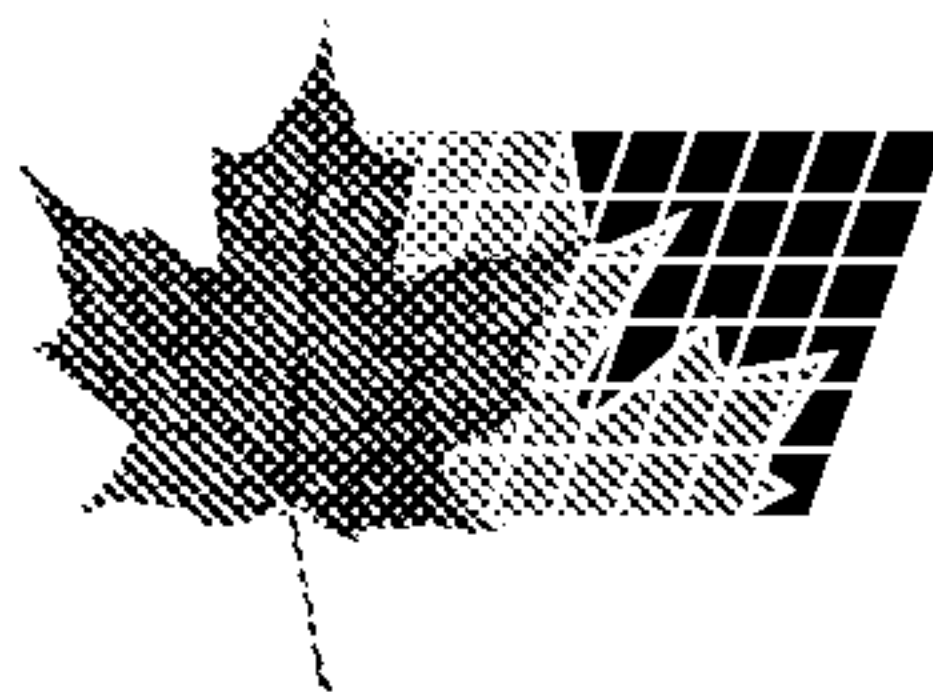




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(54) **CAPSULE PERMETTANT L'ÉCOULEMENT CONTRÔLÉ DE
SUBSTANCES ACTIVES**

(54) **CAPSULE FOR CONTROLLED RELEASE OF ACTIVE
SUBSTANCES**

(57) Capsules with a controlled release system which releases an active substance at a desired point in time and may be used in machine washing and cleaning processes and releases the active substance at a predetermined point in time of the washing process have an aperture in the capsule wall for emergence of the components contained therein and comprise (A) a substance apt to destroy the capsule wall by reaction with the capsule material and/or with a further substance, (B) a gas which under storage conditions does not react with the contents of the capsule, and (C) active substance.

Abstract

Capsules with a controlled release system which
5 releases an active substance at a desired point in time
and may be used in machine washing and cleaning
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predetermined point in time of the washing process have
an aperture in the capsule wall for emergence of the
10 components contained therein and comprise (A) a
substance apt to destroy the capsule wall by reaction
with the capsule material and/or with a further
substance, (B) a gas which under storage conditions
does not react with the contents of the capsule, and
15 (C) active substance.

CAPSULE FOR CONTROLLED RELEASE OF ACTIVE SUBSTANCES**Field of the Invention**

The present invention relates to a capsule for the controlled release of active substances and in particular to the use of this capsule in laundry detergent, cleaning product, and surfactant compositions and in pharmaceutical and cosmetic preparations.

Background of the Invention

Capsules for the controlled release of active substances are known from a multiplicity of applications. Within the pharmaceutical segment there are systems featuring what is known as delayed release, i.e., the active substances are released after a predetermined space of time following oral intake. In the case of what is known as controlled release, metering of the release of the active substances takes place within a predetermined organ. One generally customary system is the release of the active substances in the gut, with the capsules comprising a material which is resistant to gastric fluid but soluble in the gut. The capsules dissolve in the gut and the active substance is released there.

A further field of use of encapsulated active substances is that of laundry detergents and cleaning products. Finished compositions frequently include sensitive substances which may be destroyed by other components under storage conditions. These substances may be incorporated in encapsulated form into the compositions. The encapsulated materials are generally enveloped by a water-soluble shell which is dissolved by the washing water, with release ensuing.

In the known capsules, the dissolution process begins immediately, so that the rate of release of the active substances is dependent on the dissolution rate of the capsule material.

- 2 -

If the components are to be added only in one particular part of the washing process, i.e., in a specific wash cycle, then these components are usually metered by way of corresponding devices arranged in the washing machines. Domestic washing machines, for example, include reserve compartments for the prewash, the main wash, and the rinse cycle. A dishwasher machine includes reserve compartments for the detergent, and another for the rinse aid.

The field of laundry detergents and cleaning products is virtually devoid of capsules which, as in the pharmaceutical segment, are able to utilize the different pH environments within the body. Generally, the pH levels within the individual wash cycles are very similar. These cycles also show similar fluctuations in temperature in the heating and cooling phases. The prior art discloses no system which permits controlled release of the active substance in a subsequent wash or rinse cycle.

Summary of the Invention

It is an object of the present invention to provide a capsule having a controlled release system that releases an active substance at a desired point in time, i.e., at a predetermined site, following its supply. A particular object of the invention is to provide a capsule which may be used in machine washing and cleaning processes and which releases the active substance at a predetermined point in time in the washing process.

The invention accordingly provides a capsule for the controlled release of active substance, comprising

(A) a substance apt to destroy the capsule wall by means of chemical reaction with the capsule material and/or with a further substance,

- 3 -

(B) a gas which under storage conditions does not react with the other components present in the capsule, and

(C) active substance,

5 the capsule shell having an aperture for the emergence of one of the constituents present therein.

The capsule of the invention is suitable for a multiplicity of applications within the pharmaceutical
10 and cosmetic segment and also for use in machine laundry detergents and cleaning products, especially in compositions for textile laundry and for the machine cleaning of kitchen- and tableware.

15 **Detailed Description of the Invention**

The term "capsule" in the context of the present invention is not restricted to receptacles having the form of the capsules known from pharmacy. Rather, in the context of the present invention, the term
20 "capsule" denotes receptacles whose walls are sufficiently stable to withstand the volume expansion and subsequent contraction to the extent that the external medium is able to pass into the receptacle's interior. In addition to the cylindrical capsules with
25 hemispherical ends that are known from pharmacy, other geometries are of course also realizable in accordance with the invention, in particular, for example, tubular bags made of hard films, spherical, cube-shaped or tetrahedral packaging forms, etc.

30

By means of appropriate combination of the materials of capsule wall and ingredients it is possible to produce tailored capsules of the invention. The active substance and the capsule material may also be chosen,
35 for example, such that the active substance destroys the material of the capsule. In this specific case, substance A and substance C would be identical.

- 4 -

For the release of the active substance from the capsule it is not necessary for the entire capsule wall to be destroyed. Rather, for emergence of the contents from the capsule, it is sufficient for the substance A
5 to destroy parts of the capsule wall, thereby permitting the substance C (which may be identical with A) to emerge from the capsule.

The aperture that is present, in accordance with the
10 invention, in the capsule shell and which effects the release mechanism described hereinbelow may initially be closed. All that is necessary then is for the part closing the aperture to dissolve under the ambient conditions of the application, or for the aperture to
15 open up in another way, so that the activity may begin.

The release mechanism of the capsule of the invention is essentially temperature-dependent and makes use of the volume expansion of gases under increasing
20 temperature. The capsule of the invention is particularly suitable for use in an aqueous medium which in the course of the application is heated and then cooled again. If the capsule of the invention is added at room temperature to an aqueous environment
25 which is subsequently heated, the gas volume within the capsule expands and a small amount of the components A, B and/or C present therein emerges via the aperture in the capsule wall. If the system cools back down after the heating process is at an end, and/or if cold water
30 is supplied to the external environment of the capsule, then there is a volume contraction of the gas. Simultaneously with the volume contraction, substance from outside, in the aqueous medium water, is taken in via the aperture in the capsule wall. The incoming
35 water dissolves the component A, or reacts with it, as a result of which a medium develops within the capsule that leads to the destruction or dissolution of the capsule wall. Simultaneously with, or following, the

- 5 -

destruction of the capsule wall, the active substance C is released.

The shape of the capsule is arbitrary; however, it has proven advantageous if the capsule is of slightly elongated design. In an elongated shape, the solid ingredients accumulate in the bottom part and, when the capsule is used in an aqueous medium, are located below the water level. In an embodiment of this kind, the aperture in the capsule wall should also be below the water level.

The wall of the capsule of the invention should be such that it is initially inert and insoluble with respect to the external medium into which the capsule is introduced at the time of application (for example, water), and with respect to the components A, B and C present within the capsule, but at high and/or low pH values is soluble and may be destroyed, at least partially, by mechanical forces such as stirring, pressure, or abrasion. Examples of suitable materials are polymers which are soluble or dispersible in the alkaline or acidic range. Examples of suitable polymers are modified polysaccharides such as carrageenan, guar, pectin, xanthan, partially hydrolyzed cellulose, cellulose acetate, hydroxyethyl-, hydroxypropyl- and hydroxybutylcellulose, methylcellulose, and the like. Mention may further be made of proteins and modified proteins, such as gelatin. Further suitable polymers include acrylates and acrylate polymers. These materials are described later on below.

In order to meet the abovementioned requirements imposed on the capsule wall, it may be necessary to use combinations of different wall materials or else to employ a multilayer construction of the wall from different wall materials.

- 6 -

The capsule wall has an aperture for the emergence of constituents present in the capsule. This aperture should be of a size such that, at the time of volume expansion, at least one of the constituents present in the capsule is able to emerge, so as to avoid the capsule bursting as a result of the overpressure which forms. The size of this aperture is preferably less than 1 mm, in particular less than 0.5 mm. The component A is selected such that entry of external medium into the capsule is followed by dissolution or destruction of the capsule wall - for example, by the formation of an aqueous solution which has a pH which is aggressive for the capsule wall, or by the reaction of the component A with water to form a gas as a result of which, within the capsule, an overpressure is developed which leads ultimately to the destruction of the capsule and the release of the active substance.

In one preferred embodiment of the present invention, the component A is a solid acid and one material of the capsule wall is an acid-soluble polymer. Solid or crystalline acids used are preferably those which do not give off any water of crystallization at the process temperatures, examples being sulfamic acid, citric acid, and Na,KHSO₄. As acidifying agents it is also possible, for example, to use boric acid and also further alkali metal hydrogen sulfates, alkali metal dihydrogen phosphates, and other inorganic salts. Preference, however, is given to the use of organic acidifying agents, with citric acid being a particularly preferred acidifying agent. The other solid mono-, oligo- and polycarboxylic acids, however, in particular may also be used. Preferred in turn from this group are tartaric acid, succinic acid, malonic acid, adipic acid, maleic acid, fumaric acid, oxalic acid, and polyacrylic acid. Organic sulfonic acids such as sulfamic acid may likewise be used. A commercially available acidifying agent which may likewise be used

- 7 -

with preference in the context of the present invention is Sokalan[®] DCS (trademark of BASF), a mixture of succinic acid (max. 31% by weight), glutaric acid (max. 50% by weight), and adipic acid (max. 33% by weight).

In another embodiment, the component A is a substance which gives an alkaline reaction with water, and the material of the capsule wall is a polymer which is soluble in the alkaline range. Examples of solid substances which give alkaline reactions in aqueous solution are hydroxides, carbonates, hydrogen carbonates, and/or silicates, preference being given to alkali metal hydroxides, alkali metal carbonates, alkali metal hydrogen carbonates, alkali metal sesquicarbonates, alkali metal silicates, alkali metal metasilicates, and mixtures of the abovementioned substances. For the purposes of this invention, preference is given among the alkali metal salts to the potassium and in particular the sodium salts, especially sodium carbonate, sodium hydrogen carbonate, and sodium sesquicarbonate.

In a further embodiment of the present invention, the release takes place, as already mentioned above, by the formation of gas in the interior of the capsule and subsequent destruction as a result of the overpressure. In this embodiment, the component A is a substance or a mixture of substances which reacts with the incoming water to form gas. Examples of possible substances are a combination of carbonates, such as alkali metal carbonates and alkali metal hydrogen carbonates, and a solid acid, e.g., citric acid, succinic acid, or one or more of the abovementioned acidifying agents, or cobalt ammine complexes in combination with resorcinol, an example which may be mentioned of an appropriate cobalt ammine complex being $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

- 8 -

A third possible release mechanism for the active substance C is the use of swelling agents as component A. As suitable swelling agents, mention may be made of cellulose and cellulose derivatives, which
5 when water penetrates the capsule swell and lead to destruction and thus to the release of the active substance. Swelling agents, which because of their action are also referred to, inter alia, as disintegrants, increase in volume on ingress of water,
10 with firstly an increase in their own volume (swelling) and secondly the possibility, by way of the release of gases, for the generation of a pressure which bursts the capsule and causes it to break down into relatively small particles. Examples of well-known swelling agents
15 are synthetic polymers such as polyvinylpyrrolidone (PVP) or natural polymers and/or modified natural substances such as cellulose and starch and their derivatives, alginates, or casein derivatives.

20 Preferred swelling agents used in the context of the present invention are those based on cellulose. Pure cellulose has the formal empirical composition $(C_6H_{10}O_5)_n$ and, considered formally, is a β -1,4-polyacetal of cellobiose, which itself is constructed of two
25 molecules of glucose. Suitable celluloses consist of from about 500 to 5000 glucose units and, accordingly, have average molecular masses of from 50,000 to 500,000. Cellulose-based swelling agents which may be used also include, in the context of the present
30 invention, cellulose derivatives obtainable by polymer-analogous reactions from cellulose. Such chemically modified celluloses include, for example, products of esterifications and etherifications in which hydroxy hydrogen atoms have been substituted. However,
35 celluloses in which the hydroxy groups have been replaced by functional groups not attached by an oxygen atom may also be used as cellulose derivatives. The group of cellulose derivatives embraces, for example,

- 9 -

alkali metal celluloses, carboxymethylcellulose (CMC), cellulose esters and cellulose ethers, and amino-celluloses. Said cellulose derivatives are preferably not used alone as cellulose-based disintegrants but
5 instead are used in a mixture with cellulose. The cellulose derivative content of these mixtures is preferably less than 50% by weight, with particular preference less than 20% by weight, based on the cellulose-based swelling agent. The particularly
10 preferred cellulose-based swelling agent used is pure cellulose, free from cellulose derivatives.

The cellulose used as the swelling agent is preferably not incorporated into the capsule in finely divided
15 form but instead is converted before its introduction into a coarser form, by granulation or compaction, for example. The particle sizes of such disintegrants are usually above 200 μm , preferably between 300 and 1600 μm to the extent of at least 90% by weight, and in
20 particular between 400 and 1200 μm to the extent of at least 90% by weight.

As a further cellulose-based swelling agent, or as a constituent of this component, it is possible to use
25 microcrystalline cellulose. This microcrystalline cellulose is obtained by partial hydrolysis of celluloses under conditions which attack only the amorphous regions (approximately 30% of the total cellulose mass) of the celluloses and break them up
30 completely but leave the crystalline regions (approximately 70%) intact. Subsequent deaggregation of the microfibrillar celluloses resulting from the hydrolysis yields the microcrystalline celluloses, which have primary particle sizes of approximately 5 μm and may be
35 compacted, for example, to granules having an average particle size of 200 μm .

- 10 -

One further possible release mechanism for the active substance C is the use of enzymes as component A. These enzymes may, for example, be coated in which case the coating dissolves after slight ingress of water into the capsule interior, after which the enzymes break down the capsule material and thus release the active substance C. Suitable enzymes for use, in dependence on the capsule material, are all common enzymes such as proteases, amylases, cellulases, etc., which may additionally possess a function in the wash or cleaning cycle. These enzymes are described at length later on below.

As active substance C it is possible to use any substances for which controlled release is desired. In the field of drugs, any desired active substances are suitable.

In the laundry detergents and cleaning products, the kind of substances incorporated in capsule form are in particular those which under normal conditions are not stable and/or are intended for use in a later stage of the washing process. Examples of active substances incorporated in the form of capsules into laundry detergents and cleaning products are rinse-aid surfactants, textile treatment compositions (fabric softeners), enzymes, bleaches, bleaching catalysts, bleach activators, optical brighteners, dyes, fragrances, corrosion inhibitors, etc.

30

The abovementioned rinse-aid surfactants, which are used in particular in the machine washing of kitchen- and tableware, and the textile treatment compositions, such as fabric softener components, which find application in the laundering of textiles, are components which in machine washing and cleaning processes are not added until a process stage which follows the actual washing operation. Suitable rinse-aid surfactants are

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- 11 -

all nonionic surfactants, but especially fatty alcohol polyethylene glycol ethers, fatty alcohol polyethylene/polypropylene glycol ethers, mixed ethers and/or hydroxyalkyl polyethylene glycol ethers.

5

Examples of fatty alcohol polyethylene glycol ethers are those with the formula (I)



10

where R^1 is a linear or branched alkyl and/or alkenyl radical having 6 to 22, preferably 12 to 18, carbon atoms and $n1$ is numbers from 1 to 5.

15 Said substances are known commercial products. Typical examples are adducts of on average 2 or 4 mol of ethylene oxide onto technical-grade $C_{12/14}$ coconut fatty alcohol (Dehydol[®] LS-2 and LS-4, respectively, from Henkel KGaA) or adducts of on average 4 mol of ethylene
20 oxide onto $C_{14/15}$ oxo alcohols (Dobanol[®] 45-4, from Shell). The products may have a conventional or else a narrowed homolog distribution.

Fatty alcohol polyethylene/polypropylene glycol ethers
25 are nonionic surfactants of the formula (II)



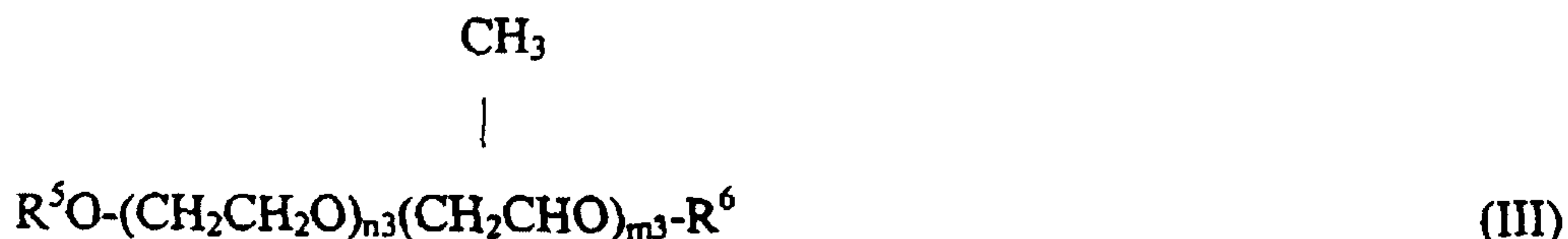
where R^4 is a linear or branched alkyl and/or alkenyl radical having 6 to 22, preferably 12 to 18, carbon atoms, $n2$ is numbers from 1 to 5 and $m2$ is numbers from
30 1 to 4.

These substances are also known commercial products. A typical example is an adduct of on average 5 mol of

- 12 -

ethylene oxide and 4 mol of propylene oxide onto technical-grade C_{12/14} coconut fatty alcohol (Dehydol[®] LS-54, from Henkel KGaA).

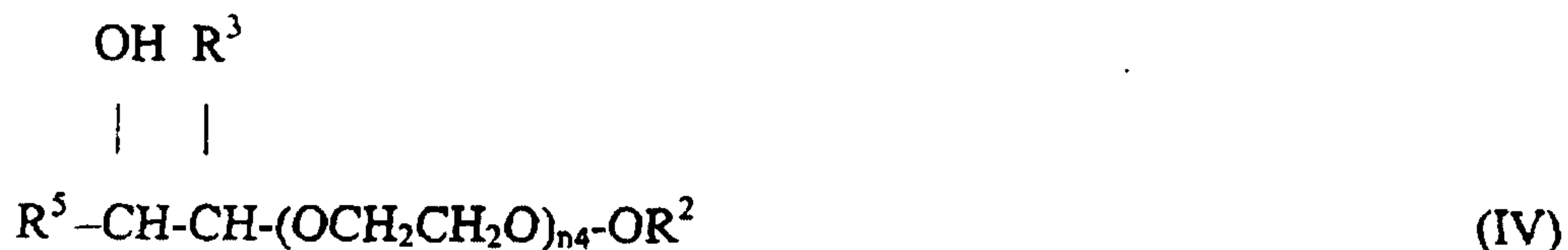
- 5 Mixed ethers are endgroup-capped fatty alcohol polyglycol ethers with the formula (III)



where R⁵ is a linear or branched alkyl and/or alkenyl radical having 6 to 22, preferably 12 to 18 carbon
10 atoms, n₃ is numbers from 1 to 10, m₃ is 0 or numbers from 1 to 4, and R⁶ is an alkyl radical having 1 to 4 carbon atoms, or a benzyl radical.

Typical examples are mixed ethers of the formula (III)
15 in which R⁵ is a technical-grade C_{12/14} cocoalkyl radical, n₃ is 5 or 10, m₃ is 0, and R⁶ is a butyl group (Dehypon[®] LS-54 and LS-104, respectively, from Henkel KGaA). The use of butyl- and/or benzyl-capped mixed ethers is particularly preferable on performance
20 grounds.

Hydroxyalkyl polyethylene glycol ethers are compounds with the general formula (IV)



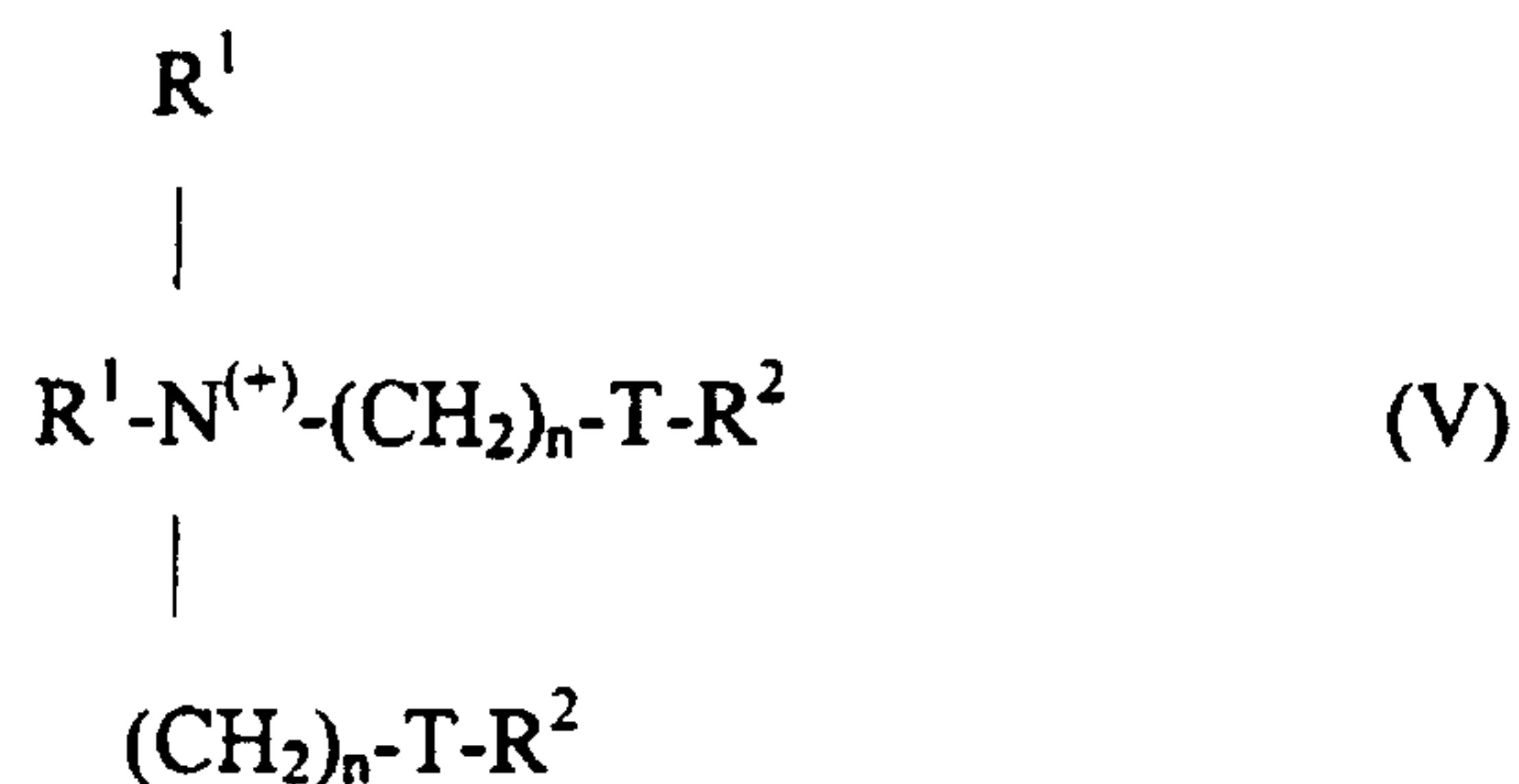
25 where R⁵ is hydrogen or a straight-chain alkyl radical having 1 to 16 carbon atoms,
R³ is a straight-chain or branched alkyl radical having 4 to 8 carbon atoms,
R² is hydrogen or an alkyl radical having 1
30 to 16 carbon atoms, and
n₄ is a number from 7 to 30,

- 13 -

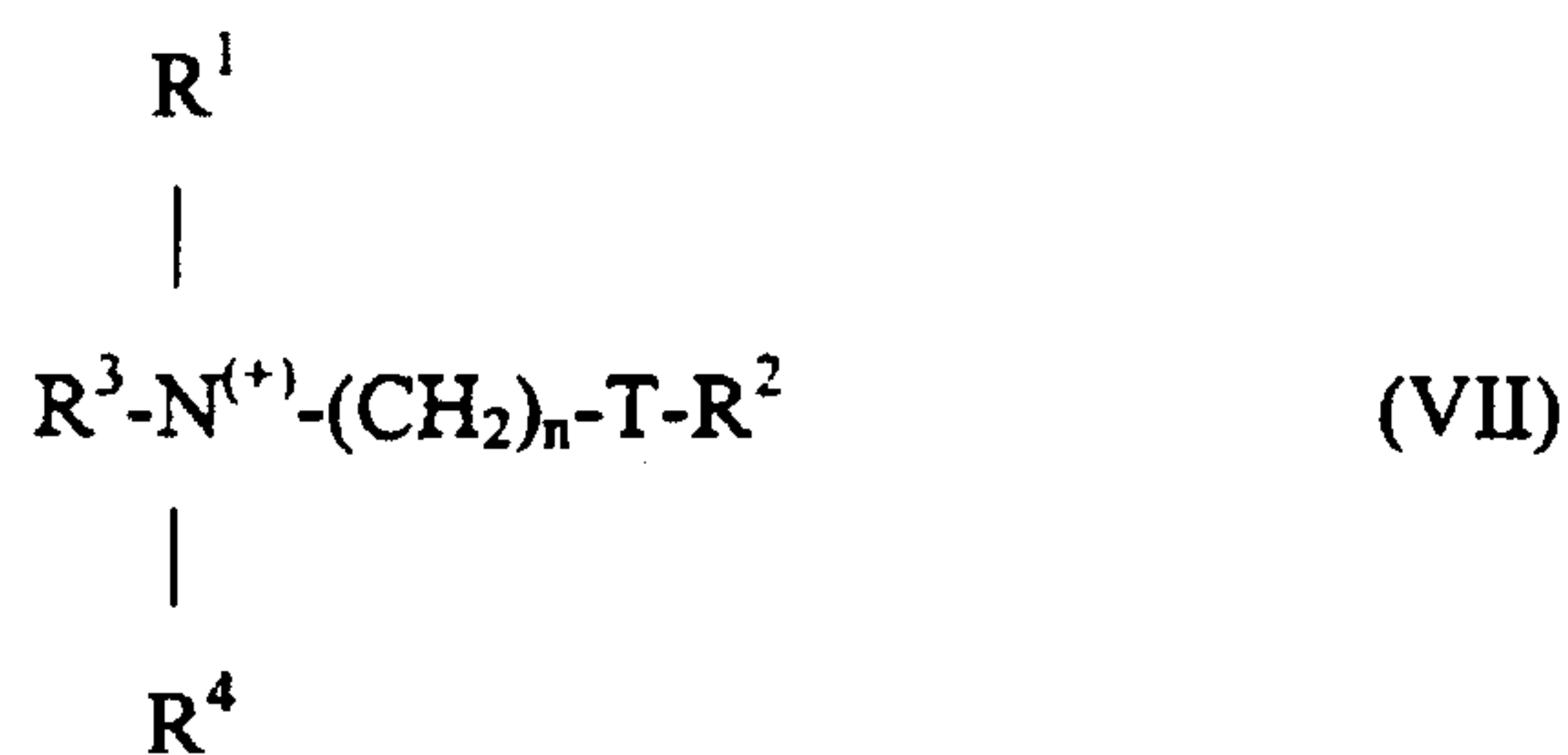
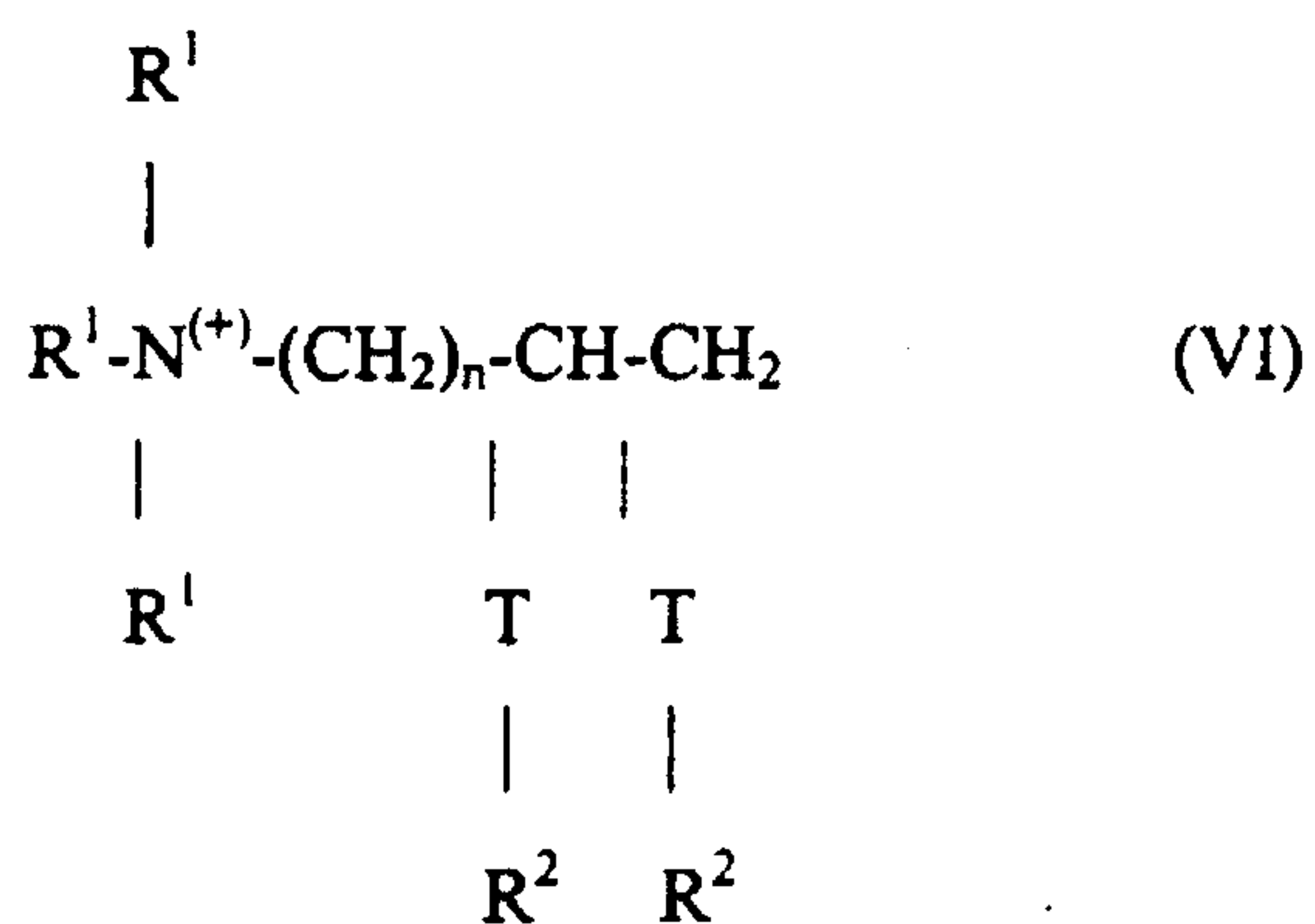
with the proviso that the total number of carbon atoms in R^5 and R^2 is from 6 to 16.

5 Examples of textile treatment compositions are, in particular, cationic surfactants. Suitable cationic surfactants are all customary surface-active substances, distinct preference being given to cationic surfactants having a textile-softening action.

10 Such cationic active substances with a textile-softening action are selected with particular preference from those which may be described by one or more of the formulae V, VI or VII:



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- 14 -

in which each group R^1 independently of the others is selected from C_{1-6} alkyl, alkenyl or hydroxyalkyl groups; each group R^2 independently of the others is selected from C_{8-28} alkyl or alkenyl groups; $R^3 = R^1$ or
5 $(CH_2)_n-T-R^2$; $R^4 = R^1$ or R^2 or $(CH_2)_n-T-R^2$; $T = -CH_2-$,
-O-CO- or -CO-O-, and n is an integer from 0 to 5.

Enzymes may be incorporated in the form of liquid or solid enzyme preparations into the capsules. Suitable
10 enzymes in this context include in particular those from the classes of the hydrolases such as the proteases, esterases, lipases or lipolytic enzymes, amylases, cellulases, and other glycosyl hydrolases, and mixtures of said enzymes. All of these hydrolases
15 contribute in the wash to removing stains such as proteinaceous, fatty or starchy stains, and instances of graying. Cellulases and other glycosyl hydrolases may, furthermore, by removing pilling and microfibrils, contribute to color retention and to increasing the
20 softness of the textile. For bleaching, and/or for inhibiting color transfer, it is also possible to use oxidoreductases. Especially suitable enzymatic active substances are those obtained from bacterial strains or fungi such as *Bacillus subtilis*, *Bacillus licheni-*
25 *formis*, *Streptomyces griseus*, *Coprinus cinereus*, and *Humicola insolens*, and also from genetically modified variants thereof. Preference is given to the use of proteases of the subtilisin type, and especially to proteases obtained from *Bacillus lentus*. Of particular
30 interest in this context are enzyme mixtures, examples being those of protease and amylase or protease and lipase or lipolytic enzymes, or of protease and cellulase or of cellulase and lipase or lipolytic enzymes, or of protease, amylase and lipase or
35 lipolytic enzymes, or of protease, lipase or lipolytic enzymes and cellulase, but especially protease and/or lipase-containing mixtures or mixtures with lipolytic enzymes. Examples of such lipolytic enzymes are the

- 15 -

known cutinases. Peroxidases or oxidases have also proven suitable in some cases. The suitable amylases include, in particular, alpha-amylases, iso-amylases, pullulanases, and pectinases. Cellulases used are preferably cellobiohydrolases, endoglucanases and -glucosidases, which are also called cellobiases, and mixtures of these. Since different types of cellulase differ in their CMCase and Avicelase activities, the desired activities may be established by means of specific mixtures of the cellulases.

In capsules intended for use in detergents for machine dishwashing, of course, different enzymes are used in order to take account of the different substrates treated and different types of soiling. Suitable enzymes in this context include in particular those from the classes of the hydrolases such as the proteases, esterases, lipases or lipolytic enzymes, amylases, glycosyl hydrolases, and mixtures of said enzymes. All of these hydrolases contribute to removing stains such as proteinaceous, fatty or starchy stains. For bleaching, it is also possible to use oxidoreductases. Especially suitable enzymatic active substances are those obtained from bacterial strains or fungi such as *Bacillus subtilis*, *Bacillus licheniformis*, *Streptomyces griseus*, *Coprinus cinereus*, and *Humicola insolens*, and also from genetically modified variants thereof. Preference is given to the use of proteases of the subtilisin type, and especially to proteases obtained from *Bacillus lentus*. Of particular interest in this context are enzyme mixtures, examples being those of protease and amylase or protease and lipase or lipolytic enzymes, or of protease, amylase and lipase or lipolytic enzymes, or of protease, lipase or lipolytic enzymes, but especially protease and/or lipase-containing mixtures or mixtures with lipolytic enzymes. Examples of such lipolytic enzymes are the known cutinases. Peroxidases

- 16 -

or oxidases have also proven suitable in some cases. The suitable amylases include, in particular, alpha-amylases, iso-amylases, pullulanases, and pectinases.

- 5 The enzymes may be adsorbed on carrier substances or embedded in coating substances in order to protect them against premature decomposition.

10 The enzymes are usually prepared in a granulated and encapsulated form and added in that form to the laundry detergent and cleaning product. In liquid cleaning products containing water, these granulated and encapsulated enzymes would dissolve, and so in that case the use of liquid enzyme concentrates is generally
15 preferred. Such liquid enzyme concentrates are based either, homogeneously, on a propylene glycol/water base or, heterogeneously, as slurry, or are present in a microencapsulated structure. The use of liquid enzyme products is likewise possible in the capsules of the
20 invention.

Preferred liquid proteases are, for example, Savinase[®] L, Durazym[®] L, Esperase[®] L, and Everlase[®] from Novo Nordisk, Optimase[®] L, Purafect[®] L, Purafect[®] OX L,
25 Properase[®] L from Genencor International, and BLAP[®] L from Biozym Ges.m.b.H.

Preferred amylases are Termamyl[®] L, Duramyl[®] L, and BAN[®] from Novo Nordisk, Maxamyl[®] WL and Purafect[®] HPAm L from
30 Genencor International.

Preferred lipases are Lipolase[®] L, Lipolase[®] ultra L and Lipoprime[®] L from Novo Nordisk and Lipomax[®] L from Genencor International.

35

Slurries or microencapsulated liquid products that may be used are, for example, products such as those designated by SL or, respectively, LCC from Novo

- 17 -

Nordisk. Said commercial liquid enzyme preparations contain, for example, from 20 to 90% by weight of propylene glycol or of mixtures of propylene glycol and water. Capsules preferred in the context of the present invention are those comprising one or more liquid amylase preparations and/or one or more liquid protease preparations.

Substances from the groups of the bleaches and bleach activators or bleaching catalysts are also suitable as ingredients for the capsules of the invention. Among the compounds used as bleaches which yield H_2O_2 in water, particular importance is possessed by sodium percarbonate. Examples of further bleaches which may be used are sodium perborate tetrahydrate and sodium perborate monohydrate, peroxyphosphates, citrate perhydrates, and H_2O_2 -donating peracidic salts or peracids, such as perbenzoates, peroxophthalates, diperazelaic acid, phthaloimino peracid, or diperodecanedioic acid. Capsules of the invention for use in cleaning products may also comprise bleaches from the group of the organic bleaches. Typical organic bleaches are the diacyl peroxides, such as dibenzoyl peroxide for example. Further typical organic bleaches are the peroxy acids, particular examples being the alkyl peroxy acids and the aryl peroxy acids. Preferred representatives are (a) peroxybenzoic acid and its ring-substituted derivatives, such as alkylperoxybenzoic acids, and also peroxy- α -naphthoic acid and magnesium monoperphthalate, (b) aliphatic or substituted aliphatic peroxy acids, such as peroxyauric acid, peroxysebacic acid, ϵ -phthalimidoperoxysebacic acid [phthalimidoperoxyhexanoic acid (PAP)], o-carboxybenzamidoperoxysebacic acid, N-nonylamidoperoxyadipic acid, and N-nonylamidopersuccinates, and (c) aliphatic and araliphatic peroxy dicarboxylic acids, such as 1,12-diperoxydicarboxylic acid, 1,9-diperoxyazelaic acid, diperoxysebacic acid, diperoxybrassylic acid, the

- 18 -

diperoxyphthalic acids, 2-decyldiperoxybutane-1,4-dioic acid, and N,N-terephthaloyldi(6-aminopercaproic acid) may be used.

5 Bleaches in the capsules of the invention used in detergents for machine dishwashing may also be substances which release chlorine or bromine. Among the suitable chlorine- or bromine-releasing materials, examples include heterocyclic N-bromoamides and
10 N-chloroamides, examples being trichloroisocyanuric acid, tribromoisocyanuric acid, dibromoisocyanuric acid, and/or dichloroisocyanuric acid (DICA) and/or salts thereof with cations such as potassium and sodium. Hydantoin compounds, such as 1,3-dichloro-
15 5,5-dimethylhydantoin, are likewise suitable.

Bleach activators, which boost the action of the bleaches, may likewise be ingredients in the capsules of the invention. Known bleach activators are compounds
20 containing one or more N-acyl and/or O-acyl groups, such as substances from the class of the anhydrides, esters, imides and acylated imidazoles or oximes. Examples are tetraacetythylenediamine TAED, tetraacetylmethylenediamine TAMD, and tetraacetylhexylene-
25 diamine TAHD, and also pentaacetylglucose PAG, 1,5-diacetyl-2,2-dioxohexahydro-1,3,5-triazine DADHT, and isatoic anhydride ISA.

Bleach activators which may be used are compounds which
30 under perhydrolysis conditions give rise to aliphatic peroxo carboxylic acids having preferably 1 to 10 carbon atoms, in particular 2 to 4 carbon atoms, and/or substituted or unsubstituted perbenzoic acid. Suitable substances are those which carry O-acyl and/or
35 N-acyl groups of the stated number of carbon atoms, and/or substituted or unsubstituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetythylenediamine (TAED), acylated

- 19 -

triazine derivatives, especially 1,5-diacetyl-
2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated
glycolurils, especially tetraacetyl glycoluril (TAGU),
N-acylimides, especially N-nonanoylsuccinimide (NOSI),
5 acylated phenolsulfonates, especially n-nonanoyl- or
isononanoyloxybenzenesulfonate (n- or iso-NOBS),
carboxylic anhydrides, especially phthalic anhydride,
acylated polyhydric alcohols, especially triacetin,
ethylene glycol diacetate, 2,5-diacetoxy-
10 2,5-dihydrofuran, N-methylmorpholiniumacetonitrile
methyl sulfate (MMA), and the enol esters known from
German Patent Applications **DE 196 16 693** and
DE 196 16 767, and also acetylated sorbitol and
mannitol and/or mixtures thereof (SORMAN), acylated
15 sugar derivatives, especially pentaacetylglucose (PAG),
pentaacetylfructose, tetraacetylxylose and octaacetyl-
lactose, and also acetylated, optionally N-alkylated
glucamine and gluconolactone, and/or N-acylated
lactams, for example, N-benzoylcaprolactam. Hydro-
20 philically substituted acyl acetals and acyllactams are
likewise used with preference. Combinations of
conventional bleach activators may also be used. In
capsules for machine dishwashing compositions, the
bleach activators are usually used in amounts from 0.1
25 to 20% by weight, preferably from 0.25 to 15% by
weight, and in particular from 1 to 10% by weight,
based in each case on the total composition.

In addition to the conventional bleach activators, or
30 instead of them, it is also possible to incorporate
what are known as bleaching catalysts into the
capsules. These substances are bleach-boosting
transition metal salts or transition metal complexes
such as, for example, Mn-, Fe-, Co-, Ru- or Mo-salen
35 complexes or -carbonyl complexes. Other bleaching
catalysts which may be used include Mn, Fe, Co, Ru, Mo,
Ti, V and Cu complexes with N-containing tripod

- 20 -

ligands, and also Co-, Fe-, Cu- and Ru-ammine complexes.

Preference is given to the use of bleach activators
5 from the group of the polyacylated alkylenediamines,
especially tetraacetylenediamine (TAED), N-acyl
imides, especially N-nonanoylsuccinimide (NOSI),
acylated phenolsulfonates, especially n-nonanoyl- or
isononanoyloxybenzenesulfonate (n- or iso-NOBS),
10 N-methylmorpholiniumacetonitrile methyl sulfate (MMA),
preferably in amounts of up to 10% by weight, in
particular from 0.1% by weight to 8% by weight,
especially from 2 to 8% by weight, and with particular
preference from 2 to 6% by weight, based on the total
15 composition.

Bleach-boosting transition metal complexes, especially
those with the central atoms Mn, Fe, Co, Cu, Mo, V, Ti
and/or Ru, preferably selected from the group of
20 manganese and/or cobalt salts and/or complexes, with
particular preference cobalt ammine complexes, cobalt
acetato complexes, cobalt carbonyl complexes, the
chlorides of cobalt or of manganese, and manganese
sulfate, are used in customary amounts, preferably in
25 an amount of up to 5% by weight, in particular from
0.0025% by weight to 1% by weight, and with particular
preference from 0.01% by weight to 0.25% by weight,
based in each case on the total composition. In
specific cases, however, it is also possible to use a
30 greater amount of bleach activator.

When used in laundry detergents and cleaning products,
the capsules of the invention may include corrosion
inhibitors for protecting the ware or the machine, with
35 special importance in the field of machine dishwashing
being possessed, in particular, by silver protectants.
The known substances of the prior art may be used. In
general it is possible to use, in particular, silver

- 21 -

protectants selected from the group of the triazoles, benzotriazoles, bisbenzotriazoles, aminotriazoles, alkylaminotriazoles, and transition metal salts or transition metal complexes. Particular preference is given to the use of benzotriazole and/or alkylaminotriazole. Frequently encountered in cleaner formulations, furthermore, are agents containing active chlorine, which may significantly reduce corrosion of the silver surface. In chlorine-free cleaners, use is made in particular of oxygen-containing and nitrogen-containing organic redox-active compounds, such as difunctional and trifunctional phenols, e.g., hydroquinone, pyrocatechol, hydroxyhydroquinone, gallic acid, phloroglucinol, pyrogallol and derivatives of these classes of compound. Inorganic compounds in the form of salts and complexes, such as salts of the metals Mn, Ti, Zr, Hf, V, Co and Ce, also find frequent application. Preference is given here to the transition metal salts selected from the group of the manganese and/or cobalt salts and/or complexes, with particular preference cobalt ammine complexes, cobalt acetato complexes, cobalt carbonyl complexes, the chlorides of cobalt or of manganese, and manganese sulfate. Similarly, zinc compounds may be used to prevent corrosion on the ware.

In shaped laundry detergent and cleaning product bodies which are preferred in the context of the present invention, the capsule comprises silver protectants from the group of the triazoles, benzotriazoles, bisbenzotriazoles, aminotriazoles, alkylaminotriazoles, and transition metal salts or transition metal complexes, with particular preference benzotriazole and/or alkylaminotriazole, in amounts of from 0.01 to 5% by weight, preferably from 0.05 to 4% by weight, and in particular from 0.5 to 3% by weight, based in each case on the weight of the total composition that comprises the capsules.

- 22 -

In order to enhance the esthetic appeal of the capsules or of the compositions that comprise the capsules, the capsules may in whole or in part be colored with appropriate dyes or comprise dyes. Preferred dyes, whose selection presents no difficulties whatsoever to the skilled worker, possess a high level of storage stability and insensitivity to the other ingredients of the compositions, and to light, and possess no pronounced affinity for the substrates treated, such as textile fibers or kitchen- or tableware items, for example, so as not to stain them.

Preference for use in capsules of the invention for textile laundering or for incorporation into textile detergents is given to all colorants which can be oxidatively destroyed in the washing process, and to mixes thereof with suitable blue dyes, known as bluing agents. It has proven advantageous to use colorants which are soluble in water or at room temperature in liquid organic substances. Examples of suitable colorants are anionic colorants, e.g., anionic nitroso dyes. One possible colorant is, for example, naphthol green (Colour Index (CI) Part 1: Acid Green 1; Part 2: 10020) which as a commercial product is available, for example, as Basacid[®] Green 970 from BASF, Ludwigshafen, Germany, and also mixtures thereof with suitable blue dyes. Further suitable colorants used include Pigmosol[®] Blue 6900 (CI 74160), Pigmosol[®] Green 8730 (CI 74260), Basonyl[®] Red 545 FL (CI 45170), Sandolan[®] Rhodamine EB400 (CI 45100), Basacid[®] Yellow 094 (CI 47005), Sicovit[®] Patent Blue 85 E 131 (CI 42051), Acid Blue 183 (CAS 12217-22-0, CI Acid Blue 183), Pigment Blue 15 (CI 74160), Supranol[®] Blue GLW (CAS 12219-32-8, CI Acid Blue 221), Nylosan[®] Yellow N-7GL SGR (CAS 61814-57-1, CI Acid Yellow 218) and/or Sandolan[®] Blue (CI Acid Blue 182, CAS 12219-26-0).

- 23 -

In the context of the choice of colorant it must be ensured that the colorants do not have too great an affinity for the textile surfaces, and especially for synthetic fibers. At the same time, it should also be borne in mind when choosing suitable colorants that colorants possess different stabilities with respect to oxidation. The general rule is that water-insoluble colorants are more stable to oxidation than water-soluble colorants. Depending on the solubility and hence also on the oxidation sensitivity, the concentration of the colorant in the laundry detergents or cleaning products varies. With readily water-soluble colorants, e.g., the abovementioned Basacid[®] Green, or the likewise abovementioned Sandolan[®] Blue, colorant concentrations chosen are typically in the range from a few 10^{-2} to $10^{-3}\%$ by weight. In the case of the pigment dyes, which are particularly preferred owing to their brightness but are less readily soluble in water, examples being the abovementioned Pigmosol[®] dyes, the appropriate concentration of the colorant in laundry detergents or cleaning products, in contrast, is typically from a few 10^{-3} to $10^{-4}\%$ by weight.

The capsules of the invention may comprise one or more optical brighteners. These substances, which are also called whiteners, are used in modern laundry detergents because even freshly washed and bleached white laundry has a slight yellow cast. Optical brighteners are organic dyes which convert a part of the invisible UV radiation of sunlight into longer-wave blue light. The emission of this blue light closes the "loophole" in the light reflected by the textile, so that a textile treated with an optical brightener appears whiter and lighter to the eye. Since the mechanism of action of brighteners necessitates that they attach to the fibers, a distinction is made in accordance with the fibers to be "dyed" between, for example, brighteners for cotton, nylon or polyester fibers. The

- 24 -

commercially customary brighteners suitable for incorporation into laundry detergents belong essentially to five structural groups: the stilbene group, the diphenylstilbene group, the coumarin-quinoline group, the diphenylpyrazoline group, and the group involving combination of benzoxazole or benzimidazole with conjugated systems. An overview of current brighteners may be found, for example, in *G. Jakobi, A. Löhr "Detergents and Textile Washing", VCH-Verlag, Weinheim, 1987, pages 94 to 100.* Examples of suitable brighteners are salts of 4,4'-bis[(4-anilino-6-morpholino-s-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid or compounds of similar structure which instead of the morpholino group carry a diethanolamino group, a methylamino group, an anilino group, or a 2-methoxyethylamino group. Furthermore, brighteners of the substituted diphenylstyryl type may be present, examples being the alkali metal salts of 4,4'-bis(2-sulfostyryl)biphenyl, 4,4'-bis(4-chloro-3-sulfostyryl)biphenyl, or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)biphenyl. Mixtures of the abovementioned brighteners may also be used.

Fragrances are added to the capsules of the invention in order to enhance the esthetic appeal of the products and to provide the consumer with not only the performance of the product but also a visually and sensorially "typical and unmistakeable" product. Also of importance here is the aspect of the long-lasting fragrancing of textiles or of the delayed release of fragrance, which masks the unpleasant alkali odor when dishwashers are opened. As perfume oils and/or fragrances it is possible to use individual odorant compounds, examples being the synthetic products of the ester, ether, aldehyde, ketone, alcohol, and hydrocarbon types. Odorant compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert-butylcyclohexyl acetate, linalyl

- 25 -

acetate, dimethylbenzylcarbinyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethyl methylphenylglycinate, allyl cyclohexylpropionate, styrallyl propionate, and benzyl salicylate. The ethers
5 include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals having 8-18 carbon atoms, citral, citronellal, citronellyloxy-acetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilial and bourgeonal; the ketones include, for
10 example, the ionones, α -isomethylionone and methyl cedryl ketone; the alcohols include anethole, citronellol, eugenol, geraniol, linalool, phenylethyl alcohol, and terpineol; the hydrocarbons include primarily the terpenes such as limonene and pinene.
15 Preference, however, is given to the use of mixtures of different odorants, which together produce an appealing fragrance note. Such perfume oils may also contain natural odorant mixtures, as obtainable from plant sources, examples being pine oil, citrus oil, jasmine
20 oil, patchouli oil, rose oil or ylang-ylang oil. Likewise suitable are clary sage oil, camomile oil, clove oil, balm oil, mint oil, cinnamon leaf oil, lime blossom oil, juniperberry oil, vetiver oil, olibanum oil, galbanum oil and labdanum oil, and also orange
25 blossom oil, neroliol, orange peel oil, and sandalwood oil.

The fragrance content of the capsules of the invention or of the compositions comprising the capsules is
30 usually up to 2% by weight of the overall formulation. The fragrances may be incorporated directly into the capsules or compositions of the invention; alternatively, it may be advantageous to apply the fragrances to carriers which intensify the adhesion of
35 the perfume on the laundry and, by means of slower fragrance release, ensure long-lasting fragrance of the textiles. Materials which have become established as such carriers are, for example, cyclodextrins, it being

- 26 -

possible for the cyclodextrin-perfume complexes to be additionally coated with further auxiliaries.

In addition, the capsules may also comprise components
5 which have a positive influence on the ease with which
oil and grease are washed off from textiles (these
components being known as soil repellents). This effect
becomes particularly marked when a textile is soiled
that has already been laundered previously a number of
10 times with a detergent of the invention comprising this
oil- and fat-dissolving component. The preferred oil-
and fat-dissolving components include, for example,
nonionic cellulose ethers such as methylcellulose and
methylhydroxypropylcellulose having a methoxy group
15 content of from 15 to 30% by weight and a hydroxypropyl
group content of from 1 to 15% by weight, based in each
case on the nonionic cellulose ether, and also the
prior art polymers of phthalic acid and/or terephthalic
acid, and/or derivatives thereof, especially polymers
20 of ethylene terephthalates and/or polyethylene glycol
terephthalates or anionically and/or nonionically
modified derivatives thereof. Of these, particular
preference is given to the sulfonated derivatives of
phthalic acid polymers and of terephthalic acid
25 polymers.

Foam inhibitors which may be present in the capsules of
the invention are suitably, for example, soaps,
paraffins or silicone oils, which may if desired have
30 been applied to carrier materials.

Graying inhibitors have the function of keeping the
dirt detached from the fiber in suspension in the
liquor and so preventing the redeposition of the dirt.
35 Suitable for this purpose are water-soluble colloids,
usually organic in nature, examples being the water-
soluble salts of polymeric carboxylic acids, glue,
gelatin, salts of ethersulfonic acids of starch or of

- 27 -

cellulose, or salts of acidic sulfuric esters of cellulose or of starch. Water-soluble polyamides containing acidic groups are also suitable for this purpose. Furthermore, soluble starch preparations and starch products other than those mentioned above may be used, examples being degraded starch, aldehyde starches, etc. Polyvinylpyrrolidone may also be used. Preference, however, is given to the use of cellulose ethers such as carboxymethylcellulose (Na salt), methylcellulose, hydroxyalkylcellulose, and mixed ethers such as methylhydroxyethylcellulose, methylhydroxypropylcellulose, methylcarboxymethylcellulose and mixtures thereof in amounts of from 0.1 to 5% by weight, based on the compositions.

Since sheetlike textile structures, especially those of filament rayon, viscose rayon, cotton and blends thereof, may tend to crease because the individual fibers are susceptible to bending, buckling, compressing and pinching transverse to the fiber direction, the capsules may comprise synthetic crease control agents. These include, for example, synthetic products based on fatty acids, fatty acid esters, fatty acid amides, fatty acid alkylol esters, fatty acid alkylolamides, or fatty alcohols, which are usually reacted with ethylene oxide, or else products based on lecithin or on modified phosphoric esters.

In order to combat microorganisms, the capsules of the invention may comprise antimicrobial active substances. In this context a distinction is made, depending on antimicrobial spectrum and mechanism of action, between bacteriostats and bactericides, fungistats and fungicides, etc. Examples of important substances from these groups are benzalkonium chlorides, alkylaryl-sulfonates, halophenols, and phenylmercuric acetate, it also being possible to do without these compounds entirely.

- 28 -

In order to prevent unwanted changes to the compositions and/or the treated textiles or substrates as a result of oxygen exposure and other oxidative processes, the capsules may comprise antioxidants. This class of compound includes, for example, substituted phenols, hydroquinones, pyrocatechols and aromatic amines, and also organic sulfides, polysulfides, dithiocarbamates, phosphites, and phosphonates.

10

Increased wear comfort may result from the additional use of antistats which are further added to the capsules of the invention. Antistats increase the surface conductivity and thus enable better dissipation of charges that are formed. External antistats are generally substances having at least one hydrophilic molecule ligand, and provide a more or less hygroscopic film on the surfaces. These antistats, which are usually surface-active, may be subdivided into nitrogen-containing (amines, amides, quaternary ammonium compounds), phosphorus-containing (phosphoric esters), and sulfur-containing (alkylsulfonates, alkyl sulfates) antistats. External antistats are described, for example, in Patent Applications FR 1,156,513, GB 873 214 and GB 839 407. The lauryl- (or stearyl-)dimethylbenzylammonium chlorides disclosed here are suitable as antistats for textiles and as additives to laundry detergents, in which case, additionally, a hand effect is obtained.

30

In order to improve the water absorption capacity, the rewettability of the treated textiles, and to facilitate ironing of the treated textiles, silicone derivatives, for example, may be used in the capsules of the invention used to treat laundry. These derivatives additionally improve the rinse-out behavior of the compositions, by virtue of their foam-inhibiting properties. Examples of preferred silicone derivatives

35

- 29 -

are polydialkylsiloxanes or alkylarylsiloxanes where the alkyl groups have one to five carbon atoms and are totally or partially fluorinated. Preferred silicones are polydimethylsiloxanes, which may if desired have
5 been derivatized and in that case are amino-functional or quaternized, or have Si-OH, Si-H and/or Si-Cl bonds. The viscosities of the preferred silicones at 25°C are in the range between 100 and 100,000 centistokes, it being possible to use the silicones in amounts of
10 between 0.2 and 5% by weight, based on the overall composition.

Finally, the capsules of the invention for textile detergents may also comprise UV absorbers, which attach
15 to the treated textiles and improve the light stability of the fibers. Compounds which have these desired properties are, for example, the compounds which are active via radiationless deactivation, and derivatives of benzophenone having substituents in position(s) 2
20 and/or 4. Also suitable are substituted benzotriazoles, acrylates which are phenyl-substituted in position 3 (cinnamic acid derivatives), with or without cyano groups in position 2, salicylates, organic Ni complexes, and also natural substances such as
25 umbelliferone and the endogenous urocanic acid.

It is of course also possible to incorporate further ingredients of laundry detergents and cleaning products, examples being builders, cobuilders, further
30 surfactants, especially anionic surfactants, etc., into the capsules of the invention. The incorporation of any pharmaceutical or cosmetic active substance is also possible without problems, so that the advantages of the controlled release may be utilized in a very wide
35 variety of fields of use with the aid of the capsules of the invention.

- 30 -

As component B it is possible to use any desired gas compatible with the other components in the capsule. Examples are air, N₂, O₂, noble gases and noble gas mixtures, and CO₂.

5

The capsules of the invention may be produced in various ways. One possibility is to fill prefabricated capsule parts comprising the abovementioned materials with components A and C and then to fit the capsule parts together. Prefabricated capsule parts are available commercially in the form of so-called hard capsules. The amount of the gas component B is determined by the amount of components A and C introduced. If the capsule parts are filled in air, then the gas component is air. Where a gas other than air is to be used as the gas component, filling generally takes place under the corresponding gas atmosphere.

20 After the capsule has been sealed, it is provided with the aperture, usually by means of a pointed article with the appropriate diameter. Alternatively, use may also be made of capsule shells which have already been perforated beforehand.

25

A further mode of production consists in the preparation of soft capsules. This takes place industrially by the so-called Scherer process. In this process, two strips of the capsule wall materials (e.g., gelatin strips) are combined in counter-rotating shaping rolls, with capsule shaping and capsule filling taking place simultaneously. The capsule aperture may in this case be made during the capsule shaping/filling process, or else in a downstream process step.

35

As already mentioned, in order to obtain the stated properties of the capsule wall it may be sensible or necessary to apply one or more layers of further wall

- 31 -

materials to the capsules. This can be done, for example, by means of immersion processes, film coating, or in the fluidized bed process.

- 5 It is also possible to produce microcapsules of the invention which allow the release mechanism. In this case it is possible to have recourse to the common production processes, followed by the making of one or more microholes.

10

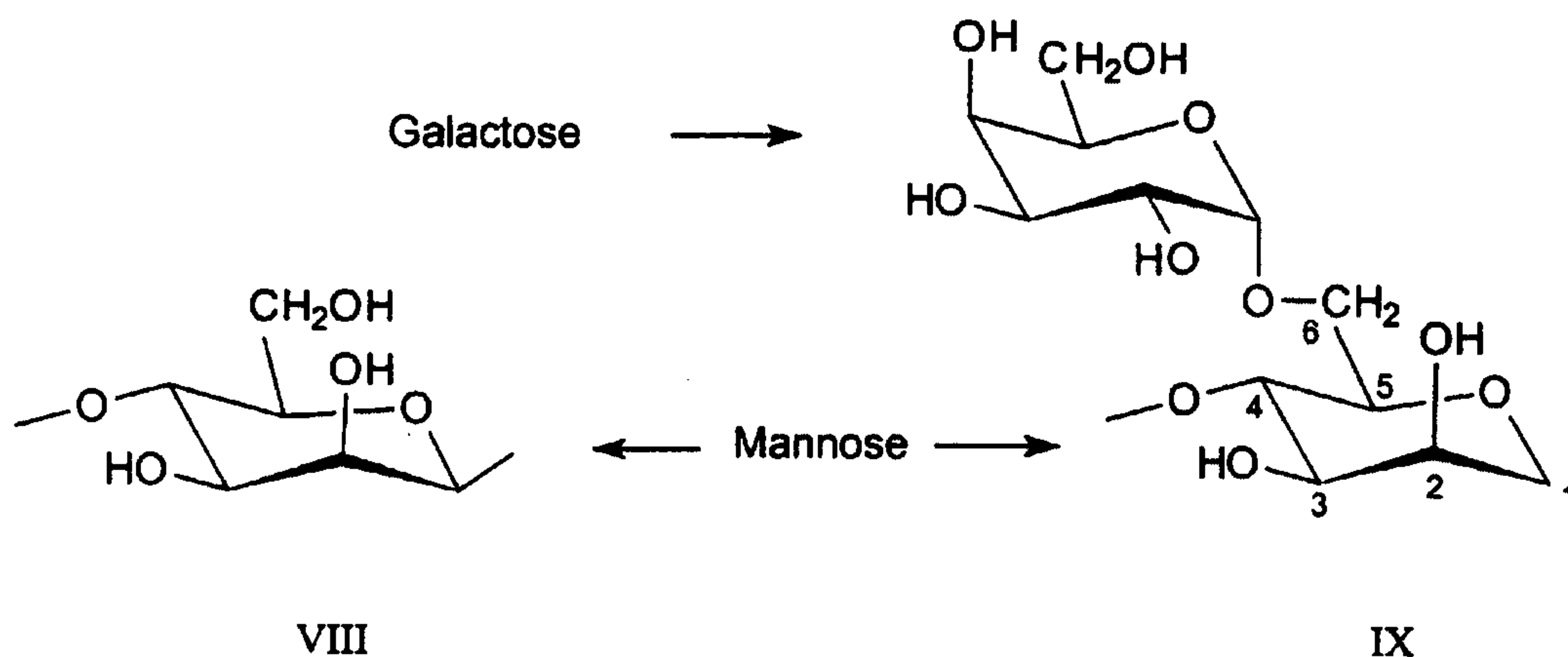
Appropriate capsule materials are, as already mentioned, polymers in particular. The materials mentioned earlier on above, such as carrageenan, guar, pectin, xanthan, cellulose and its derivatives, and
15 gelatin, are described below.

Carrageenan is a formed extract, with a composition similar to that of agar, of North Atlantic red algae which belong to the Florideae, and is named for the
20 Irish coastal town of Carragheen. The carrageenan, precipitated from the hot-water extract of the algae, is a colorless to sandy-colored powder having molecular masses of 100,000-800,000 and a sulfate content of approximately 25%, which is very readily soluble in
25 warm water. In carrageenan, three principal constituents are distinguished: the gel-forming κ fraction consists of D-galactose 4-sulfate and 3,6-anhydro- α -D-galactose, having alternate glycoside linkages in the 1,3 and 1,4 positions (agar, in contrast, contains
30 3,6-anhydro- α -L-galactose). The non-gelling λ fraction is composed of D-galactose 2-sulfate with 1,3-glycoside linkages and of D-galactose 2,6-disulfate residues with 1,4 linkages, and is readily soluble in cold water. ι -Carrageenan, composed of D-galactose 4-sulfate in
35 1,3 linkage and 3,6-anhydro- α -D-galactose 2-sulfate in 1,4 linkage, is both water-soluble and gel-forming. Further types of carrageenan are likewise labeled with Greek letters: α , β , γ , μ , ν , ξ , π , ω , χ . The nature of

- 32 -

cations present (K, NH₄, Na, Mg, Ca) also influences the solubility of the carrageenans. Semisynthetic products which contain only one ionic type and are likewise possible for use in capsule materials in the context of the present invention are also called carrag(h)eenates.

The guar which may be used as a capsule material in the context of the present invention, also called guar gum, is a grayish white powder obtained by milling the endosperm of the guar bean (*Cyamopsis tetragonolobus*), which belongs to the family of the Leguminosae and was originally endemic in the Indian and Pakistani region but has since been cultivated in other countries as well, for example, in the southern USA. The principal constituent of guar, with up to about 85% by weight of the dry matter, is guaran (guar gum, *Cyamopsis* gum); secondary constituents are proteins, lipids, and cellulose. Guaran itself is a polygalactomannan, i.e., a polysaccharide whose linear chain is composed of unsubstituted mannose units (see formula VIII) and mannose units substituted in the C6 position by a galactose residue (see formula IX) in β -D-(1 $\rightarrow$ 4) linkage.



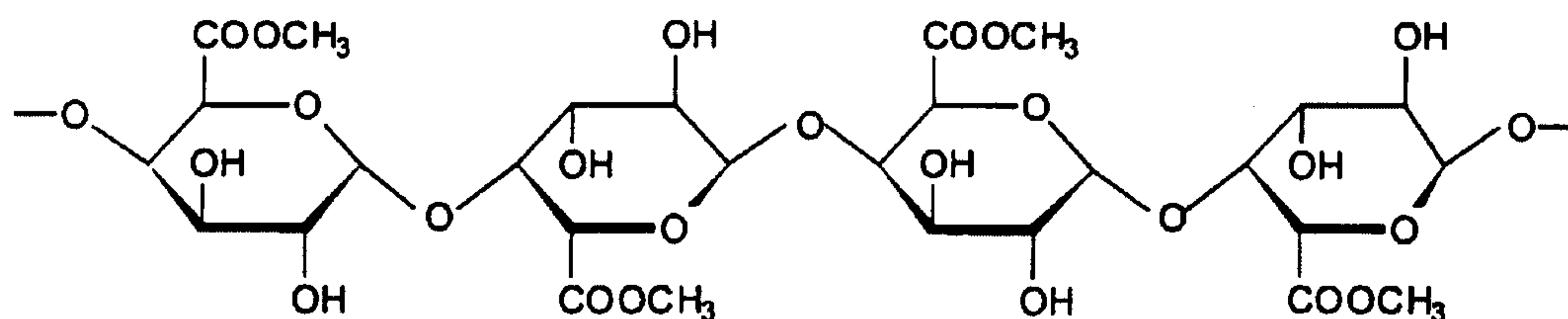
25

The ratio of VIII:IX is approximately 2:1; the IX units, in contrast to what was originally assumed, are not strictly alternating but are instead arranged in

- 33 -

pairs or triplets in the polygalactomannan molecule. Data on the molecular mass of guaran vary with values of approximately $2.2 \cdot 10^5$ - $2.2 \cdot 10^6$ g/mol, depending on the degree of purity of the polysaccharide - the high value
 5 was determined on a highly purified product - significantly and correspond to approximately 1350-13,500 sugar units/macromolecule. Guaran is insoluble in the majority of organic solvents.

10 The pectins, which are likewise suitable for use as capsule material, are high molecular mass glycosidic plant substances which are very widespread in fruits, roots, and leaves. Pectins consist essentially of chains of 1,4- α -glycosidically linked galacturonic acid
 15 units with 20-80% of their acid groups esterified with methanol, a distinction being made between high-esterification (>50%) and low-esterification (<50%) pectins. The pectins have a folded leaf structure which positions them in the center between starch and
 20 cellulose molecules. Their macromolecules also contain some glucose, galactose, xylose and arabinose, and have weakly acidic properties.

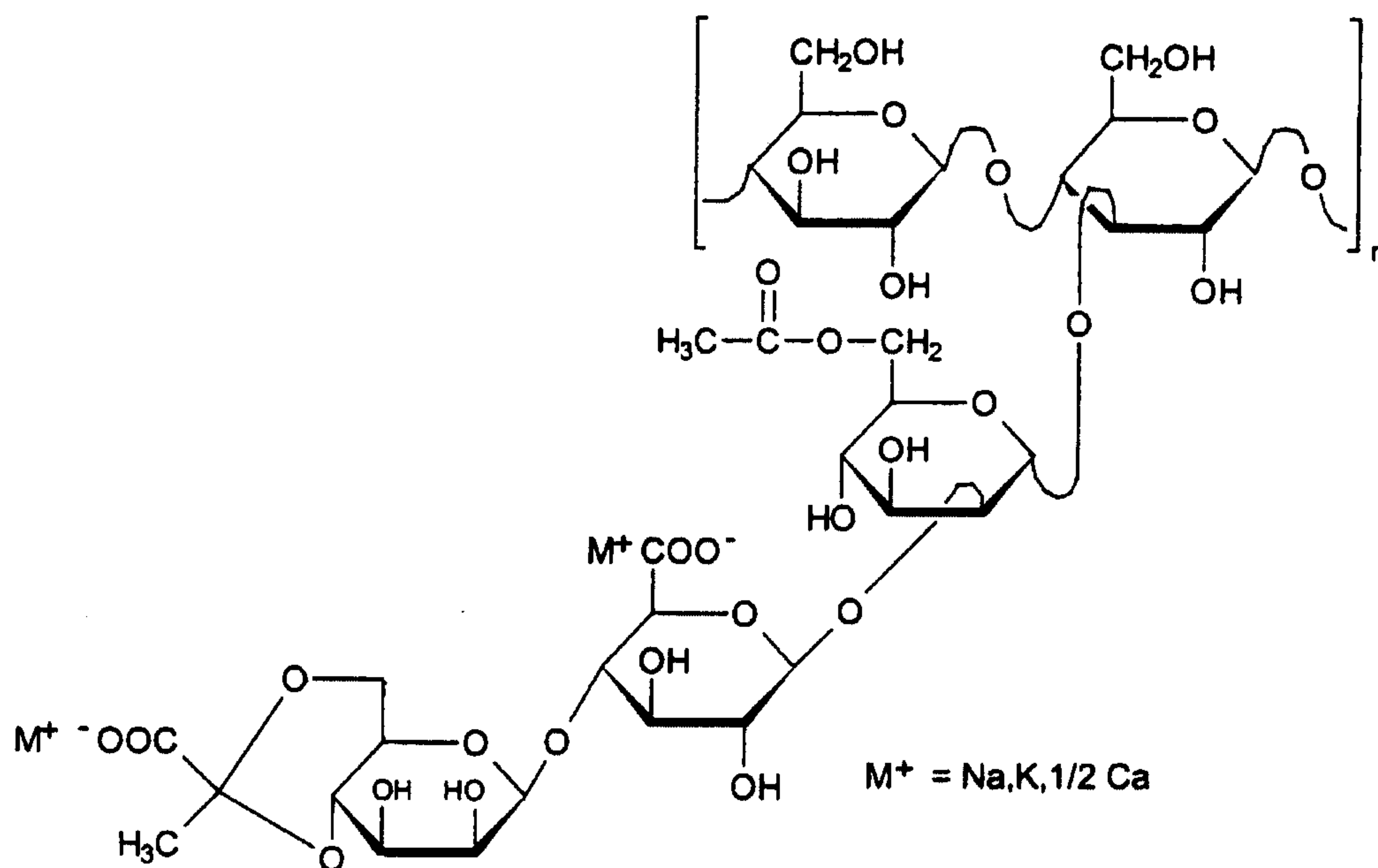


Fruit pectin contains 95%, beet pectin up to 85%
 25 galacturonic acid. The molecular masses of the various pectins vary between 10,000 and 500,000. The structural properties as well are highly dependent on the degree of polymerization; for example, the fruit pectins in the dried state form asbestoslike fibers while the flax
 30 pectins form fine, granular powders.

- 34 -

The pectins are prepared by extraction with dilute acids predominantly from the inner portions of citrus fruit peels, fruit residues, or sugar beet chips.

- 5 Xanthan may also be used as a capsule material in accordance with the invention. Xanthan is a microbial anionic heteropolysaccharide produced by *Xanthomonas campestris* and certain other species under aerobic conditions, having a molecular mass of from 2 to 10 15 million daltons. Xanthan is formed of a chain comprising β -1,4-linked glucose (cellulose) with side chains. The structure of the subgroups comprises glucose, mannose, glucuronic acid, acetate, and pyruvate, the viscosity of the xanthan being determined 15 by the number of pyruvate units. Xanthan may be described by the following formula:



Basic unit of xanthan

- 20 The celluloses and their derivatives have already been described above as capsule ingredients. The capsules may of course also be produced from such materials. In addition to cellulose and cellulose derivatives, it is

- 35 -

also possible to use (modified) dextrans, starch, and starch derivatives as capsule materials.

Suitable nonionic organic capsule materials are
5 dextrans, examples being oligomers and polymers of
carbohydrates obtainable by partial hydrolysis from
starches. The hydrolysis may be conducted in accordance
with customary processes - for example, acid- or
enzyme-catalyzed processes. The products in question
10 are preferably hydrolysis products having average
molecular masses in the range from 400 to
500,000 g/mol. Preference is given to a polysaccharide
having a dextrose equivalent (DE) in the range from 0.5
to 40, in particular from 2 to 30, DE being a
15 customary measure of the reducing action of a
polysaccharide in comparison with dextrose, which
possesses a DE of 100. Dextrans suitable for use
include not only maltodextrans having a DE of between 3
and 20 and dry glucose syrups having a DE of between 20
20 and 37 but also what are known as yellow dextrans and
white dextrans having higher molecular masses in the
range from 2000 to 30,000 g/mol.

The oxidized derivatives of such dextrans comprise the
25 reaction products with oxidizing agents capable of
oxidizing at least one alcohol function of the
saccharide ring to the carboxylic acid function.
Oxidized dextrans of this kind and processes for
preparing them are known, for example, from European
30 Patent Applications **EP-A-0 232 202**, **EP-A-0 427 349**,
EP-A-0 472 042 and **EP-A-0 542 496** and International
Patent Applications **WO 92/18542**, **WO 93/08251**,
WO 93/16110, **WO 94/28030**, **WO 95/07303**, **WO 95/12619** and
WO 95/20608. Likewise suitable is an oxidized
35 oligosaccharide in accordance with German Patent
Application **DE-A-196 00 018**. A product oxidized at C₆
of the saccharide ring may be particularly
advantageous.

- 36 -

Starch as well may be used as capsule material for the capsules of the invention. Starch is a homoglycan in which the glucose units are linked α -glycosidically.

5 Starch is composed of two components of different molecular weight: approximately 20-30% straight-chain amylose (MW approx. 50,000-150,000) and 70-80% branched-chain amylopectin (MW approx. 300,000-2,000,000), with small amounts of lipids, phosphoric

10 acids, and cations being present as well. Whereas amylose forms long, helical, interlooped chains comprising approximately 300-1200 glucose molecules, owing to the 1,4 linkage, in the case of amylopectin the chain branches by 1,6 linkage, after on average

15 25 glucose units, to form a treelike structure comprising approximately 1500-12,000 molecules of glucose. In addition to straight starch, starch derivatives obtainable by polymer-analogous reactions from starch are also suitable for preparing capsules in

20 the context of present invention. Examples of such chemically modified starches include products of esterifications and etherifications in which hydroxy hydrogen atoms have been substituted. Alternatively, starches in which the hydroxy groups have been replaced

25 by functional groups not attached via an oxygen atom may be used as starch derivatives. The group of the starch derivatives includes, for example, alkali metal starches, carboxymethylstarch (CMS), starch esters and ethers, and amino starches.

30

Among the proteins and modified proteins, gelatin is of outstanding significance as capsule material. Gelatin is a polypeptide (molecular mass: approx. 15,000- >250,000 g/mol) obtained principally by hydrolysis

35 under acidic or alkaline conditions of the collagen present in the skin and bones of animals. The amino acid composition of gelatin corresponds largely to that of the collagen from which it was obtained, and varies

- 37 -

as a function of its provenance. The use of gelatin as a water-soluble envelope material is extremely widespread, especially in pharmacy, in the form of hard or soft gelatin capsules.

5

Further polymers suitable for use as capsule materials are synthetic polymers, which are preferably water-swellaable and/or water-soluble. These polymers hail in particular from the following groups:

10

a) water-soluble nonionic polymers from the group of

a1) polyvinylpyrrolidones

a2) vinylpyrrolidone-vinyl ester copolymers

15

a3) cellulose ethers

a4) (modified) polyvinyl alcohols

b) water-soluble amphoteric polymers from the group of

20

b1) alkylacrylamide-acrylic acid copolymers

b2) alkylacrylamide-methacrylic acid copolymers

b3) alkylacrylamide-methylmethacrylic acid copolymers

25

b4) alkylacrylamide-acrylic acid-alkylaminoalkyl-(meth)acrylic acid copolymers

b5) alkylacrylamide-methacrylic acid-alkylamino-alkyl(meth)acrylic acid copolymers

30

b6) alkylacrylamide-methylmethacrylic acid-alkyl-aminoalkyl(meth)acrylic acid copolymers

b7) alkylacrylamide-alkyl methacrylate-alkylamino-ethyl methacrylate-alkyl methacrylate copolymers

b8) copolymers of

35

b8i) unsaturated carboxylic acid

- 38 -

b8ii) cationically derivatized unsaturated
carboxylic acids

b8iii) if desired, further ionic or nonionic
monomers

5

c) water-soluble zwitterionic polymers from the
group of

10 c1) acrylamidoalkyltrialkylammonium chloride-
acrylic acid copolymers and their alkali metal
and ammonium salts

c2) acrylamidoalkyltrialkylammonium chloride-
methacrylic acid copolymers and their alkali
metal and ammonium salts

15 c3) methacroylethyl betaine-methacrylate
copolymers

d) water-soluble anionic polymers from the group of

20 d1) vinyl acetate-crotonic acid copolymers

d2) vinylpyrrolidone-vinyl acrylate copolymers

d3) acrylic acid-ethyl acrylate-N-tert-butylacryl-
amide terpolymers

25 d4) graft polymers of vinyl esters, esters of
acrylic acid or methacrylic acid alone or in a
mixture, copolymerized with crotonic acid,
acrylic acid or methacrylic acid with poly-
alkylene oxides and/or polyalkylene glycols

30 d5) grafted and crosslinked copolymers from the
copolymerization of

d5i) at least one monomer of the nonionic
type,

d5ii) at least one monomer of the ionic
type,

35 d5iii) polyethylene glycol, and

- 39 -

- d5iv) a crosslinker
- d6) copolymers obtained by copolymerizing at least one monomer from each of the three following groups:
 - 5 d6i) esters of unsaturated alcohols and short-chain saturated carboxylic acids and/or esters of short-chain saturated alcohols and unsaturated carboxylic acids,
 - 10 d6ii) unsaturated carboxylic acids,
 - d6iii) esters of long-chain carboxylic acids and unsaturated alcohols and/or esters of the carboxylic acids of group d6ii) with saturated or unsaturated,
 - 15 straight-chain or branched C₈₋₁₈ alcohol
- d7) terpolymers of crotonic acid, vinyl acetate and an allyl or methallyl ester
- d8) tetra- and pentapolymers of
 - d8i) crotonic acid or allyloxyacetic acid
 - 20 d8ii) vinyl acetate or vinyl propionate
 - d8iii) branched allyl or methallyl esters
 - d8iv) vinyl ethers, vinyl esters or straight-chain allyl or methallyl esters
- 25 d9) crotonic acid copolymers with one or more monomers from the group consisting of ethylene, vinylbenzene, vinyl methyl ether, acrylamide and water-soluble salts thereof
- d10) terpolymers of vinyl acetate, crotonic acid and vinyl esters of a saturated aliphatic α -branched monocarboxylic acid
- 30
- e) water-soluble cationic polymers from the group of

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- e1) quaternized cellulose derivatives
- e2) polysiloxanes with quaternary groups
- e3) cationic guar derivatives
- e4) polymeric dimethyldiallylammonium salts and
5 their copolymers with esters and amides of
acrylic acid and methacrylic acid
- e5) copolymers of vinylpyrrolidone with quater-
nized derivatives of dialkylaminoacrylate and
-methacrylate
- 10 e6) vinylpyrrolidone-methoimidazolinium chloride
copolymers
- e7) quaternized polyvinyl alcohol
- e8) polymers indicated under the INCI designations
Polyquaternium 2, Polyquaternium 17, Poly-
15 quaternium 18, and Polyquaternium 27.

Water-soluble polymers in the sense of the invention
are those polymers which are soluble to the extent of
more than 2.5% by weight at room temperature in water.

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The capsules of the invention may be prepared from
individual polymers of those mentioned above;
alternatively, mixtures or multi-layer laminar
constructions of the polymers may be used. The polymers
25 are described in more detail below.

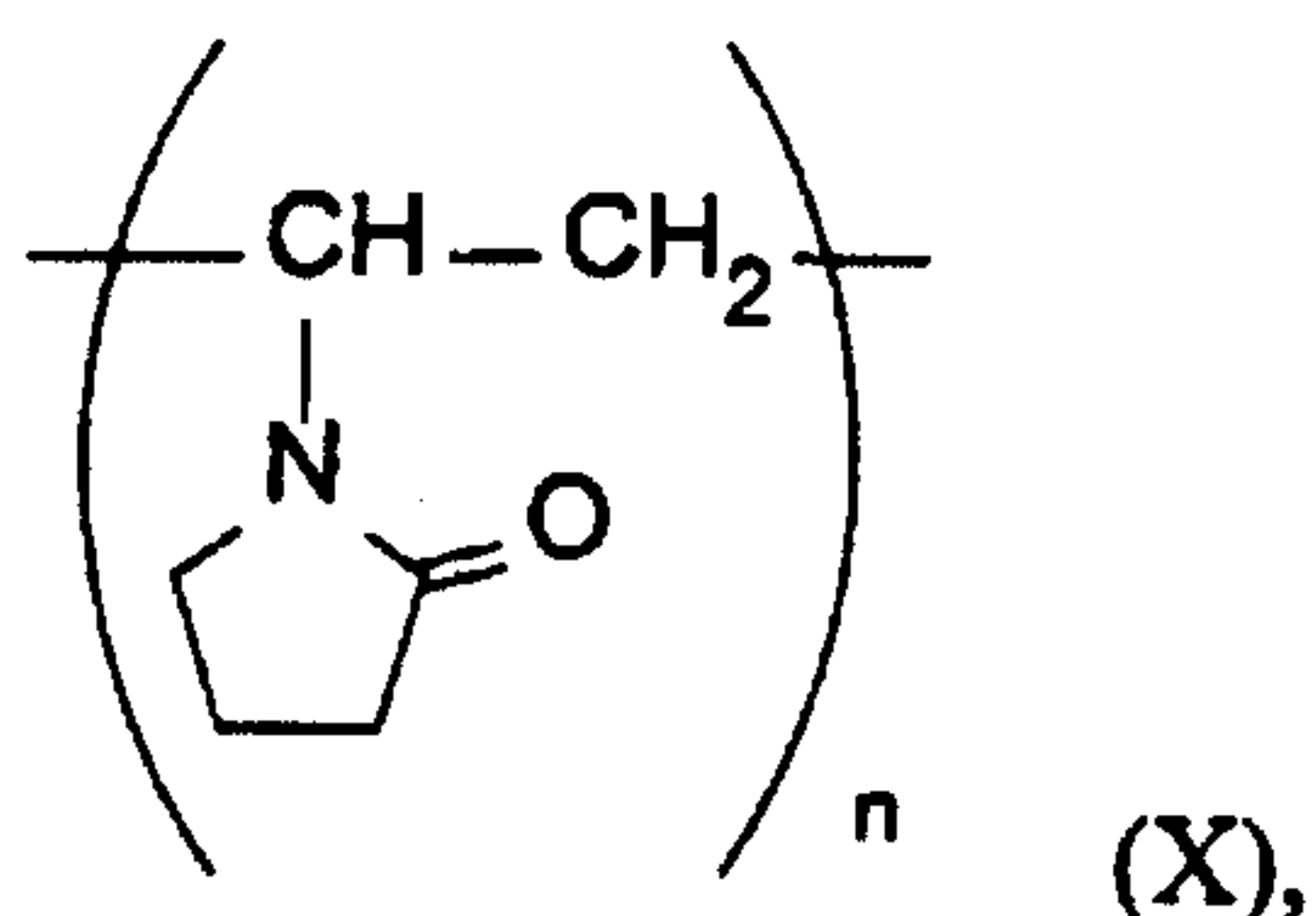
Water-soluble polymers which are preferred in
accordance of the invention are nonionic. Examples of
suitable nonionic polymers are the following:

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- polyvinylpyrrolidones, as marketed, for example,
under the designation Luviskol® (BASF). Polyvinyl-
pyrrolidones are preferred nonionic polymers in the
context of the invention.

- 41 -

Polyvinylpyrrolidones [poly(1-vinyl-2-pyrrolidin-ones)], abbreviated PVP, are polymers of the general formula (X)



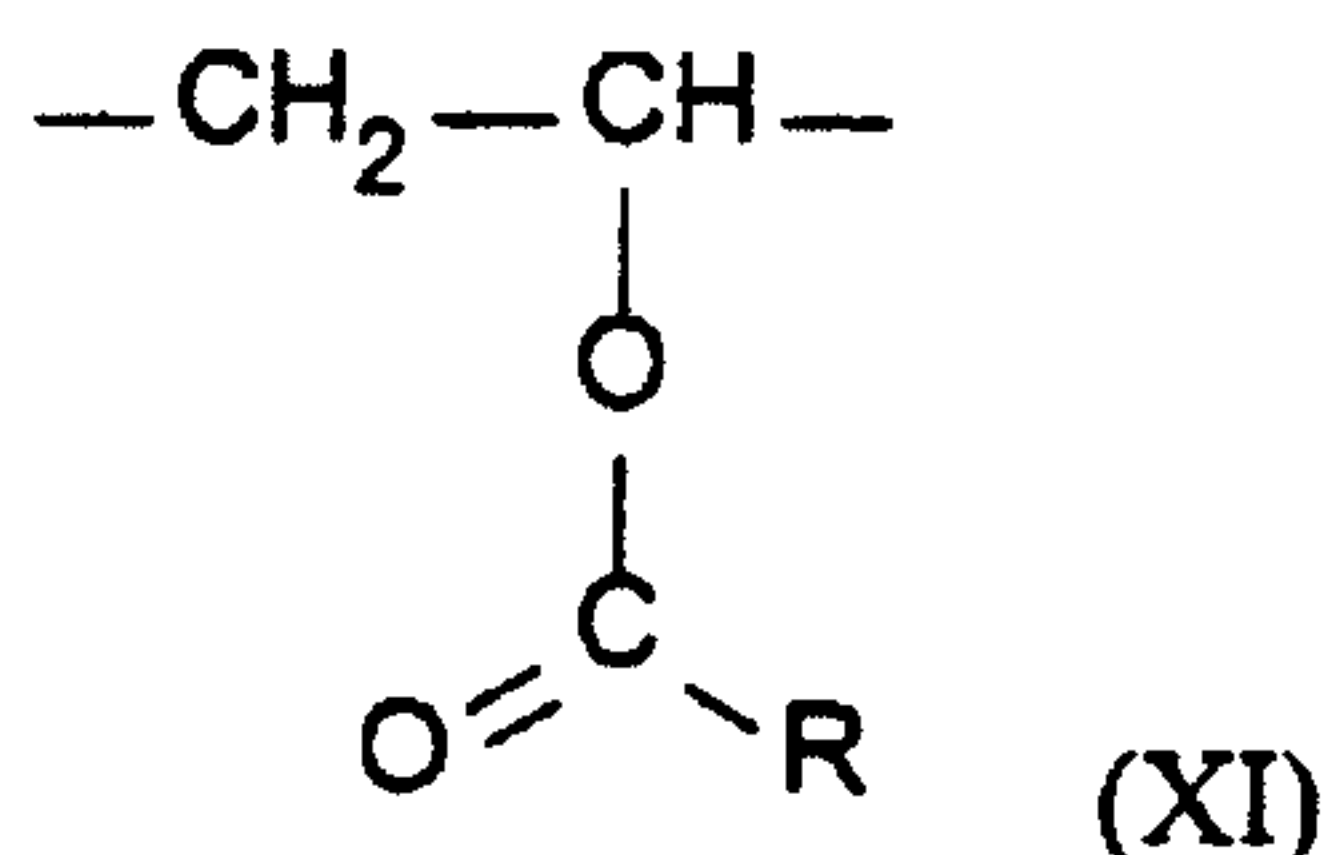
5 prepared by free-radical addition polymerization of 1-vinylpyrrolidone by processes of solution or suspension polymerization using free-radical initiators (peroxides, azo compounds). The ionic polymerization of the monomer yields only products having low molecular
10 masses. Commercially customary polyvinylpyrrolidones have molecular masses in the range from approx. 2500-750,000 g/mol, which are characterized by stating the K values and - depending on the K value - have glass transition temperatures of 130-175°. They are supplied
15 as white, hygroscopic powders or as aqueous solutions. Polyvinylpyrrolidones are readily soluble in water and a large number of organic solvents (alcohols, ketones, glacial acetic acid, chlorinated hydrocarbons, phenols, etc).

20

- Vinylpyrrolidone-vinyl ester copolymers, as marketed for example under the trademark Luviskol® (BASF). Luviskol® VA 64 and Luviskol® VA 73, each vinylpyrrolidone-vinyl acetate copolymers, are
25 particularly preferred nonionic polymers.

The vinyl ester polymers are polymers obtainable from vinyl esters and featuring the grouping of the formula (XI)

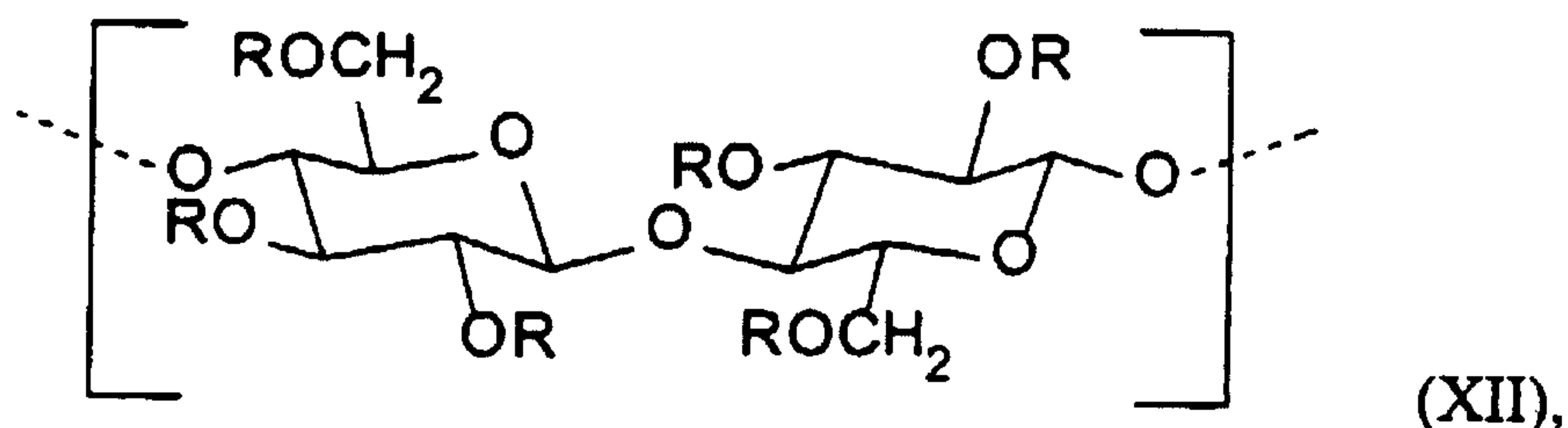
- 42 -



as the characteristic basic structural unit of the macromolecules. Of these, the vinyl acetate polymers (R = CH₃) with polyvinyl acetates, as by far the most important representatives, have the greatest industrial significance.

The vinyl esters are polymerized free-radically by various processes (solution polymerization, suspension polymerization, emulsion polymerization, and bulk polymerization). Copolymers of vinyl acetate with vinylpyrrolidone comprise monomer units of the formulae (I) and (II)

- Cellulose ethers, such as hydroxypropylcellulose, hydroxyethylcellulose and methylhydroxypropylcellulose, as marketed for example under the trademarks Culminal[®] and Benecel[®] (AQUALON). Cellulose ethers may be described by the general formula (XII)



where R is H or an alkyl, alkenyl, alkynyl, aryl, or alkylaryl radical. In preferred products, at least one R in formula (XII) is -CH₂CH₂CH₂-OH or -CH₂CH₂-OH. Cellulose ethers are prepared industrially by etherifying alkali metal cellulose (e.g., with ethylene oxide). Cellulose ethers are

- 43 -

characterized by way of the average degree of substitution, DS, and/or by the molar degree of substitution, MS, which indicate how many hydroxyl groups of an anhydroglucose unit of cellulose have reacted with the etherifying reagent or how many moles of the etherifying reagent have been added on, on average, to one anhydroglucose unit. Hydroxyethylcelluloses are water-soluble above a DS of approximately 0.6 and, respectively, an MS of approximately 1. Commercially customary hydroxyethyl- and hydroxypropylcelluloses have degrees of substitution in the range of 0.85-1.35 (DS) and 1.5-3 (MS), respectively. Hydroxyethyl- and -propylcelluloses are marketed as yellowish white, odorless and tasteless powders in greatly varying degrees of polymerization. Hydroxyethyl- and -propylcelluloses are soluble in cold and hot water and in some (water-containing) organic solvents, but insoluble in the majority of (anhydrous) organic solvents; their aqueous solutions are relatively insensitive to changes in pH or addition of electrolyte.

Polyvinyl alcohols, denoted PVAL for short, are polymers of the general structure



including small fractions of structural units of the



type. Since the corresponding monomer, the vinyl alcohol, is unstable in free form, polyvinyl alcohols are prepared by way of polymer-analogous reactions by hydrolysis, but industrially in particular by alkali-catalyzed transesterification of polyvinyl acetates

- 44 -

with alcohols (preferably methanol) in solution. These industrial processes also make it possible to obtain PVALs having a predeterminable residual fraction of acetate groups.

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Commercially customary PVAL (e.g., Mowiol[®] grades from Hoechst) are commercialized as yellowish white powders or granules having degrees of polymerization in the range of approx. 500-2500 (corresponding to molecular masses of approximately 20,000-100,000 g/mol) and have different degrees of hydrolysis of 98-99 or 87-89 mol%. They are, therefore, partially hydrolyzed polyvinyl acetates having a residual acetyl group content of approximately 1-2 or 11-13 mol%.

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The water-solubility of PVAL may be reduced by after-treatment with aldehydes (acetalization), by complexing with Ni salts or Cu salts, or by treatment with dichromates, boric acid and/or borax, and so adjusted to desired levels.

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Further polymers suitable in accordance with the invention are water-soluble amphopolymers. The generic term amphopolymers embraces amphoteric polymers, i.e., polymers whose molecule includes both free amino groups and free -COOH or SO₃H groups and are capable of forming inner salts; zwitterionic polymers whose molecule contains quaternary ammonium groups and -COO⁻ OR -SO₃⁻ groups, and polymers containing -COOH or SO₃H groups and quaternary ammonium groups. An example of an amphopolymer which may be used in accordance with the invention is the acrylic resin obtainable under the designation Amphomer[®], which constitutes a copolymer of tert-butylaminoethyl methacrylate, N-(1,1,3,3-tetramethylbutyl)acrylamide, and two or more monomers from the group consisting of acrylic acid, methacrylic acid and their simple esters. Likewise preferred amphopolymers are composed of unsaturated carboxylic

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- 45 -

acids (e.g., acrylic and methacrylic acid),
cationically derivatized unsaturated carboxylic acids,
(e.g., acrylamidopropyltrimethylammonium chloride),
and, if desired, further ionic or nonionic monomers, as
5 evident, for example, from German Laid-Open
Specification 39 29 973 and the prior art cited
therein. Terpolymers of acrylic acid, methyl acrylate
and methacrylamidopropyltrimonium chloride, as avail-
able commercially under the designation
10 Merquat® 2001 N, are particularly preferred amphi-
polymers in accordance with the invention. Further
suitable amphoteric polymers are, for example, the
octylacrylamide-methyl methacrylate-tert-butylamino-
ethyl methacrylate-2-hydroxypropyl methacrylate
15 copolymers available under the designations Amphomer®
and Amphomer® LV-71 (DELFT NATIONAL).

Examples of suitable zwitterionic polymers are the
addition polymers disclosed in German Patent
20 Applications DE 39 29 973, DE 21 50 557, DE 28 17 369
and DE 37 08 451. Acrylamidopropyltrimethylammonium
chloride-acrylic acid or -methacrylic acid copolymers
and their alkali metal salts and ammonium salts are
preferred zwitterionic polymers. Further suitable
25 zwitterionic polymers are methacryloylethyl betaine-
methacrylate copolymers, which are obtainable com-
mercially under the designation Amersette® (AMERCHOL).

Anionic polymers that are suitable in accordance with
30 the invention include:

- vinyl acetate-crotonic acid copolymers, as in
commercialized, for example, under the designation
Resyn® (NATIONAL STARCH), Luviset® (BASF) and
35 Gafset® (GAF).

In addition to monomer units of the above formula (II), these polymers also have monomer units of the general formula (IV):



- 5
- Vinylpyrrolidone-vinyl acrylate copolymers, obtainable for example under the trademark Luviflex[®] (BASF). A preferred polymer is the vinylpyrrolidone-acrylate terpolymer obtainable under the designation Luviflex[®] VBM-35 (BASF).
 - 10
 - Acrylic acid-ethyl acrylate-N-tert-butylacrylamide terpolymers, which are marketed for example under the designation Ultrahold[®] strong (BASF).
 - 15
 - Graft polymers of vinyl esters, esters of acrylic acid or methacrylic acid alone or in a mixture, copolymerized with crotonic acid, acrylic acid or methacrylic acid with polyalkylene oxides and/or polyalkylene glycols
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Such grafted polymers of vinyl esters, esters of acrylic acid or methacrylic acid alone or in a mixture with other copolymerizable compounds onto polyalkylene glycols are obtained by polymerization under hot conditions in homogeneous phase, by stirring the polyalkylene glycols into the monomers of the vinyl esters, esters of acrylic acid or methacrylic acid, in the presence of free-radical initiators.

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Vinyl esters which have been found suitable are, for example, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate, and esters of acrylic acid or methacrylic acid which have been found suitable are those obtainable with low molecular weight aliphatic alcohols, i.e., in particular, ethanol, propanol,

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- 47 -

isopropanol, 1-butanol, 2-butanol, 2-methyl-1-propanol,
2-methyl-2-propanol, 1-pentanol, 2-pentanol,
3-pentanol, 2,2-dimethyl-1-propanol, 3-methyl-
1-butanol; 3-methyl-2-butanol, 2-methyl-2-butanol,
5 2-methyl-1-butanol, and 1-hexanol.

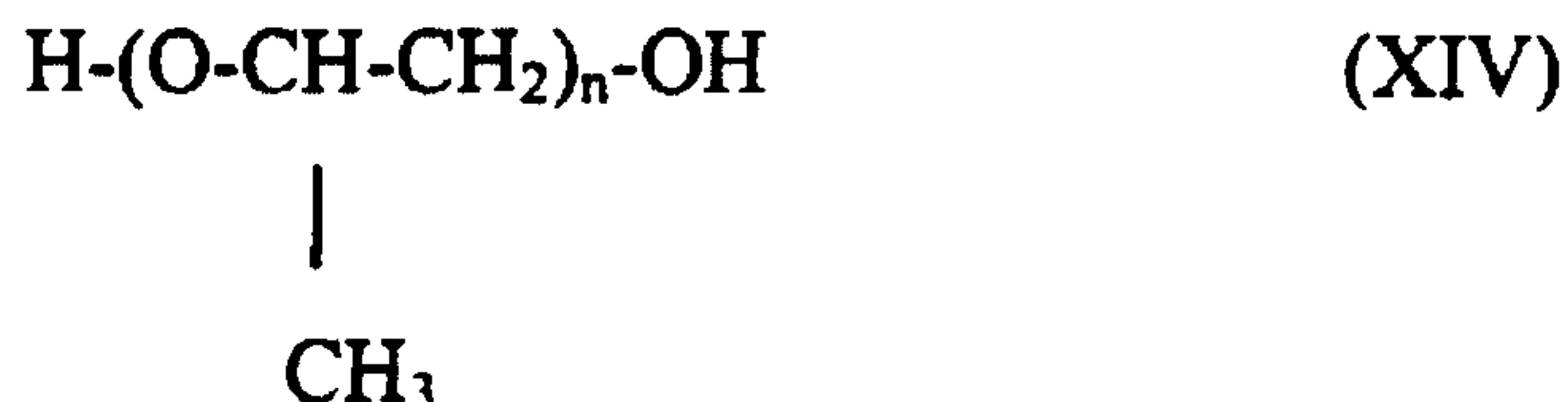
Suitable polyalkylene glycols include in particular
polyethylene glycols and polypropylene glycols.
Polyethylene glycols are polymers of ethylene glycol
10 which satisfy the general formula XIII



in which n may adopt values between 1 (ethylene glycol)
15 and several thousand. For polyethylene glycols there
exist various nomenclatures, which may lead to
confusion. It is common in the art to state the average
relative molecular weight after the letters "PEG", so
that "PEG 200" characterizes a polyethylene glycol
20 having a relative molecular mass of from about 190 to
about 210. For cosmetic ingredients, a different
nomenclature is used, in which the abbreviation PEG is
provided with a hyphen and the hyphen is followed
directly by a number which corresponds to the number n
25 in the abovementioned formula XIII. According to this
nomenclature (known as the INCI nomenclature, CTFA
International Cosmetic Ingredient Dictionary and
Handbook, 5th Edition, The Cosmetic, Toiletry and
Fragrance Association, Washington, 1997), for example,
30 PEG-4, PEG-6, PEG-8, PEG-9, PEG-10, PEG-12, PEG-14, and
PEG-16 may be used. Polyethylene glycols are available
commercially, for example, under the trade names
Carbowax[®] PEG 200 (Union Carbide), Emkapol[®] 200 (ICI
Americas), Lipoxol[®] 200 MED (HÜLS America), Polyglycol[®]
35 E-200 (Dow Chemical), Alkapol[®] PEG 300 (Rhone-Poulenc),
Lutrol[®] E300 (BASF), and the corresponding trade names
with higher numbers.

- 48 -

Polypropylene glycols (abbreviation PPGs) are polymers of propylene glycol which satisfy the general formula XIV



5 in which n may adopt values between 1 (propylene glycol) and several thousand. Industrially significant in this case are, in particular, di-, tri- and tetrapropylene glycol, i.e., the representatives where
10 n = 2, 3 and 4 in formula VI.

In particular, it is possible to use the vinyl acetate copolymers grafted onto polyethylene glycols and the polymers of vinyl acetate and crotonic acid grafted
15 onto polyethylene glycols.

- Grafted and crosslinked copolymers from the copolymerization of

- i) at least one monomer of the nonionic type,
- 20 ii) at least one monomer of the ionic type,
- iii) polyethylene glycol, and
- iv) a crosslinker

The polyethylene glycol used has a molecular weight of
25 between 200 and several million, preferably between 300 and 30,000.

The nonionic monomers may be of very different types and include the following preferred monomers: vinyl
30 acetate, vinyl stearate, vinyl laurate, vinyl propionate, allyl stearate, allyl laurate, diethyl maleate, allyl acetate, methyl methacrylate, cetyl vinyl ether, stearyl vinyl ether, and 1-hexene.

- 49 -

The nonionic monomers may equally be of very different types, among which particular preference is given to the presence in the graft polymers of crotonic acid, allyloxyacetic acid, vinylacetic acid, maleic acid, acrylic acid, and methacrylic acid.

Preferred crosslinkers are ethylene glycol dimethacrylate, diallyl phthalate, ortho-, meta- and para-divinylbenzene, tetraallyloxyethane, and polyallylsaccharoses containing 2 to 5 allyl groups per molecule of saccharin.

The above-described grafted and crosslinked copolymers are formed preferably of:

- i) from 5 to 85% by weight of at least one monomer of the nonionic type,
- ii) from 3 to 80% by weight of at least one monomer of the ionic type,
- iii) from 2 to 50% by weight, preferably from 5 to 30% by weight, of polyethylene glycol, and
- iv) from 0.1 to 8% by weight of a crosslinker, the percentage of the crosslinker being shaped by the ratio of the overall weights of i), ii) and iii).

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- Copolymers obtained by copolymerizing at least one monomer from each of the three following groups:

- i) esters of unsaturated alcohols and short-chain saturated carboxylic acids and/or esters of short-chain saturated alcohols and unsaturated carboxylic acids,
- ii) unsaturated carboxylic acids,
- iii) esters of long-chain carboxylic acids and unsaturated alcohols and/or esters of the carboxylic acids of group ii) with saturated

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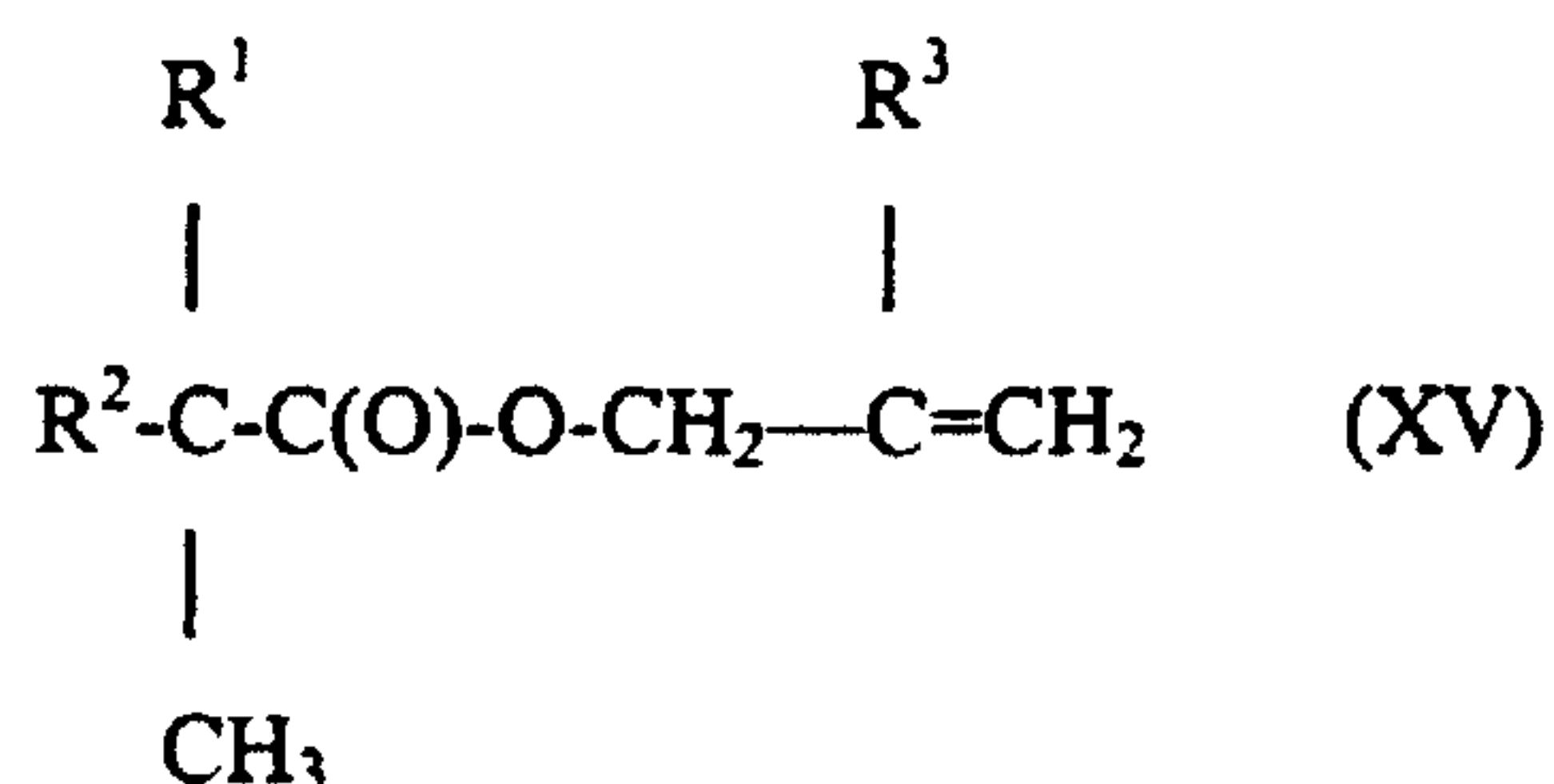
- 50 -

or unsaturated, straight-chain or branched
C₈₋₁₈ alcohols

Short-chain carboxylic acids and alcohols here are
5 those having 1 to 8 carbon atoms, it being possible for
the carbon chains of these compounds to be interrupted,
if desired, by divalent hetero-groups such as -O-,
-NH-, and -S-.

10 - Terpolymers of crotonic acid, vinyl acetate, and an
allyl or methallyl ester

These terpolymers contain monomer units of the general
formulae (II) to (IV) (see above) and also monomer
15 units of one or more allyl or methallyl esters of the
formula XV:



in which R³ is -H or -CH₃, R² is -CH₃ or -CH(CH₃)₂ and R¹
is -CH₃ or a saturated straight-chain or branched C₁₋₆
20 alkyl radical and the sum of the carbon atoms in the
radicals R¹ and R² is preferably 7, 6, 5, 4, 3 or 2.

The abovementioned terpolymers result preferably from
the copolymerization of from 7 to 12% by weight of
25 crotonic acid, from 65 to 86% by weight, preferably
from 71 to 83% by weight, of vinyl acetate and from 8
to 20% by weight, preferably from 10 to 17% by weight,
of allyl or methallyl esters of the formula XV.

30 - Tetra- and pentapolymers of
i) crotonic acid or allyloxyacetic acid
ii) vinyl acetate or vinyl propionate

- 51 -

- iii) branched allyl or methallyl esters
 - iv) vinyl ethers, vinyl esters or straight-chain allyl or methallyl esters
- 5 - Crotonic acid copolymers with one or more monomers from the group consisting of ethylene, vinylbenzene, vinyl methyl ether, acrylamide and the water-soluble salts thereof
- 10 - Terpolymers of vinyl acetate, crotonic acid and vinyl esters of a saturated aliphatic α -branched monocarboxylic acid.

Particularly appropriate capsule materials among the
15 anionic polymers are polycarboxylates/polycarboxylic acids, polymeric polycarboxylates, polyaspartic acid, polyacetals, and dextrans, which are described below.

Examples of organic capsule materials which may be used
20 are the polycarboxylic acids which may be used in the form of their sodium salts but also in free form. Polymeric polycarboxylates are, for example, the alkali metal salts of polyacrylic acid or of polymethacrylic acid, examples being those having a relative molecular
25 mass of from 500 to 70,000 g/mol.

The molecular masses reported for polymeric polycarboxylates, for the purposes of this document, are weight-average molecular masses, M_w , of the respective
30 acid form, determined fundamentally by means of gel permeation chromatography (GPC) using a UV detector. Measurement was made against an external polyacrylic acid standard, which owing to its structural similarity to the polymers under investigation provides realistic
35 molecular weight values. These figures differ markedly from the molecular weight values obtained using polystyrenesulfonic acids as the standard. The

- 52 -

molecular masses measured against polystyrenesulfonic acids are generally much higher than the molecular masses reported in this document.

5 Suitable polymers are, in particular, polyacrylates, which preferably have a molecular mass of from 2000 to 20,000 g/mol. Owing to their superior solubility, preference in this group may be given in turn to the short-chain polyacrylates, which have molecular masses
10 of from 2000 to 10,000 g/mol, and with particular preference from 3000 to 5000 g/mol.

Also suitable are copolymeric polycarboxylates, especially those of acrylic acid with methacrylic acid
15 and of acrylic or methacrylic acid with maleic acid. Copolymers which have been found particularly suitable are those of acrylic acid with maleic acid, containing from 50 to 90% by weight acrylic acid and from 50 to 10% by weight maleic acid. Their relative molecular
20 mass, based on free acids, is generally from 2000 to 70,000 g/mol, preferably from 20,000 to 50,000 g/mol, and in particular from 30,000 to 40,000 g/mol.

In order to improve the solubility in water, the
25 polymers may also contain allylsulfonic acids, such as allyloxybenzenesulfonic acid and methallylsulfonic acid, for example, as monomers.

Particular preference as capsule materials is also
30 given to biodegradable polymers comprising more than two different monomer units, examples being those comprising, as monomers, salts of acrylic acid and of maleic acid, and also vinyl alcohol or vinyl alcohol derivatives, or those comprising, as monomers, salts of
35 acrylic acid and of 2-alkylallylsulfonic acid, and also sugar derivatives.

- 53 -

Further preferred copolymeric capsule materials are those described in German Patent Applications **DE-A-43 03 320** and **DE-A-44 17 734**, whose monomers are preferably acrolein and acrylic acid/acrylic salts, and, respectively, acrolein and vinyl acetate.

Similarly, further preferred capsule materials that may be mentioned include polymeric amino dicarboxylic acids, their salts or their precursor substances. Particular preference is given to polyaspartic acids and their salts and derivatives.

Further suitable capsule materials are polyacetals, which may be obtained by reacting dialdehydes with polyol carboxylic acids having 5 to 7 carbon atoms and at least 3 hydroxyl groups. Preferred polyacetals are obtained from dialdehydes such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof and from polyol carboxylic acids such as gluconic acid and/or glucoheptonic acid.

Further polymers which may be used with preference as capsule materials are cationic polymers. Among the cationic polymers, the permanently cationic polymers are preferred. "Permanently cationic" refers according to the invention to those polymers which independently of the pH of the composition (i.e., both of the capsule and of the remaining composition that may be present) have a cationic group. These are generally polymers which include a quaternary nitrogen atom, in the form of an ammonium group, for example.

Examples of preferred cationic polymers are the following:

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- Quaternized cellulose derivatives, as available commercially under the designations Celquat[®] and Polymer JR[®]. The compounds Celquat[®] H 100, Celquat[®]

- 54 -

- L 200 and Polymer JR[®] 400 are preferred quaternized cellulose derivatives.
- Polysiloxanes with quaternary groups, such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethylsilylamodimethicone), Dow Corning[®] 929 emulsion (comprising a hydroxyl-amino-modified silicone, also referred to as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker), and Abil[®]-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxanes, Quaternium-80),
 - Cationic guar derivatives, such as in particular the products marketed under the trade names Cosmedia[®] Guar and Jaguar[®],
 - Polymeric dimethyldiallylammonium salts and their copolymers with esters and amides of acrylic acid and methacrylic acid. The products available commercially under the designations Merquat[®] 100 (poly(dimethyldiallylammonium chloride)) and Merquat[®] 550 (dimethyldiallylammonium chloride-acrylamide copolymer) are examples of such cationic polymers.
 - Copolymers of vinylpyrrolidone with quaternized derivatives of dialkylamino acrylate and methacrylate, such as, for example, with diethyl sulfate-quaternized vinylpyrrolidone-dimethylamino methacrylate copolymers. Such compounds are available commercially under the designations Gafquat[®] 734 and Gafquat[®] 755.
 - Vinylpyrrolidone-methoimidazolinium chloride copolymers, as offered under the designation Luviquat[®].
 - Quaternized polyvinyl alcohol
- and also polymers known under the designations
- Polyquaternium 2
 - Polyquaternium 17,
 - Polyquaternium 18, and

- 55 -

- Polyquaternium 27,
having quaternary nitrogen atoms in the polymer main
chain. These polymers are designated in accordance with
the INCI nomenclature; detailed information can be
5 found in the CTFA International Cosmetic Ingredient
Dictionary and Handbook, 5th Edition, The Cosmetic,
Toiletry and Fragrance Association, Washington, 1997,
which is expressly incorporated herein by reference.
- 10 Cationic polymers which are preferred in accordance
with the invention are quaternized cellulose
derivatives and also polymeric dimethyldiallylammonium
salts and copolymers thereof. Cationic cellulose
derivatives, especially the commercial product Polymer®
15 JR 400, are especially preferred cationic polymers.

The capsules of the invention may be used, for example,
in pharmaceutical and cosmetic preparations, and in
surfactant, laundry detergent, rinse, laundering aid,
20 cleaning product, and textile aftertreatment
compositions. It is possible, for example, to provide a
laundry detergent and cleaning composition comprising
only the capsules of the invention, which are dosed by
the user into the washing machine or dishwasher. Of
25 course, it is also possible to add the capsules to an
otherwise completely formulated cosmetic composition or
to a laundry detergent and cleaning composition in
order to give said composition additional utility
through the controlled release of certain active
30 substances.

The compositions to which the capsules of the invention
are added may be liquid, gellike, pasty, pulverulent or
granular, or in the form of compact tablets, with
35 hardly any limits imposed on formulation freedom.

By virtue of the temperature-controlled release
mechanism from the capsules of the invention it is

- 56 -

possible to attain controlled release of the capsule ingredients, which opens up new performance dimensions to the products.

5 For example, it is possible to add the capsules of the invention to a particulate detergent for machine dishwashing. In this case the capsules of the invention are designed so that the release of the ingredients is initiated only after cooling of the medium surrounding
10 them (the detergent liquor). On cooling, the medium surrounding the capsule enters the capsule, where it triggers a reaction which at least partially destroys the capsule wall. The duration of this procedure, and thus the time between the cooling of the external
15 medium and the release of the active substances from the capsule, may be varied by way of the thickness of the capsule wall, the physical and/or chemical stability of the capsule wall, the nature of the reaction destroying the capsule wall, and/or the
20 aggressiveness of the ingredients toward the capsule wall following entry of the external medium. For instance, capsules of the invention may be produced which do not release their ingredients in the main wash cycle (and also in optional prewash cycles) in a
25 domestic dishwasher. The main wash cycle is followed by intermediate wash cycles with cold water, so that the external medium enters into the capsule. Appropriate formulation of the capsule ensures that the active substances are not released until the rinse cycle,
30 where they develop their action. Thus, for example, rinse surfactants, acidifying agents or scale inhibitors may be ingredients of the capsules, thereby bringing about a rinse-clean effect. In addition to this chemical formulation, a physical formulation may
35 be necessary depending on the type of dishwasher, so that the capsules of the invention are not pumped off in the machine when the water is changed and hence are no longer available for the rinse cycle. Standard

- 57 -

domestic dishwashers, upstream of the detergent-liquor pump, which pumps the water or cleaning solution from the machine after the individual cleaning cycles, comprise a sieve insert, intended to prevent clogging
5 of the pump by food residues. If the user cleans heavily soiled kitchen- and tableware, then this sieve insert requires regular cleaning, which is a simple option owing to the ease of access and removeability. The capsules of the invention, then, are preferably so
10 designed in terms of their size and shape that they do no pass through the sieve insert of the dishwasher even after the cleaning cycle, i.e., after exposure to agitation in the machine and to the detergent solution. This ensures that capsules of the invention are present
15 in the dishwasher in the rinse cycle, these capsules releasing the active substance(s) under the action of the colder water after the main wash cycle, by at least partial destruction of the capsule wall, and so bringing the desired clean-rinse effect. Particulate
20 machine dishwashing compositions that are preferred in the context of the present invention are those wherein the capsules of the invention they comprise have particle sizes of between 1 and 20 mm, preferably between 1.5 and 15 mm, and in particular between 2 and
25 12 mm.

In particulate dishwashing compositions of this kind, the capsules of the invention, having the sizes stated above, may project from the matrix of the other
30 particulate ingredients; alternatively, the other particles may likewise have sizes within the stated range, so that, overall, a detergent composition is formulated that comprises large detergent particles and capsules. Especially if the capsules of the invention
35 are colored, i.e., have a red, blue, green, or yellow color, for example, it is advantageous for the appearance of the product, i.e. of the overall detergent composition, if the capsules are visibly

- 58 -

larger than the matrix comprising the particles of the other ingredients of the detergent composition. Here, preference is given to particulate machine dishwashing compositions which (not taking into account the capsules) have particle sizes between 200 and 3000 μm , preferably between 300 and 2500 μm , and in particular between 400 and 2000 μm .

If detergent compositions of this kind are formulated as a powder mixture, then - especially if there are large differences between the sizes of capsules and detergent matrix - on the one hand partial separation may occur when the pack is shaken, and on the other hand dosing may be different in two successive washing operations, since the user does not always automatically dose equal quantities of detergent and capsules. If it is desired technically to use an identical amount for each washing operation, this can be realized by the packaging - familiar to the skilled worker, of the compositions of the invention in water-soluble film bags. The present invention also provides particulate machine dishwashing compositions wherein one dose unit is welded in a water-soluble film bag. Of course, other cosmetic or pharmaceutical preparations or laundry detergent and cleaning compositions, such as textile detergents, for example, may also be provided in an entirely analogous manner.

By this means, the user need only insert a bag, containing for example a detergent powder and a plurality of visually distinctive capsules, into the dosing drawer of his or her dishwasher. This embodiment of the present invention is therefore a visually attractive alternative to conventional detergent tablets.

The detergent compositions of the invention may be prepared in conventional manner. A process for

- 59 -

preparing pulverulent machine dishwashing compositions with a rinse-clean effect, in which a conventional pulverulent machine dishwashing composition is mixed with capsules of the invention comprising surfactants and/or acidifying agents and/or scale inhibitors, is
5 therefore also provided with the present invention.

The above-described desired retention of the capsules in the machine, even when the water is changed, may be
10 realized not only by the abovementioned enlargement of the capsules but also by a reduction in the size of the holes in the sieve insert. In this way, it is possible for formulate machine dishwashing compositions having a uniform average particle size of less than, for
15 example, from 4 to 12 mm. For this purpose, the product of the invention, in which the capsules as well have relatively low particle sizes, is provided with a sieve insert which replaces or covers the insert present in the machine. The present invention additionally
20 provides a kit of parts comprising a pulverulent machine dishwashing composition of the invention and a sieve insert for domestic dishwashers.

As already mentioned, the novel combination of
25 composition and sieve insert permits the formulation of compositions in which the capsules as well have relatively low particle sizes. Kits of parts of the invention wherein the particle sizes of the machine dishwashing composition (taking into account the
30 capsules) are in the range from 400 to 2500 μm , preferably from 500 to 1600 μm , and in particular from 600 to 1200 μm , are preferred.

In order to prevent blockages of the added sieve insert
35 by food residues, the mesh size or hole size chosen should not be too small. Here, preference is given to kits of parts of the invention wherein the mesh size or hole size of the sieve insert is from 1 to 4 mm and the

- 60 -

rinse aid particles are larger than this mesh size or hole size of the sieve insert.

The kit of parts of the invention is not restricted to the particular form of the sieve insert in which said insert replaces or covers the insert present in the machine. In accordance with the invention it is also possible and preferred to provide the kit of parts with a sieve insert having the form of a basket which may be hung in a known manner in the dishwasher - on the cutlery basket, for example. In this way, a sieve insert of such design replaces the dispensing cup, i.e., the user doses the machine dishwashing composition of the invention directly into this sieve insert, which acts in the manner described above in the wash and rinse cycles.

The above example was based closely on conditions in standard domestic dishwashers. It is readily evident that, in an entirely analogous manner, pulverulent laundry detergents may be formulated which release, for example, fabric softener active substances only after the main wash cycle, from capsules of the invention comprising such active substances. In the fields of pharmacy, cosmetics, rinsing, and cleaning products in general, as well, in an entirely analogous manner, it is possible to formulate compositions which release the desired active substance from the capsules of the invention.

30

It is of course also possible to add the capsules of the invention to compact compositions or to incorporate them into them. For example, laundry detergent and cleaning product tablets may be produced which comprise one or more of the capsules of the invention. In this case, the capsule(s) may be attached either on or in the tablet. The first-mentioned embodiment may be realized, for example, by adhesively bonding one or

- 61 -

more capsules onto a conventionally produced tablet. The last-mentioned embodiment comprises, for example, the insertion of one or more capsules of the invention into the cavities of pre-produced tablets which have
5 depressions or holes passing through them. Particularly attractive from a visual standpoint is the insertion of a capsule of the invention into a ring-shaped tablet.

Examples

10

Production of capsules for use in machine dishwashing compositions

Example 1

15

The bottom parts of hard gelatin capsules of size 000 (volume 1.37 ml) and those of size 0 (volume 0.68 ml) from the company WEPA were filled with the substances shown in Table 1. Subsequently, the capsules were put together and the top and bottom parts were firmly
20 bonded. The capsules were coated with a basic polyacrylate (Eudragit® E from Röhm), giving a polymer coat with a thickness of between 0.2 and 0.3 mm. The aperture, with a diameter of 0.5 mm, was made in the bottom part of the capsule with the aid of a needle.

25

Subsequently, the capsule prepared in this way was placed in a glass beaker containing warm water at 20°C. The water was heated to 65°C (stage I); after reaching this temperature, the capsule remained at this
30 temperature for 10 minutes. The capsule was then placed for 5 minutes into water at 35°C (stage II), which was subsequently heated again to 65°C (stage III). This experimental procedure simulates the temperature/time regime of a universal program at 65°C in a dishwasher.

35

The ingredients of the individual capsules, and the capsule weight during the procedure and at the end of the experiment, are shown in Table 1 below.

- 62 -

Table 1

Capsule contents	Amount [g]	Capsule weight			
		Initial	Stage I	Stage II	Stage III
Polytergent ^{®1}	1.4	1.72	1.65	1.10	-
Polytergent ^{®1} (70%); Citric anhydride/ soda (30%)	0.7	0.90	?	0.55	-
Polytergent ^{®1} (70%) PEG 1550 ² (15%) citric anhydride/soda (15%)	0.7	0.95	0.80	0.4	-

Citric anhydride and soda were used in a weight ratio of 1:1

- 5 ¹ Polytergent[®] SLF-18 B 45: ethylene oxide-propylene
oxide block copolymer (alcohol alkoxylate from
Olin Chemicals, softening point 25-45°C)
- ² Polyethylene glycol with a molecular weight of
1550

10

Example 2

In this example, hard gelatin capsules of size 000
(volume 1.37 ml) from WEPA were treated further as
follows: the bottom part of the capsules was initially
15 prepared with 80-100 mg of polyethylene glycol
(PEG 3000), an inner coating being applied in the
region of the capsule end. Subsequently, the bottom
part of the capsule was filled with the following
composition:

20

Ingredient	Amount [% by weight]
Polytergent [®] SLF18B45	74.8
Sulfamic acid	14.0
Cetylstearyl alcohol	11.2

- 63 -

The amount of contents in the capsules was 1.3 g. Following the assembly of the capsule, the residual volume of air enclosed in the capsule was 10% of the total volume.

5

Various coatings were subsequently applied to the capsules, the composition of said coatings being indicated, in % by weight, in the table below.

Ingredient	Formulation 1	Formulation 2	Formulation 3
Eudragit® E	100.0	73.0	-
Vitacel® P 290	-	27.0	53.0
Eudragit® S 12.5 P	-	-	47.0

10

The following capsules were produced:

Type 1: 0.25 mm coat of formulation 2

Type 2: 0.04 mm coat of formulation 1, then 0.15 mm
15 coat of formulation 3

The capsules were subsequently provided with a hole (diameter 0.5 mm) at the capsule end.

20 The capsules produced in this way were each used together with a tablet-form detergent in a 55°C and a 65°C program in standard commercial dishwashers (Bosch S 712, Miele G 590). The rinse aid tank of the machines was emptied prior to the tests, so that any rinse-clean
25 effects arising are brought about by the capsules of the invention.

Observation over the running time of the different programs revealed no visual changes in the capsules of
30 type 1 and of type 2 during the wash cycle and the intermittent rinsing. During the final rinse cycle, the capsules broke down and the contents were released.

- 64 -

In all of the tests, the rinse-clean effects on glasses, plates and pans were at least equivalent to those found in comparative tests with conventional rinse-aid dosing via the automatic mechanism of the
5 machine.

The invention may be varied in any number of ways as would be apparent to a person skilled in the art and all obvious equivalents and the like are meant to fall
10 within the scope of this description and claims. The description is meant to serve as a guide to interpret the claims and not to limit them unnecessarily.

- 65 -

CLAIMS

1. A capsule for the controlled release of an active
5 substance, comprising
 - (A) a substance apt to destroy the capsule wall by means of reaction with the capsule material and/or with a further substance,
 - (B) a gas which under storage conditions does not
10 react with the contents of the capsule, and
 - (C) the active substance,the capsule wall having an aperture for the emergence of the components present therein.
- 15 2. The capsule as claimed in claim 1, wherein the material used for the capsule wall is an acid-soluble, alkali-soluble or water-soluble polymer or a polymer which softens at relatively high temperatures.
- 20 3. The capsule as claimed in claim 1 or 2, wherein the aperture in the capsule wall has a size of up to 1 mm.
- 25 4. The capsule as claimed in any of claims 1 to 3, wherein component A is selected from crystalline acids and/or bases, from components or mixtures which in reaction with water form a gas, and/or from substances which are swellable in water.
- 30 5. The capsule as claimed in any of claims 1 to 4, wherein said gas is selected from air, N₂, O₂, and CO₂.
- 35 6. The use of the capsule as claimed in any of claims 1 to 5 in machine cleaning compositions for cleaning textiles and hard surfaces.

- 66 -

7. The use as claimed in claim 6, wherein the active substance is selected from rinse-aid surfactants, textile treatment compositions (fabric softeners), enzymes, bleaches, bleaching catalysts, bleach activators, and/or optical brighteners.
5
8. The use as claimed in claim 7, wherein said rinse-aid surfactants are selected from nonionic surfactants, preferably selected from the group of
10 fatty alcohol polyethylene glycol ethers, fatty alcohol polyethylene/polypropylene glycol ethers, mixed ethers and/or hydroxyalkyl polyethylene glycol ethers.
- 15 9. The use of the capsule as claimed in any of claims 1 to 5 for delivering cosmetic or pharmaceutical active substances.
- 20 10. The use as claimed in claim 6, wherein kitchenware and tableware are cleaned.