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PROCESS OF PRODUCING FILMS, COATINGS AND IMPREGNATIONS

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The present invention relates to a process for the preparation of films, coatings, impregnations and bondings.

Films, coatings, impregnations and bondings resistant to water have already been prepared with the aid of aqueous dispersions of organic film-forming polymerization products which after drying were no longer dispersible in water. It has also been proposed to employ for the same purpose aqueous dispersions of water-insoluble polyvinyl compounds containing a small amount of hydrophilic groups which rendered such dispersions more stable, but films, impregnations and coatings thus prepared are, however, not sufficiently resistant to water.

We have now found that films, coatings, impregnations and bondings well resistant to water can be prepared with advantage industrially from water-insoluble organic film-forming polymerization products containing a small amount of hydrophilic groups and shape-stable at ordinary temperature by separating the said polymerization products from the aqueous dispersions resulting from the emulsion polymerization of the corresponding monomers without plasticizing them, redispersing them in water, applying the dispersion thus obtained to a substratum, evaporating the water and rendering the residue plastic at least for a short time. It has been found that by this treatment the polymerization products lose their property of being redispersible and, therefore, become resistant to water. In separating the said polymerization products from the aqueous dispersions resulting from the emulsion polymerization it must be carefully avoided, that they come into the plastic state either by the action of heat or solvents, since otherwise they would no longer be redispersible. The water, contained in the dispersions must, therefore, be removed at temperatures as low as possible and organic solvents must be excluded.

For rendering the films, coatings or impregnations produced with the aid of the said polymerization products at least transiently plastic, they are exposed, for example to the action of heat. In practice, it is sufficient to heat the polymerization products to sintering. A water-resistant layer is thus obtained after cooling. Alternatively, the polymerization products are rendered plastic by adding to the redispersed polymerization products volatile solvents or non-volatile plasticizers; a water-resistant layer of the polymerization product will then be obtained already at room temperature after the water of the dispersion and the volatile solvent, if any present, have evaporated.

The use of such dispersions of the said redispersible polymerization products offers considerable advantages in practice, because the polymerization products can be stored and marketed in a solid state and the consumer only needs to disperse them before use. Hitherto the dispersions themselves had to be stored and shipped to the consumer, so that the large amounts of water in the dispersions were transported and big containers required, which facts made the manipulation of the products very inconvenient and, in addition, caused increased charges for transport. The redispersible polymerization products used according to the present invention in contradistinction to the dispersions hitherto practically exclusively used are not subject to coagulation under the influence of frost or shaking during the transport or prolonged storage.

Suitable water-insoluble organic film-forming polymerization products possessing a stable shape at ordinary temperature and forming stable dispersions with water are, for example, interpolymerization products of one or more water-insoluble vinyl compounds, as for example acrylic nitrile, styrene, vinyl ketones, vinyl chloride, acrylic esters, vinyl esters, vinyl ethers, butadiene or their homologues or substitution products or methacrylic or fumaric or maleic acid esters on the one hand with small proportions of one or more water soluble polymerizable compounds, as for example such as contain a carboxylic acid, carboxylic amide, hydroxyl or amino group, for example acrylic acid, methacrylic acid, maleic acid and fumaric acid, or their amides or water-soluble metal salts, furthermore methylol vinylmethyl ketone, acrylic acid ethanol amine esters, as also N-vinyl compounds, for example N-vinyl pyrrolidone or N-vinylpiperidone on the other hand. Polymerization products in which hydrophilic groups are produced by a chemical after-treatment, for example carboxylic or hydroxyl groups by the saponification of ester groups, can also be employed. Polymerization products which possess no stable shape, i. e. which are plastic and exhibit some flow already at ordinary temperature, are not suitable in the present process, since they are not redispersible and, therefore, do not fulfill one of the requirements of the present invention.

The dispersions to be used according to the present invention can be admixed with the substances usual in the production of films, coatings

and impregnations, as, for instance, pigments, dyes, fillers and the like substances.

The following examples serve to illustrate how the present invention may be carried out in practice, but the invention is not restricted to these examples. The parts are by weight.

Example 1

800 parts of vinyl chloride and 200 parts of vinyl benzoate are emulsified in a solution of 30 parts of sodium octodecane sulphonate, 30 parts of the reaction product of 1 mol. of octodecyl alcohol with 20 mols of ethylene oxide, 60 parts of acrylic acid and 10 parts of potassium persulphate in 3000 parts of water and polymerized in a pressure-tight vessel at 50° C. The dispersion obtained is dried below 60° C., yielding a white polymerization product which is hard at ordinary temperature and can be redispersed to a stable dispersion by treating with water rendered weakly alkaline.

A fabric made of staple fibres from regenerated cellulose is immersed into a 5 per cent dispersion prepared from the dry powder, and dried in the air. The resulting size can be easily removed with water. However, if the sized fabric is dried at a temperature above the sintering point of the polymerization product, for example, at about 100° C., the size becomes highly resistant to washing.

Example 2

500 parts of vinyl chloride and 500 parts of vinyl acetate are emulsified in a solution of 60 parts of sodium octodecane sulphonate, 60 parts of acrylic acid and 10 parts of potassium persulphate in 3000 parts of water and polymerized in a vessel resistant to pressure at 45° C. The dispersion thus prepared is freed from water, for example, by being atomized below 40° C. in known manner. A white polymerization product is obtained which is hard at ordinary temperature and gives a stable dispersion when treated with water rendered weakly alkaline.

Cotton linters are immersed into an aqueous dispersion containing 5 per cent of the dry powder and 40 per cent (with reference to the polymerization product) of butylacetate and dried in the open air at ordinary temperature. A size fast to washing in a marked degree is thus obtained.

By spraying a concentrated dispersion of the dried powder on to metallic surfaces and then exposing the article to temperatures of between 90° and 120° C., durable and waterproof coatings are obtained.

Example 3

750 parts of styrene and 250 parts of acrylic acid methyl ester are emulsified in a solution of 10 parts of the sodium salt of octodecane sulphonic acid, 10 parts of the reaction product of 1 mol of octodecyl alcohol with 20 mols of ethylene oxide, 20 parts of acrylic acid and 5 parts of potassium persulphate in 1000 parts of water and polymerized at from 75° to 90° C. There is obtained an about 50 per cent. aqueous dispersion of the polymerization product from which either the water is evaporated at ordinary temperature or which is freed from the water as quickly as possible at a moderately raised temperature, for example by atomizing in a "Krause" drier. The white polymerization product thus obtained is hard at ordinary temperature and can be repassed into a stable dispersion with water rendered weakly alkaline.

This dispersion of the dry powder of about 50 per cent strength is admixed with 30 parts of dibutyl phthalate as plasticizing agent and if desired with pigments and applied to plaster or masonry. Coatings which are fast to washing, rubbing and weathering are thus obtained.

Example 4

800 parts of styrene and 200 parts of methacrylic acid methyl ester are emulsified in a solution of 30 parts of sodium octodecane sulphonate, 3 parts of sodium persulphate and 40 parts of monomeric acrylic acid in 1000 parts of water and polymerized at from 80 to 85° C. The polymerization product obtained in the form of a dispersion of about 50 per cent is dried by atomizing at from about 60 to 65° C. A fine white powder is thus obtained which can again be made into a stable dispersion by treating with ammoniacal water.

By admixing 100 parts of an about 50 per cent of the aqueous dispersion prepared from the dry powder with 17 parts of dibutyl phthalate and 35 parts of water and applying the mixture onto paper or leather a glossy water-proof finish is obtained.

Example 5

500 parts of styrene and 500 parts of methacrylic acid methyl ester are emulsified in a solution of 30 parts of sodium octodecane sulphonate, 3 parts of sodium persulphate and 20 parts of monomeric acrylic acid in 1000 parts of water and polymerized at from 80 to 85° C. The polymerization product obtained in an about 50 per cent dispersion is dried by atomizing at from about 60 to 65° C. A fine white powder is obtained which can again be made into a stable dispersion by means of ammoniacal water.

By admixing 100 parts of an about 50 per cent dispersion from the dry powder with 35 parts of butyl phthalate and 35 parts of water and applying the mixture, if desired with an addition of pigments, to plaster and masonry, coatings fast to washing, rubbing and weathering are obtained.

Example 6

500 parts of vinyl benzoate and 500 parts of methacrylic acid methyl ester are emulsified in a solution of 30 parts of sodium octodecane sulphonate, 5 parts of sodium persulphate and 40 parts of monomeric acrylic acid in 1000 parts of water and polymerized at from 80 to 85° C. The polymerization product obtained in the form of a dispersion of about 50 per cent strength is dried by atomizing at about 60 to 65° C. A fine white powder is obtained which can again be made into a stable dispersion by means of alkaline water.

A mixture of 100 parts of an about 35 per cent dispersion of the dry powder and of 35 parts of tricresylphosphate is employed for bonding paper with paper, leather with leather, leather with wood or leather with paper. After drying, the joints between the said materials are very strong and resistant to water.

Example 7

10,000 parts of vinyl benzoate are emulsified in a solution of 200 parts of sodium octodecane sulphonate, 100 parts of an interpolymerization product from 75 parts of acrylic acid and 25 parts of dimethylaminoethyl vinyl ether, 400 parts of monomeric acrylic acid and 50 parts of sodium persulphate in 10,000 parts of water and polymerized at from 60 to 85° C. The polymerization product thus obtained in a dispersion of 50 per

cent strength is dried on a vacuum drying roller at between 30 and 35° C. A white powder is obtained which can again be made into a stable dispersion by means of alkaline water.

100 parts of an about 30 per cent aqueous dispersion from the dry powder are mixed with 5 parts of tricresylphosphate and made up with water to form a five per cent dispersion. Cell wool is plunged into this dispersion and then allowed to dry at 80° C. A finish highly resistant to washing is obtained.

Example 8

500 parts of vinyl chloride, 250 parts of vinyl acetate and 250 parts of vinyl benzoate are emulsified in a solution of 90 parts of sodium octodecane sulphonate, 20 parts of sodium polyacrylate, 10 parts of potassium persulphate and 40 parts of the sodium salt of monomeric acrylic acid in 3000 parts of water and polymerized at from 45 to 50° C. in a pressure-tight vessel. After drying the dispersion of the polymerization by atomizing at a temperature of from about 50 to 55° C., a fine white powder is obtained which can again be made up into a stable dispersion by means of water.

100 parts of an about 30 per cent aqueous dispersion prepared from the dry powder are mixed with 30 parts of tributylphosphate and the mixture is used for bonding wood to wood, paper to wood, cotton to cotton, cotton to wood or cotton to paper. Strong and water-proof joints are obtained after drying.

Example 9

1000 parts of styrene are emulsified in a solution of 30 parts of the product obtained by acting with chlorine and sulphur dioxide on a mixture of paraffinic hydrocarbons containing from 9 to 15 carbon atoms in the molecule and saponifying the resulting product with sodium hydroxide solution, 5 parts of sodium persulphate and 30 parts of monomeric acrylic acid in 1000 parts of water, and polymerized at from 85 to 90° C. By drying the dispersion of the polymerization product on a vacuum drying roller at 50° C., a fine powder is obtained which can again be made up into a stable dispersion by means of alkaline water.

By mixing 100 parts of a dispersion prepared from the dry powder with 5 parts of dibutyl phosphate and spraying the mixture onto metallic surfaces, water-proof coatings are obtained after drying at a temperature of from 110 to 150° C.

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