and/or where the cavity for forming the open pouch in process step a) itself comprises two or more compartments.

12. A water-soluble container obtainable by the process according to any one of the preceding claims.

13. The water-soluble container according to claim 12 having one compartment or two or more compartments.

14. Use of the process according to any one of claims 1 to 11 for the production of a detergent pod or dishwashing pod.

15. Use of the water-soluble container according to claims 12 or 12 for dosing detergent into a laundry machine or a dishwashing machine.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/065298

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D17/04 B65D65/46 C08F20/06 C08F2/30
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D B65D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2017/158002 A1 (BASF SE [DE]) 21 September 2017 (2017-09-21) page 1, line 37 - line 39 claims; examples -----	1-15
Y	WO 2006/124484 A1 (PROCTER & GAMBLE [US]; CATALFAMO VINCENZO [US]; DENOME FRANK WILLIAM [) 23 November 2006 (2006-11-23) page 2, line 30 - line 31 page 12, line 18 - page 13, line 26 example 2 -----	1-15
Y	EP 0 513 692 A1 (AIR PROD & CHEM [US]) 19 November 1992 (1992-11-19) the bridging paragraph; page 2 - page 3 page 1, line 51 - line 55 examples -----	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 September 2019	26/09/2019

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2019/065298

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