

Production of dipped articles

5 The present invention relates to a process for producing dipped articles, in which a former is dipped into an aqueous latex dipping formulation in order to form a continuous polymer film on the surface of the shaped former.

10 Aqueous latices (aqueous polymer dispersions) are widely known. They are fluid systems whose disperse phase in the aqueous dispersion medium comprises polymer coils (referred to as polymer particles) consisting of a plurality of intertwined polymer chains and is in disperse distribution.

15 Unlike polymer solutions, latices do not form thermodynamically stable systems. Instead, the system attempts to reduce the polymer/dispersion medium interface by combining small primary particles to form larger, secondary particles, a process which
20 can be prevented for a relatively long period, in the state of disperse distribution in the aqueous medium, by adding dispersants (substances which are able to stabilize the dispersed polymer/aqueous dispersion medium interface).

25 This means that aqueous polymer dispersions contain the potential, given controlled deactivation of the dispersant by a partial or complete fusion of the dispersed polymer particles, to form a coherent polymer matrix.

30 Whereas chemical linking of different polymer chains within the polymer particles tends generally to be disadvantageous in terms of the formation of the aforementioned polymer matrix, subsequent chemical linking (crosslinking), after the polymer matrix has
35 formed, of the polymer chains which make up said matrix is often desirable in order to establish specific mechanical properties (elasticity, for example).

This set of circumstances is known and is employed to produce
40 dipped articles from aqueous polymer dispersions which are obtainable by free-radical aqueous emulsion polymerization of a mixture of monomers containing at least one ethylenically unsaturated group, at least 30 % by weight of said mixture consisting of monomers containing two conjugated ethylenically
45 unsaturated double bonds.

When a free-radical aqueous emulsion polymerization of this kind is conducted at temperatures which are not too high, possibly with the use of common molecular weight regulators such as mercaptans (eg. tert-dodecyl mercaptan or n-dodecyl mercaptan), it is generally the case that essentially only one of the two conjugated ethylenically unsaturated double bonds takes part in the polymerization reaction.

Consequently, aqueous polymer dispersions are obtained whose dispersed polymer coils consist of polymer chains which on the one hand are substantially noncrosslinked (ie. not chemically bonded to one another) but on the other hand still have ethylenically unsaturated double bonds which - following the formation of the desired polymer matrix by reputedly suitable sulfur-based vulcanization systems, which are incorporated into the aqueous polymer dispersion, with or without further auxiliaries and normally before the polymer matrix is formed, so as to give aqueous latex formulations (referred to below as aqueous latex dipping formulations) - can be activated in conjunction with elevated temperature and can be induced to undergo targeted reaction with the formation of intramolecular crosslinks, by means of which it is possible to establish a degree of crosslinking which is in tune with the desired performance properties.

Typical aqueous latex dipping formulations include (cf. eg. Kautschuk-Handbuch [Rubber handbook], Volume 4, Berliner Union Verlag, Stuttgart, 1961, p. 247):

30	Component	Parts by weight
	polymer in disperse distribution	100
	sulfur	0.25 to 2.5
	zinc oxide as vulcanization activator	0.25 to 10
35	vulcanization accelerator	0.5 to 1.5
	antiaging agent	0.5 to 1.0
	insoluble mineral fillers	0 to 10
	colorants	0 to 1.5
40	plasticizers	0 to 10

The use of vulcanization accelerators is necessary because of the slowness of the sulfur to react and because of the second olefinically unsaturated group of the copolymerized conjugated diene. The most important accelerators are thiazoles (also called mercapto accelerators), such as 2-mercaptobenzothiazole, its zinc salt and dibenzothiazyl disulfide, sulfenamides, such as

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benzothiazyl-2-cyclohexylsulfenamide,
benzothiazyl-2-tert-butylsulfenamide,
benzothiazyl-2-sulfenmorpholide and
benzothiazyl-dicyclo-hexylsulfenamide, guanidines, such as
5 diphenylguanidine, di-ortho-tolylguanidine and
ortho-tolylbiguanidine, thiurams, such as tetramethylthiuram
disulfide and tetraethylthiuram disulfide, dithiocarbamates, such
as zinc N-dimethyldithiocarbamate, zinc N-diethyldithiocarbamate,
zinc N-dibutyldithiocarbamate, zinc N-ethylphenyldithiocarbamate
10 and zinc N-pentamethylenedithiocarbamate, thiolene substances,
such as ethylenethiourea, diethylenethiourea and
diphenylthiourea, and also aldehyde-amine condensation products,
for example those of butyraldehyde and aniline. In many cases,
mixtures of vulcanization accelerators are also used.

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To produce their optimum activity the vulcanization accelerators
normally require the addition of zinc oxide as activator.

20 The reactivity with sulfur of the unsaturated groups which are
still present in the latex dipping formulation has the effect, on
the one hand, of making the vulcanization possible but also, on
the other hand, of inducing a sensitivity toward reactive
influences such as O₂ or UV radiation. A consequence of this
interaction is that the latex may become hard and brittle
25 (aging). Bacterial attack on the organic polymer is an additional
source of aging. To counter these effects, it is therefore usual
to add antiaging agents, such as Wingstay® L, to the latex
dipping formulation. The addition of fillers and/or plasticizers
makes it possible to influence the physical properties of the
30 dipped article.

In the dipping process, then, a shaped former is immersed in the
aqueous latex dipping formulation and a coherent polymer film is
35 deposited as a polymer matrix on the surface of the shaped former
through controlled coagulation. The shaped former is then removed
from the aqueous latex dipping formulation and dried, the polymer
film enveloping the shaped former is vulcanized by the action of
heat, and then the vulcanized dipped article (eg. nipples,
40 condoms, medical gloves, surgical gloves, industrial gloves,
household gloves, fingerstalls, balloons or specialty products
for medical use) is removed from the former and, if desired, is
washed, dried and possibly treated with powder or chlorinated.

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To carry out the controlled coagulation on the surface of the solid, two different principles have been realized in the prior art:

5 a) electrolyte coagulation

and

10 b) thermocoagulation.

Electrolyte coagulation uses an aqueous latex dipping formulation whose aqueous latex is stabilized in its disperse distribution predominantly by means of suitable anionic emulsifiers.

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In this document the term emulsifiers refers to surfactants whose relative molecular weight is ≤ 1000 and which, on dissolution in water (at 25°C and 1 atm) until a critical micelle concentration is obtained are able to reduce the surface tension σ of the water
20 by at least 25 % (based on the surface tension of pure water). By contrast, the term surfactant as used here refers merely to an amphiphilic substance which is able when dissolved in water (at 25°C and 1 atm) to reduce the surface tension of pure water. The attributive adjective amphiphilic indicates that surfactants have
25 both hydrophilic and hydrophobic groups. Anionic emulsifiers are those in which the hydrophilic groups in the aqueous medium carry a negative charge, these hydrophilic groups being opposed by small, monovalent cations which have little effect on the surface-active properties of the anionic emulsifi-
30 er, such as alkali metal or ammonium ions.

By oriented adsorption of the anionic emulsifier on the essentially nonpolar surface of the dispersed polymer particles, the latter acquire a negative surface charge, and are thereby
35 stabilized in their disperse distribution through the mutual repulsion of like charges.

Nonionic emulsifiers, on the other hand, possess no ionic charge
40 in the aqueous medium. The hydrophilicity of their hydrophilic group is instead generally brought about by the polarity of an increased number of covalently bonded oxygens.

The principle of electrolyte coagulation, then, is based on the
45 immersion into the aqueous latex dipping formulation of a former on whose surface there is adsorbed as coagulant an electrolyte (a substance which dissociates into anion and cation in the presence



of water) whose cation interacts with the anionic emulsifier group in such a way that it brings about controlled reduction of the stabilizing effect of said emulsifier group and initiates the desired coagulation.

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While electrolyte coagulation therefore uses an aqueous latex dipping formulation which reacts sensitively to addition of an electrolyte, thermocoagulation requires an aqueous latex dipping formulation which reacts sensitively to an increase in
10 temperature. To achieve this, coagulants are added which become active only above a certain temperature, the coagulation point. If a former at elevated temperature is immersed into an aqueous latex dipping formulation which has been thermally sensitized in this way, coagulation takes place at the surface of said former
15 and continues until the surface temperature of this former lies permanently below the preset coagulation point of the aqueous latex dipping formulation.

20 The preparation of dipped articles on the basis of pure thermocoagulation is described in the prior art (Kautschuk-Handbuch [Rubber Handbook], Volume 4, Berliner Union Verlag, Stuttgart, 1961, pp. 252-256; High Polymer Latexes, D.C. Blackley, Vol.2, MacLaren & Sons Ltd., London, 1966, p. 532; DE-AS 12 43 394; DE-A 14 94 037; Ullmanns Encyclopädie der
25 technischen Chemie [Ullmann's Encyclopedia of Industrial Chemistry], Verlag Chemie, Weinheim, Vol. 13 (Hormone-Keramik), 1977, p. 676; Bayer-Mitteilungen für die Gummi-Industrie, Vol. 32, Annual series 63, pp. 56-69;).

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It is advantageous insofar as high thicknesses of the deposited polymer matrix can be obtained in a relatively short time in the course of dipping.

35 A disadvantage of the abovementioned technique is that, for uniform thicknesses of the dipped article, formers are required whose temperature and heat capacity are uniform within very narrow limits. Moreover, particularly high removal rates are necessary in order to obtain a uniform film thickness along the
40 length of the former. Furthermore, the mechanical properties of the resulting dipped article are in many cases not entirely satisfactory.

The preparation of dipped articles on the basis of pure
45 electrolyte coagulation has likewise been described in the prior art (eg. US-A 2 880 189; EP-A 378 380; EP-A 456 333; Kautschuk-Handbuch (Rubber Handbook), Volume 4, Berliner Union

- Verlag, Stuttgart, 1961, pp. 246-252; High Polymer Latices, D.C. Blackley, Vol.2, Maclaren & Sons Ltd., London, 1966, pp. 530-532; Ullmanns Encyclopädie der technischen Chemie [Ullmann's Encyclopedia of Industrial Chemistry], Verlag Chemie, Weinheim, 5 Vol. 13 (Hormone-Keramik), 1977, p. 676; Bayer-Mitteilungen für die Gummi-Industrie, Vol. 32, Annual series 63, pp. 56-69;).

The advantages of preparing dipped articles by electrolyte coagulation are the increased reproducibility in the thickness of
 10 the dipped articles and the favorable mechanical properties which result. A disadvantage is the increased dipping time required for a predetermined film thickness, which is caused by the coagulation electrolyte taking a certain time to diffuse through the gradually thickening film and to bring about coagulation of
 15 further parts of the aqueous latex dipping composition.

It is an object of the present invention, in the light of the above, to provide a process for producing dipped articles, in
 20 which a former is dipped into an aqueous latex dipping formulation, which process combines the advantages of electrolyte coagulation with those of thermocoagulation.

We have found that this object is achieved by a process for
 25 producing dipped articles, in which a former at a temperature T on whose surface an electrolyte is adsorbed as coagulant is dipped, normally at 1 atm, into an aqueous latex dipping formulation comprising an aqueous polymer dispersion obtained by the method of free-radical aqueous emulsion polymerization of
 30 monomers containing at least one ethylenically unsaturated group, at least 30 % by weight of which monomers consist of monomers containing two conjugated ethylenically unsaturated double bonds, and which, based on the weight of the dispersed polymer, has had added to it

35	from 0.25 to 2.5 % by weight of	sulfur
	from 0.25 to 10 %, preferably from 0.5 to 5.0 %, by weight of	zinc oxide
40	from 0.5 to 1.5 % by weight of	vulcanization accelerator
	from 0.5 to 1.0 % by weight of	antiaging agent
45	from 0 to 10 % by weight of	insoluble mineral fillers

from 0 to 1.5 % by weight of	colorants and
from 0 to 10 % by weight of	plasticizer

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with the proviso that

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- the electrolyte adsorbed on the surface of the former is a Brønsted acid and/or a salt,
- the free-radical aqueous emulsion polymerization takes place in the presence of dispersants of which at least 50 % by weight consists of water-soluble alkali metal salts and/or ammonium salts of the monosulfonic acids of C₁₀-C₂₀ hydrocarbons,
- the aqueous latex dipping formulation comprises, as added thermal coagulant, a nonionic organosilicon surfactant which contains polyether groups and has a cloud point in the range from 20 to 60°C, preferably from 30 to 40°C, and
- the temperature T is above the cloud point of the organosilicon surfactant. T is expediently ≥ 40 to $\leq 150^\circ\text{C}$. Advantageously, T is from 60 to 90°C.

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The cloud point is that temperature at which the aqueous solution of the polyether-modified organosilicon compound, which is clear at 25°C, breaks down into two phases in the course of an increase in temperature (the cloud point is usually based on a 4 % strength by weight aqueous solution of the surfactant). The novel action of the abovementioned organosilicon surfactants is presumed to be based on their ability at low temperature to dissolve in an aqueous medium with hydration. When the temperature is increased, spontaneous dehydration apparently takes place when the cloud point is reached, with phase separation as a result of bonding of adducts to themselves and to the sulfonates employed as emulsifiers, which brings about the sudden latex coagulation.

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At their simplest, the polyether-modified nonionic organosilicon surfactants which are to be used in accordance with the invention (and are known and commercially available) are polyether-modified siloxanes containing hydrophobic groups, as described, for example, in DE-B 12 43 394, DE-B 17 94 418 and DE-A 14 94 037. However, they also embrace those polyether-modified nonionic organosilicon surfactants in which the polyether-modified

- organosilicon compound is grafted as hydrophilic moiety onto the polymer of a conjugated diene, preferably poly-1,2-butadiene, as hydrophobic moiety, as disclosed, for example, in DE-A 32 18 676, DE-A 23 21 557 and DE-C1 37 18 588. Suitable modifying polyether
- 5 groups are homo- and copolymers of alkylene oxides such as ethylene oxide, propylene oxide or isobutylene oxide. Preference is given to homopolymers of ethylene oxide. In general, the number-average relative molecular mass of the nonionic polyether-modified organosilicon surfactants to be used in
- 10 accordance with the invention is >1000 and <50,000. Preferred such surfactants are the commercial products Basensol® HA 5 (cloud point: 38°C) from BASF AG and Coagulant WS (cloud point: 32°C) from Bayer AG.
- 15 Based on the amount of dispersed polymer present in the aqueous latex dipping formulation to be used in accordance with the invention, the additional amount of polyether-modified organosilicon compound required in accordance with the invention is generally from 0.1 to 5 % by weight.
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- Among the alkali metal and/or ammonium salts of the C₁₀-C₂₀ hydrocarbonsulfonates to be used in accordance with the invention for the free-radical aqueous emulsion polymerization, the sodium
- 25 salts are preferred.
- Specific examples which may be mentioned are sodium dodecylsulfonate, sodium myristylsulfonate and sodium stearyl sulfonate as sulfonates of aliphatic C₁₀-C₂₀ hydrocarbons,
- 30 and sodium dodecylbenzenesulfonate as an alkylarylsulfonate. It is of course also possible to employ mixtures of such C₁₀-C₂₀ hydrocarbonsulfonates, as are widely available commercially (eg. C₁₀-, C₁₂- and C₁₃-alkylbenzenesulfonate mixtures or C₁₄-, C₁₅-, C₁₆- and C₁₇-alkanesulfonate mixtures).
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- For the free-radical aqueous emulsion polymerization and in accordance with the invention, it is usual to use from 0.1 to 5 % by weight, in most cases from 0.5 to 2 % by weight, of the water-soluble alkali metal and/or ammonium salts of the
- 40 monosulfonic acids of C₁₀-C₂₀ hydrocarbons, based on the amount of the resulting dispersed emulsion polymer.
- In addition to the alkali metal and/or ammonium salts of the monosulfonic acids of C₁₀-C₂₀ hydrocarbons which are required in
- 45 accordance with the invention, up to 50 % of the total weight of the dispersants employed for the free-radical aqueous emulsion polymerization may be accounted for by other dispersants.



Examples of these are other anionic and/or nonionic emulsifiers and/or surfactants, such as ethoxylated mono-, di- and trialkylphenols (degree of EO: 3 to 100, alkyl: C₄-C₁₂), ethoxylated fatty alcohols (degree of EO: 3 to 100, alkyl:

- 5 C₈-C₁₈), alkali metal and ammonium salts of alkyl sulfates (alkyl: C₈-C₁₆), of sulfuric acid half-esters of ethoxylated alkanols (degree of EO: 1 to 70, alkyl: C₁₂-C₁₈), of aryl sulfates and of alkylaryl sulfates (alkyl: C₉ to C₁₈) and of C₈-C₁₈ fatty acids and disproportionated resin acids obtained from rosin (Dresinates).
- 10 Of course, other suitable such dispersants are protective colloids such as polyvinyl alcohols, cellulose derivatives, copolymers containing vinylpyrrolidone, or polycondensates of naphthalenesulfonic acid and formaldehyde. Unlike emulsifiers and surfactants, they are not capable of forming micelles in the
- 15 aqueous polymerization medium and generally have relative molecular weights of > 1000. Moreover, they have hardly any effect on the surface tension of water. Suitable polycondensates of naphthalenesulfonic acid and formaldehyde (or water-soluble salts thereof), for example, have a relative molecular weight of
- 20 4000 to 8000. A combination of emulsifiers and protective colloids will frequently be employed when there is a desire, with monomers to be polymerized which are of markedly different solubility in water, for aqueous polymer dispersions whose dispersed polymer particles are, chemically speaking, of maximum
- 25 uniformity. The diameter of the resulting emulsion polymer particles is usually determined by the absolute amount of emulsifier employed. The weight-average diameter is preferably from 80 to 300 nm, particularly preferably from 100 to 250 nm, and with very particular preference from 100 to 200 nm.

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The amount of other dispersants employed (in addition to the sulfonates which are necessary in accordance with the invention) is advantageously not more than 25 %, or not more than 10 %, of the total weight thereof. Favorable embodiments of the invention

35 are those in which no additional dispersants are used.

- For preparing the aqueous polymer dispersion which forms the basis of the aqueous latex dipping formulation to be used in
- 40 accordance with the invention, the monomer mixture to be polymerized by the method of free-radical aqueous emulsion polymerization may comprise monomers containing only two conjugated ethylenically unsaturated groups (monomers A) or else may additionally comprise comonomers which are different from the monomers A and contain at least one ethylenically unsaturated
- 45 group. Frequently, the proportion of the monomers A in the monomer mixture to be polymerized in accordance with the invention is from 30 to 90 % by weight, often from 40 to 70 % by



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weight and in many cases from 50 to 70 % by weight. Examples of possible monomers A are butadiene, 2-methylbutadiene, 2,3-dimethylbutadiene, 1,3-pentadiene or 2,4-pentadiene, or mixtures thereof. Monoethylenically unsaturated comonomers which at atmospheric pressure (1 atm) and 25°C have an increased molal water-solubility (greater than that of acrylonitrile) (monomers B) are generally included in the mixture of monomers which is to be polymerized in amounts of up to 10 % by weight, often from 3 to 8 % by weight. Examples of common monomers B are α,β -monoethylenically unsaturated C_3 - C_6 mono- and dicarboxylic acids, such as acrylic, methacrylic, maleic, fumaric and itaconic acids, their salts (especially the alkali metal salts and the ammonium salt), their amides, for example acrylamide and methacrylamide, and also vinylsulfonic acid and its water-soluble salts (especially the alkali metal salts and the ammonium salt) and N-vinylpyrrolidone. It is of course also possible to employ the monomers B as a mixture. While butadiene is the preferred monomer A, methacrylic acid is preferred as monomer B.

The proportion of other copolymerizable monomers containing an ethylenically unsaturated group (monomers C) may be up to 70 % by weight. Frequently the proportion of the monomers C is from 10 to 70 %, often from 30 to 60 %, and in many cases from 30 to 50 %, by weight. Examples of suitable monomers C are vinyl-aromatic monomers, such as styrene, vinyltoluene or o-chlorostyrene, acrylonitrile, methacrylonitrile and esters of acrylic or methacrylic acid with C_1 - C_8 alkanols, and the mixtures of these monomers, among which styrene, acrylonitrile and methyl methacrylate and mixtures thereof are particularly suitable as monomers C.

Consequently, suitable aqueous dispersions of free-radical aqueous emulsion polymers are those obtained from monomer mixtures consisting of

from 30 to 100 % by weight of	monomers A,
from 0 to 10 % by weight of	monomers B and
from 0 to 70 % by weight of	monomers C.

These comprise free-radical aqueous emulsion polymers of monomer mixtures consisting of

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- from 30 to 100 % by weight of at least one monomer from the group consisting of butadiene, 2-methylbutadiene and 2,3-dimethylbutadiene,
- 5 from 0 to 10 % by weight of at least one monomer from the group consisting of acrylic, methacrylic, maleic, fumaric and itaconic acids and acrylamide and methacrylamide, and
- 10 from 0 to 70 % by weight of at least one monomer from the group consisting of styrene, acrylonitrile and methyl methacrylate.
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In particular, they include free-radical aqueous emulsion polymers of monomer mixtures consisting of

- 20 from 30 to 100 % by weight of butadiene,
from 0 to 10 % by weight of methacrylic acid, and
from 0 to 70 % by weight of acrylonitrile.

25 The abovementioned monomer mixtures likewise produce suitable free-radical aqueous emulsion polymers if the proportions by weight of the abovementioned combinations of monomers A, B and C break down as follows:

- 30 from 30 to 90 % by weight of monomers A,
from 1 to 10 % by weight of monomers B, and
from 9 to 60 % by weight of monomers C.

35 or

- from 40 to 80 % by weight of monomers A,
from 1 to 10 % by weight of monomers B and
40 from 19 to 50 % by weight of monomers C.

or

- 45 from 45 to 70 % by weight of monomers A
from 3 to 10 % by weight of monomers B and

from 27 to 45 % by weight of monomers C.

This is particularly the case if the monomers A are only butadiene, the monomers B are only methacrylic acid and the
5 monomers C are only acrylonitrile.

As already mentioned, to limit the degree of crosslinking the free-radical aqueous emulsion polymerization generally takes
10 place in the presence of molecular weight regulators (chain transfer agents) such as, for example, mercaptans (alkanethiols), advantageously of 3 to 15 carbons. In general, tert-dodecyl mercaptan and/or n-dodecyl mercaptan are employed as such regulators. The free-radical aqueous emulsion polymerization
15 typically takes place in the presence of from 0.1 to 3 % by weight, frequently from 0.5 to 1.5 % by weight, of such regulators, based on the monomers which are to be polymerized.

Suitable free-radical polymerization initiators for carrying out
20 the aqueous emulsion polymerization are in principle all those which are able to initiate such a polymerization. They may include both peroxides and azo compounds. To limit the degree of crosslinking of the resulting emulsion polymer, preference is given to initiator systems decomposing at $\leq 55^{\circ}\text{C}$. Consequently,
25 preference is given to the use of combined systems composed of at least one reducing agent and at least one peroxide and/or hydroperoxide, since the reducing agents activate the formation of free radicals and thus enable the novel free-radical aqueous emulsion polymerization to start at low temperatures.

30 Examples of suitable reducing agents are ascorbic acid, acetone bisulfite, sodium hydroxymethanesulfinate, sodium sulfite, sodium bisulfite or sodium dithionite. With particular preference the abovementioned combined (redox initiator) systems also include a
35 small amount of a metal compound which is soluble in the polymerization medium and whose metallic component can exist in two or more valence states.

Examples of such metal compounds are iron(II) salts such as
40 iron(II) sulfate. Instead of a water-soluble iron(II) salt, use is frequently made of a combination of water-soluble Fe/V salts. Redox initiator systems of this kind, containing such a metal compound, are of advantage insofar as they enable the novel
45 free-radical aqueous emulsion polymerization to start at even lower temperatures. Examples of such redox initiator systems are ascorbic acid/iron(II) sulfate/hydrogen peroxide or sodium dithionite and/or sodium formaldehyde sulfoxylate/iron(II)

sulfate/paramenthane hydroperoxide or diisopropylbenzene hydroperoxide or cumene hydroperoxide. In many cases, redox initiator systems of this kind, containing a metal compound, also have added to them a small amount of a chelating agent, so as to ensure that the metallic component is in solution and is not removed from the reaction system as a result, for example, of a precipitation reaction. Examples of such chelating agents are the sodium salts of ethylenediaminetetraacetic acid. Often, the metallic component is actually added directly in the form of a chelate complex.

Based on the monomers to be polymerized, the amount of initiator to be used is generally from 0.01 to 5 % by weight, in most cases from 0.01 to 1 % by weight. In accordance with the invention, polymerization is normally carried out under inert gas. Sodium dithionite is likewise suitable as a scavenger of residual oxygen. Moreover, in order to stabilize the pH of the aqueous dispersion medium during the emulsion polymerization it is possible to add pH buffers, such as alkali metal phosphates. The addition of small amounts of strong electrolytes, such as potassium sulfate, potassium chloride and/or sodium sulfate, is known to make it easier to establish the desired polymer particle diameter through its controlling influence in the particle formation phase.

Very generally, the temperature, nature and quantity of molecular weight regulator, and conversion of the polymerization are advantageously matched to one another so as to give aqueous polymer dispersions whose crosslinking density is such that the transversal nuclear-magnetic relaxation time of the protons bonded chemically to the polymer ($^1\text{H}_T$) is from 2.5 to 4.5 ms. These values relate to a sample of the respective aqueous polymer dispersion from which a film is formed at 25°C and is then dried at 80°C for 2 h, measured on the sample at 140°C and a ^1H resonance frequency of 20 MHz. The relationship between $^1\text{H}_T$ and that the crosslinking density is pointed out, for example, in Macromolecules 27 (1994) 2111-2119. It rests ultimately on the facts that the transversal nuclear-magnetic relaxation time of an atomic nucleus which has a magnetic moment is a measure of its mobility in an external magnetic field, on the one hand, and that the crosslinking of mutually different polymer chains restricts their mobility, on the other hand. Therefore, the lower the mobility of a polymer chain, the greater the crosslinking density and the shorter the transversal nuclear-magnetic relaxation time of atomic nuclei which are bonded chemically to this polymer chain and have a magnetic moment.

The conversion of the free-radical aqueous emulsion polymerization is stopped, if required, generally by adding polymerization inhibitors such as dimethylhydroxylamine, and then still unreacted monomers are removed in a manner known per se by
5 deodorization (preferably stripping and/or steam distillation).

The realization of a free-radical aqueous emulsion polymerization as described above is disclosed, for example, in DE-A 195 45 096.

10 The simplest embodiment of the free-radical aqueous emulsion polymerization comprises introducing the entirety of the polymerization batch, with the exception of part of the polymerization initiator, into the polymerization vessel as
15 initial charge, initiating the polymerization by heating this charge to the polymerization temperature, and continuing the free-radical aqueous emulsion polymerization until the desired conversion is obtained, by successive addition of the remaining free-radical initiator and maintenance of the polymerization
20 temperature. If monomers are used which at the end of polymerization are difficult to remove, as residues, from the product mixture (eg. acrylonitrile), it may be expedient in the latter stage of polymerization to increase the relative proportion of more easily removable monomer types (for example
25 butadiene) by making a separate addition.

An alternative embodiment of the free-radical aqueous emulsion polymerization is offered by the method of continuous monomer feed. In this case, only a small part of the monomers to be
30 polymerized are charged initially to the polymerization vessel, and are expediently subjected to initial polymerization in the presence of an added seed latex, and then the remaining amount of the monomers to be polymerized is supplied continuously to the polymerization vessel in accordance with the rate at which they
35 are consumed, while maintaining the polymerization.

In general, the aqueous polymer dispersions to be used in accordance with the invention are prepared with a solids content of from 30 to 70 % by volume, usually from 40 to 50 % by volume.
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To prepare the aqueous latex dipping formulation to be used for the novel process, the required vulcanization system, with or without further auxiliaries, and the nonionic polyether-modified organosilicon surfactant are customarily incorporated into the
45 aqueous polymer dispersion obtained by the method of free-radical aqueous emulsion polymerization.

The thermal sensitizer is advantageously incorporated last. The remaining substances to be incorporated essentially comprise solids, which to develop their action need to be incorporated in as finely divided a form as possible. Powders generally have a high absorption capacity for water and are therefore difficult to incorporate, in the dry state, into aqueous polymer dispersions, since they remove serum from the latex and thereby in some cases induce coagulation. Other finely divided solids have a coagulating effect as a result not of a particularly high absorption capacity but of the fact that they possess a high positive surface charge. Consequently, the powder solids need to be prepared, prior to their incorporation into the latex, such that they are unable to bring about coagulation for either of the above reasons. They are therefore expediently made into a paste with water, to which protective colloids are normally added (generally by treatment in a ballmill for at least 24 hours). These colloids also prevent subsequent agglomeration of the powder particles, and have a high affinity for them. Protective colloids which are suitable from this standpoint are, for example, the water-soluble alkali metal salts of naphthalenesulfonic acid-formaldehyde condensates (eg. Tamol[®] NN 4501 from BASF AG; a 45 % strength aqueous solution of the sodium salt of a naphthalenesulfonic acid-formaldehyde condensate having a number-average relative molecular weight of 6500) or the water-soluble alkali metal salts of the partial mixed esters (C₁-C₆ alkanols) of styrene-maleic anhydride copolymers (eg. K-Scripset[®] 540, produced by mixing 625 g of water, 250 g of 10 % strength aqueous potassium hydroxide solution and 125 g of Scripset 540 from Monsanto (partial methyl/isobutyl mixed ester of a styrene-maleic anhydride (1:<1 molar) copolymer with a weight-average relative molecular weight of 180,000)). In many cases thickeners as well are added to the aqueous paste (examples being Collatex[®] AS/RK, Collatex A/RN or Collatex A/RE from Kelco; these compounds are ammonium alginates whose 1 % strength aqueous solution preferably has a viscosity of 350-650 mPa·s (20°C, Brookfield viscometer, model LV, 60 rpm, spindle 3)), in order to obtain a pastelike consistency. Vulcanization accelerators which can be used include both water-soluble and water-insoluble compounds. Water-insoluble accelerators are preferred, since they are not absorbed by porous dip-formers. Among these, those which are important in practice include in particular the ultra-accelerators of the dithiocarbamate group (eg. zinc N-diethyldithiocarbamate, zinc N-dimethyldithiocarbamate, zinc N-dibutyldithiocarbamate or zinc N-phenylethyldithiocarbamate) and the less strongly accelerating compounds of the mercaptobenzothiazole class (eg. zinc mercaptobenzothiazole). These solid vulcanization accelerators are

expediently likewise incorporated in the form of an aqueous paste.

Another part of the auxiliaries to be incorporated comprises
5 viscous liquids (eg. Wingstay S = antiaging agent (antioxidant)),
which are generally incorporated in aqueous emulsion form. In
this case, the emulsifiers and/or surfactants used are preferably
those which would also be suitable for carrying out the
free-radical aqueous emulsion polymerization and which have a
10 particularly high affinity for the liquid to be emulsified.
Further antiaging agents are Naugawhite® and Proxel® XL2 (bacte-
ricide).

15 Examples of possible mineral fillers, which are insoluble in the
aqueous medium, are quartz flour and also calcium silicates or
aluminum silicates. Particularly suitable colorants are the
Vulkanosol dyes and the Halizarin® pigments from BASF AG. Pos-
sible plasticizers are oils such as mineral oil, paraffin oil or
20 dibenzyl ether, which would likewise be incorporated in aqueous
emulsion form.

Suitable electrolytes present in adsorbed form on the former
surface include, in accordance with the invention and with the
25 character of the anionic sulfonate group, salts of monovalent or
polyvalent cations, such as calcium nitrate, calcium chloride,
aluminum sulfate, magnesium nitrate or zinc nitrate, which
preferably have good solubility in water, and also Brønsted acids,
especially strong examples such as formic, acetic or lactic acid.
30 Mixtures of such electrolytes are also suitable, of course. The
application of the electrolyte to the surface of the former is
preferably carried out by first of all dipping the former into a
solution of the electrolyte and then drying it. Suitable solvents
are lower alcohols, such as methyl and ethyl alcohol, water
35 and/or a mixture thereof. To avoid the coagulant solution
coalescing as it runs off from the former, and thus not uniformly
wetting it, the initial dipping solution generally and
conventionally includes a wetting agent (eg. ethoxylated
alkylphenols such as Lutensol® AP 10 in aqueous dipping solu-
40 tions). Materials which have proven suitable for the former are
glass, porcelain, ceramic or a light metal which must, however,
be free from Cu and Mn. In many cases these materials are also
enveloped in a textile fabric which serves as the base for the
subsequent dipped article. Heated formers are also suitable, of
45 course. The aqueous latex dipping formulation into which the for-
mer is immersed in the course of the novel process is generally
at from 10 to 40°C, usually from 10 to 30°C, and normally below

the cloud point of the nonionic organosilicon surfactant. Following the novel dipping of the former into the aqueous latex dipping formulations, the polymer film deposited on the surface of the former is generally washed in water, dried, vulcanized in hot
5 air and finally pulled off, washed again in water if desired, and treated with powder or chlorinated if required. It is of course also possible to carry out a plurality of sequential dipping operations in order to obtain particularly high film thicknesses.

10 With a low dipping time, the novel process ensures films which are of increased thickness, of improved reproducibility and of a quality which corresponds to that obtained on electrolyte dipping alone. Moreover, the resulting films have an enhanced handle, a
15 requirement made of medical gloves in particular. By varying the polymer content of the aqueous latex dipping formulation, the dipping time required for a particular film thickness can additionally be influenced. Higher polymer contents generally require shorter dipping times. In many cases, the aqueous latex
20 dipping formulation is rendered alkaline using NH_3 and prior to dipping is left to stand for a prolonged period (maturation). During this period, some of the ZnO dissolves, which in the case of carboxylated polymers frequently proves advantageous. In some cases, an alkali metal hydroxide, for example NaOH , is used
25 instead of NH_3 . The novel process is suitable, for example, for producing dipped articles with a film thickness of from 0.04 mm to 2 mm. The dipped articles involved are those known per se, ie. gloves, condoms, nipples, inflation balloons, fingerstalls, etc.

30 Examples

A) Preparation of latices LI and LII suitable for producing dipped articles

35 LI: Polymerization took place under N_2 and with the addition of Na dithionite, which in this case acted as an oxygen scavenger.

40 A polymerization vessel (stirred pressure reactor made from V2A stainless steel) was charged with a mixture

of

45 52 kg of water,
 23.52 kg of butadiene (47.3 % by weight),
 20.82 kg of acrylonitrile (41.9 % by weight),

18

2.90 kg of methacrylic acid (5.8 % by weight),

3.47 kg of a 40 % strength by weight aqueous solution of Na salt of secondary alkanesulfonic acid (C₁₃/C₁₇ mixture),

5 1.03 kg of a 45 % strength by weight aqueous solution of the naphthalenesulfonic acid-formaldehyde condensate corresponding to Tamol NN 4501 (number-average relative molecular weight: 6500),

10 86 g of sodium sulfate and

 40 g of a 40 % strength by weight aqueous solution of the disodium salt of ethylenediamine tetraacetic acid

15

and was cooled to 8°C.

20 Still at this temperature, 1.5 g of sodium dithionite and then

 4 g of sodium formaldehyde-sulfoxylate,
 609 g of tert-dodecyl mercaptan and

25 1.5 g of Sequestrene[®] Na-Fe (mixed Na-Fe salt of ethylenediaminetetraacetic acid)

30 were added at once. Subsequently, 9.0 g of a 90.5 % strength aqueous solution of cumene hydroperoxide were added all at once and then polymerization was carried out, still at 8°C, to a conversion of 40 mol %. Then, all at once, a mixture of

35 0.45 g of Sequestrene Na-Fe,
 4 g of sodium formaldehyde-sulfoxylate and
 400 g of water

40 and

11 g of a 90.5 % strength by weight aqueous solution of cumene hydroperoxide,

45 again all at once, were added, and the polymerization was continued, still at 8°C, to a conversion of 60 mol %. The polymerization temperature was subsequently raised to 10°C

19

and the polymerization was continued at this temperature until a polymerization conversion of 75 mol % had been reached.

5 Then, in a single addition,

2.51 kg of butadiene (5 % by weight) and
a mixture of

10 0.45 g of Sequestrene Na-Fe,
4 g of sodium formaldehyde-sulfoxylate and
3.7 kg water

15 and

11 g of a 90.5 % strength by weight aqueous solution of
cumene hydroperoxide

20 again all at once, were added and the polymerization was
continued at 15°C until a polymerization conversion of
98 mol % had been reached.

25 By adding a mixture of

590 g of 25 % strength by weight aqueous ammonia,
30 g of diethylhydroxylamine and
30 500 g of water

the polymerization stopped at the abovementioned conversion.
The solids content of the resulting aqueous polymer
dispersion was 45.5 % by weight.

35

Following the addition of 500 g of a 50 % strength by weight
aqueous solution of Naugawhite and 100 g of water, the
remaining monomers were largely removed by steam stripping.
The final aqueous polymer dispersion had a solids content of
40 44.7 % by weight. The weight-average polymer particle
diameter $\bar{d}_w$ was 110 nm and the film had a $^{1H}T_2$ value of
4.1 ms.

LII: Polymerization took place under N₂.

45 A feed supply vessel I was filled with a feed stream I
consisting of

20

11.1 kg of acrylonitrile (24 % by weight),
 22.7 kg of butadiene (49.1 % by weight),
 1.38 kg of methacrylic acid (2.9 % by weight) and
 5 305 g of tert-dodecyl mercaptan

10 A feed supply vessel II was filled with a feed stream II consisting of

5 kg of water and
 2.4 kg of a 40 % strength by weight aqueous solution
 15 of the Na salt of secondary alkanesulfonic acid (C₁₃-/C₁₇ mixture).

A polymerization vessel (stirred pressure reactor made of V2A stainless steel) was charged with a mixture
 20 of

12.9 g of the disodium salt of
 ethylenediaminetetraacetic acid,
 5.53 kg of butadiene (12 % by weight),
 25 5.54 kg of acrylonitrile (12 % by weight),
 760 g of a 33.5 % by weight aqueous polystyrene
 dispersion ($\bar{d}_w=30$ nm, containing as dispersant
 20 % by weight, based on the mass of
 polystyrene, of Na dodecylbenzenesulfonate) as
 30 seed latex
 and
 37.6 kg of water

35 and was conditioned at 53°C. Then 930 g of ammonium peroxodisulfate were added to the polymerization vessel, and the resulting mixture was polymerized at 53°C for 0.5 h. Subsequently, still at 53°C, feed stream I (over a period of
 40 7 h) and feed stream II (over a period of 9 h) were fed into the polymerization vessel, starting at the same time. After all of feed stream II had been added, the polymerization mixture was stirred at 53°C for 8 h more. The polymerization was then stopped by adding a mixture of

45 180 g of 25% by weight strength aqueous NH₃,
 1600 g of water,

21

46 g of hydroxylamine sulfate and
4.5 g of Na dodecylbenzenesulfonate.

5 The solids content of the resulting aqueous polymer dispersion was 49.8 % by weight.

10 After adding a mixture of 500 g of water and 2.4 kg of a 40 % strength by weight aqueous solution of the Na salt of secondary alkanesulfonic acid (C₁₃/C₁₇ mixture), the remaining monomers were largely removed by steam stripping.

15 The final aqueous polymer dispersion had a solids content of 48.6 % by weight. The weight-average polymer particle diameter $\bar{d}_w$ was 180 nm and the film had a t_{HT2} value of 2.6 ms.

B) Preparation of latex dipping formulations LTI to LTIII and comparison latex dipping formulations VLTI to VLTIII.

20 LTI: Into the entire quantity of the aqueous polymer dispersion LI obtained there were incorporated, as protection against aging, a mixture of

25 953 g of Wingstay-S,
8.5 g of Na dodecylbenzenesulfonate and
944 g of water

30 and a mixture of

35 1 kg of water,
1.98 kg of a 25 % strength by weight aqueous potassium Dresinate solution (Dresinat 214 K from Abieta Chemie GmbH in Gersthofen, DE) and
480 g of a 9.5 % by weight aqueous Proxel XL2 mixture.

40 220 g of the resulting aqueous formulation were removed and adjusted to a pH of 9 using concentrated aqueous NH₃, and the following constituents were added:

45 2 g of a mixture of

625 g of water,
125 g of K-Scripset and

22

- 250 g of 10 % strength by weight aqueous potassium hydroxide solution;
- 5 10 g of a 10 % strength by weight aqueous solution of the Na salt of a naphthalenesulfonic acid condensate corresponding to Tamol NN 4501, with a relative number-average molecular weight of 6500;
- 10 7 g of an aqueous formulation of finely divided ZnO, comprising
- 1000 g of ZnO,
- 15 10 g of Collatex AS/RK,
- 50 g of a 45 % strength by weight aqueous solution of the Na salt of a naphthalenesulfonic acid condensate corresponding to Tamol NN 4501 and
- 20 910 g of water;
- 1.6 g of an aqueous formulation of finely divided sulfur, comprising
- 25 910 g of water,
- 60 g of a 45 % strength by weight aqueous solution of the Na salt of a naphthalenesulfonic acid condensate corresponding to Tamol NN 4501,
- 30 30 g of Collatex AS/RK and
- 1000 g of sulfur;
- 1 g of an aqueous formulation of finely divided zinc mercaptobenzothiazole, comprising
- 35 940 g of water,
- 1000 g of zinc mercaptobenzothiazole,
- 40 50 g of a 45 % strength aqueous solution of the Na salt of a naphthalenesulfonic acid condensate corresponding to Tamol NN 4501 and
- 10 g of Collatex AS/RK;
- 45 1 g of an aqueous formulation of finely divided zinc N-diethyldithiocarbamate, comprising

23

5 940 g of water,
 1000 g of zinc N-diethyldithiocarbamate,
 50 g of a 45 % strength by weight aqueous solution
 of the Na salt of a naphthalenesulfonic acid
 condensate corresponding to Tamol NN 4501 and
 10 g of Collatex AS/RK;

10 the formulation was then diluted to a solids content of
 40 % by weight and left at 25°C for 24 h (maturation).
 Then a mixture of 1.8 g of water and 0.2 g of Basensol HA
 5 was added, for thermal sensitization, and maturation
 was continued at 25°C for 24 h. The resulting coagulation
 temperature was 44°C.

15 VLTII: As LTI, but no Basensol HA 5 was added.

 LTII: Into the entire quantity of the aqueous polymer
 dispersion LII obtained there were incorporated, as
20 protection against aging:

 46.2g of hydroxylamine sulfate,
 4.6 g of Na dodecylbenzenesulfonate,
 1.60 kg of water,
25 924 g of a 50 % by weight aqueous Naugawhite mixture
 and
 370 g of a 9.5 % by weight aqueous Proxel XL2
 mixture.

30 215 g of the resulting aqueous formulation were removed
 and formulated correspondingly in the same way as the
 aqueous polymer dispersion LI, containing added antiaging
 agent, was formulated to give LTI.

35 However, only 2 g instead of 7 g of the aqueous ZnO
 formulation were added. Also, 2 g instead of 1.6 g of the
 aqueous sulfur formulation were added. Moreover, the
 amount of Basensol HA 5 added was 0.8 g (dissolved in
40 7.2 g of water) rather than 0.2 g, and dilution was to a
 solids content of 25 % by weight. The resulting
 coagulation temperature was 41°C.

 VLTII: As LTII, but no Basensol HA 5 was added.

45

LTIII: As LTII, but the amount of Basensol HA 5 added was 0.9 g (dissolved in 8.1 g of water). In addition, only 1 g of aqueous sulfur formulation but 5 g of aqueous ZnO formulation were added. After dilution to a solids content of 25 % by weight, the coagulation temperature was 42°C.

VLIII: As LTIII, but no Basensol HA 5 was added.

10 C) Production of dipped articles

15 The dip-formers used were three ceramic cylinders (10 cm in diameter, 28 cm long, 16 cm immersion depth) VKH1, KH2 and KH3, which were at 70°C and differed only in that KH2 and KH3 carried an adsorbed surface layer of $\text{Ca}(\text{NO}_3)_2$, which had been applied as follows:

20 KH2: The clean ceramic cylinder was first heated to 70°C and then dipped at an immersion rate of 100 mm/sec into a solution of

25 350 g of calcium nitrate,
 639 g of water,
 10 g of glacial acetic acid and
 1 g of Lutensol AP10

30 in which it was left for 0.1 sec. The former was then removed (at a rate of 20 mm/sec) and dried at 70°C for 180 sec.

KH3: Like KH2, but the calcium nitrate solution consisted of

35 130 g of calcium nitrate,
 639 g of water,
 10 g of glacial acetic acid and
 1 g Lutensol AP10.

40 Moreover, the dip-formers VKH1, KH2 and KH3 were dipped in the aqueous latex dipping formulations which were at 25°C (in the case of pure thermal coagulation the rate of immersion was 50 mm/sec and the rate of removal was 65 mm/sec;
45 otherwise, the parameters were 65 mm/sec and 10 mm/sec respectively). After a defined residence time, the dip-formers were removed again and left at 25°C for 5 min.



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Subsequently, the dip-former, with its film deposited in the course of dipping, was immersed in water at 40°C for 5 minutes for the purpose of washing the films. It was then dried at 70°C for 30 min and subsequently vulcanized at 120°C for 30 min (in each case in air of the appropriate temperature). The film formed was then pulled off and a sample removed from it (type 2 in accordance with ISO 37:1994(E)) was analyzed at 23°C at 50 % relative atmospheric humidity (determination of the film thickness FD in μm ; determination of the tensile force ZK (mPa) required for extension 100 %, 200 %, 300 % and 500 %, standardized to the product of width and thickness of the testing site, the correspondingly standardized tear strength RK (mPa) and the elongation of break RD (increase in length of sample until tearing occurred, relative to the initial length, in %) in accordance with ISO 37:1994(E)). The results obtained were as follows:

Dip-former	Latex dipping formulation	Residence time	FD	ZK100	ZK200	ZK300	ZK500	RK	RD
KH2	LT II	10 sec	162	1.73	2.52	3.59	9.97	22.06	590
KH2	VLT II	10 sec	105	1.74	2.54	3.57	8.85	22.35	616

With the novel procedure in comparison with pure electrolyte coagulation, an identical residence time led to a film having essentially the same set of properties but with a thickness increased by more than 50 %.

VKH1	LTII	3 sec	117	1.02	1.29	1.56	2.53	10.17	727
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With pure thermal coagulation, the mechanical properties of the resulting film were unsatisfactory.

Dip-former	Latex dipping formulation	Residence time	FD	ZK100	ZK200	ZK300	ZK500	RK	RD
KH2	LT III	10 sec	181	1.99	3.05	4.55	13.76	25.79	567
KH2	VLT III	10 sec	110	1.97	3.08	4.58	13.45	23.63	563

With the novel procedure in comparison with pure electrolyte coagulation, an identical residence time led to a film having substantially the same set of properties but with a thickness increased by more than 50 %.

VKH1	LTIII	3 sec	124	1.26	1.63	2.06	4.12	16.31	681
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With pure thermal coagulation, the mechanical properties of the resulting film were unsatisfactory.

5	Dip-former	Latex dipping formulation	Residence time	FD
	KH3	LT III	10 sec	153
	KH3	VLT III	10 sec	92

10	Dip-former	Latex dipping formulation	Residence time	FD	RK
	KH2	LT I	10 sec	178	45.23
	KH2	VLT I	10 sec	140	46.55
	KH1	LT I	3 sec	204	37.39

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We claim:

1. A process for producing dipped articles, in which a former at a temperature T on whose surface an electrolyte is adsorbed as coagulant is dipped into an aqueous latex dipping formulation comprising an aqueous polymer dispersion obtained by the method of free-radical aqueous emulsion polymerization of monomers containing at least one ethylenically unsaturated group, at least 30 % by weight of which monomers consist of monomers containing two conjugated ethylenically unsaturated double bonds, and which, based on the weight of the dispersed polymer, has had added to it,

15	from 0.25 to 2.5 % by weight of	sulfur
	from 0.25 to 10 % by weight of	zinc oxide
	from 0.5 to 1.5 % by weight of	vulcanization accelerator
20	from 0.5 to 1.0 % by weight of	antiaging agent
	from 0 to 10 % by weight of	insoluble mineral fillers
	from 0 to 1.5 % by weight of	colorants and
25	from 0 to 10 % by weight of	plasticizer

with the proviso that

- 30
- the electrolyte adsorbed on the surface of the former is a Brønsted acid and/or a salt,
- 35
- the free-radical aqueous emulsion polymerization takes place in the presence of dispersants of which at least 50 % by weight consists of water-soluble alkali metal salts and/or ammonium salts of the monosulfonic acids of C₁₀-C₂₀ hydrocarbons,
- 40
- the aqueous latex dipping formulation comprises, as added thermal coagulant, a nonionic organosilicon surfactant which contains polyether groups and has a cloud point in the range from 20 to 60°C, and

45



- the temperature T is above the cloud point of the organosilicon surfactant.
2. A process as claimed in claim 1, wherein the cloud point of the added organosilicon surfactant is from 30 to 40°C.
3. A process as claimed in claim 1 or 2, wherein the temperature T is $\geq 40^{\circ}\text{C}$ to $\leq 150^{\circ}\text{C}$.
4. A process as claimed in claim 1 to 3, wherein the temperature T is from 60 to 90°C.
5. A process as claimed in claim 1 to 4, wherein the free-radical aqueous emulsion polymerization takes place in the presence of dispersants of which at least 75 % by weight consists of water-soluble alkali metal and/or ammonium salts of the monosulfonic acids of C₁₀-C₂₀ hydrocarbons.
6. A process as claimed in claim 1 to 4, wherein the free-radical aqueous emulsion polymerization takes place in the presence of dispersants which exclusively consists of water-soluble alkali metal and/or ammonium salts of the monosulfonic acids of C₁₀-C₂₀ hydrocarbons.
7. A process as claimed in claim 1 to 6, wherein a C₁₀-C₁₃-alkylbenzenesulfonate is used as at least one alkali metal and/or ammonium salt of a monosulfonic acid of C₁₀-C₂₀ hydrocarbons.
8. A process as claimed in claim 1 to 6, wherein a C₁₃-C₁₈-alkanesulfonate is used as at least one alkali metal and/or ammonium salt of a monosulfonic acid of C₁₀-C₂₀ hydrocarbons.
9. A process as claimed in claim 1 to 8, wherein Basensol HA 5 is employed as nonionic organosilicon surfactant containing polyether groups.
10. A process as claimed in claim 1 to 8, wherein Coagulant WS is employed as nonionic organosilicon surfactant containing polyether groups.



11. A process as claimed in claim 1 to 10, wherein the weight-average diameter of the dispersed polymer particles is from 80 to 300 nm.
- 5 12. A process as claimed in claim 1 to 10, wherein the weight-average diameter of the dispersed polymer particles is from 100 to 250 nm.
- 10 13. A process as claimed in claim 1 to 10, wherein the weight-average diameter of the dispersed polymer particles is from 100 to 200 nm.
- 15 14. A process as claimed in claim 1 to 13, wherein the aqueous polymer dispersion has been obtained by the method of free-radical aqueous emulsion polymerization of a monomer mixture of
- 20 from 30 to 100 % by weight of at least one monomer which has two conjugated ethylenically unsaturated groups (monomers A),
- 25 from 0 to 10% by weight of one or more monoethylenically unsaturated monomers whose molal solubility in water at 25°C and 1 atm is greater than the corresponding molal solubility in water of acrylonitrile (monomers B), and
- 30 from 0 to 70% by weight of one or more monoethylenically unsaturated monomers whose molal solubility in water at 25°C and 1 atm is $\leq$ the corresponding molal solubility in water of acrylonitrile (monomers C).
- 35 15. A process as claimed in claim 14, wherein the monomers A comprise at least one monomer from the group consisting of butadiene, 2-methylbutadiene, 2,3-dimethylbutadiene, 1,3-pentadiene and 2,4-pentadiene.
- 40 16. A process as claimed in claim 14 or 15, wherein the monomers B used comprise one or more monomers from the group consisting of α,β -monoethylenically unsaturated C_3 - C_6 mono- and dicarboxylic acids, their salts, their amides, vinylsulfonic acid, its salts, and N-vinylpyrrolidone.
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17. A process as claimed in claim 14 to 16, wherein the monomers C used comprise one or more monomers from the group consisting of styrene, vinyltoluene, o-chlorostyrene, acrylonitrile, methacrylonitrile and esters of acrylic or methacrylic acid with C₁-C₈ alkanols.
18. A process as claimed in claim 14 to 17, wherein butadiene is employed exclusively as monomer A.
19. A process as claimed in claim 14 to 18, wherein methacrylic acid is employed exclusively as monomer B.
20. A process as claimed in claim 14 to 19, wherein acrylonitrile or styrene is employed as monomer C.
21. A process as claimed in claim 14 to 20, wherein the composition of the monomer mixture to be polymerized by the method of free-radical aqueous emulsion polymerization is
- from 30 to 90 % by weight of monomers A,
from 1 to 10 % by weight of monomers B and
from 9 to 60 % by weight of monomers C,
22. A process as claimed in claim 14 to 21, wherein the composition of the monomer mixture to be polymerized by the method of free-radical aqueous emulsion polymerization is
- from 45 to 70 % by weight of monomers A,
from 3 to 10 % by weight of monomers B and
from 27 to 45 % by weight of monomers C.
23. A process as claimed in claim 22, wherein the monomer A is butadiene, the monomer B is methacrylic acid and the monomer C is acrylonitrile.
24. A process as claimed in claim 14 to 23, wherein the film of the aqueous polymer dispersion obtained in the course of free-radical aqueous emulsion polymerization has a transversal nuclear magnetic relaxation time of the protons bonded chemically to the polymer, ¹H T₂, of from 2.5 to 4.5 ms.

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