

1 565 529

- (21) Application No. 51970/76 (22) Filed 13 Dec. 1976
- (31) Convention Application No. 2556327
- (32) Filed 13 Dec. 1975 in
- (33) Federal Republic of Germany (DE)
- (44) Complete Specification published 23 April 1980
- (51) INT CL³ C08F 220/00 (C08F 220/00 212/08)
- (52) Index at acceptance
C3P 202 210 220 222 230 316 320 322 324 FE



(54) PROCESS FOR THE PREPARATION OF AQUEOUS PLASTICS DISPERSIONS

5 (71) We, HOECHST AKTIENGESELLSCHAFT, a Body Corporate
organised according to the laws of the Federal Republic of Germany, of 6230
Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby
declare the invention, for which we pray that a patent may be granted to us, and the
method by which it is to be performed to be particularly described in and by the
following statement:— 5

This invention relates to the preparation of aqueous polymer dispersions and
in particular to dispersions to be used for treating substrates.

10 Primers for preparing and solidifying substrates for subsequent coatings should
be able to allow the binder to penetrate the substrate thoroughly to ensure good
solidification after drying and to reduce the absorption power. The primer
therefore has to form a good ground coat for subsequent paint layers, and must also
be resistant to water, saponification and atmospheric influence. These
15 requirements have hitherto been met by solvent containing primers. However,
these primers have had various disadvantages, for example, the solvents can be
physiologically dangerous, and can also cause a fire risk; the tools used for applying
the primers have to be cleaned with solvents; the molecular weight of the binder
has to be maintained within a certain range since, at high molecular weight, the
viscosity of the primers is too high and does not allow a high binder concentration.

20 In contrast to solvent containing primers, aqueous plastics dispersions have
none of the above disadvantages: they do not contain inflammable or
physiologically intolerable solvents, the tools may be cleaned with water, and in
particular, such dispersions may have high solids contents even when the molecular
weight of the binders is high, without the viscosity being too great. They have the
25 added advantage that residual water in the paint coating dries more easily and more
rapidly than solvent residues. Furthermore, provided that their
emulsifier/protective colloid systems are compatible, a greater range of plastics
dispersions may be blended so that the scope of properties may be widely varied by
such mixtures.

30 Despite the advantages of aqueous systems, they have not as yet been
commercially successful in practice. Although water-soluble binders penetrate the
substrates well, because they are either not sufficiently water-resistance and/or
stable to saponification or when the plastics dispersions give coatings which are
stable to water and saponification, their depth of penetration is insufficient to
35 solidify and seal the substrate. It has been observed by copolymerizing optically
brightening monomers, the previously used dispersions do not penetrate cavities
and capillaries of the substrate to any significant extent due to their large average
particle diameter, but only form a film on the surface.

40 German Patent Specification No. 1,925,353 proposes a two-step process
according to which vinyl ester copolymer dispersions having particle sizes of less
than 0.2 μ are obtained. However, the manufacturing process is complicated and
the polymers obtained are not sufficiently stable to water and saponification.

45 The present invention provides a process for the preparation of a finely
distributed plastics dispersion, which comprises incorporating a monomer mixture
comprising:

I from 20 to 80% by weight of a hardening component comprising styrene or
methyl methacrylate or a styrene/methyl methacrylate mixture.

II from 20 to 80% by weight of a plasticising component comprising an ester of
one or more linear or branched alcohols having from 2 to 8 carbon atoms and

acrylic acid and/or an ester of one or more linear or branched alcohols having from 4 to 8 carbon atoms and methacrylic acid,

III from 0.1 to 5% by weight of an amide of an α, β -unsaturated carboxylic acid, and

IV from 0.1 to 5% by weight of an α, β -unsaturated monocarboxylic acid, in the form of the pure monomer mixture or a preliminary emulsion, simultaneously with an initiator, with an aqueous liquor containing an anionic emulsifier, said monomers being used in such an amount that the solids content of the final dispersion does not exceed 45% by weight, polymerising said monomers in said aqueous liquor to form said dispersion, and causing the dispersion so formed to have a pH in the range of from 7 to 10.

The monomers should be selected according to the rules known to those skilled in the art, for example, so that stable dispersions may be obtained and that the film-forming temperatures of the copolymers are in the range known to be favourable for coating techniques, that is, advantageously from about -10 to $+25^{\circ}\text{C}$.

The hardening component may consist wholly of styrene or wholly of methyl methacrylate, but it is especially advantageous for the hardening component to consist wholly of styrene.

In the case where the hardening component comprises a styrene/methyl methacrylate mixture, the proportion of methyl methacrylate in that mixture advantageously does not exceed 15% by weight.

Examples of the plasticising component are ethylacrylate, propylacrylate, isopropylacrylate and the acrylic or methacrylic acid esters of butyl alcohol and 2-ethylhexyl alcohol.

Further α, β -unsaturated copolymerisable monomers such as acrylonitrile, hydroxyethyl-methacrylate, hydroxypropyl-methacrylate, vinyl toluene or vinyl xylene may be concomitantly used in order to modify the properties of the copolymer. The total quantity of any such copolymerisable monomer preferably does not exceed 10% by weight, and more especially does not exceed 5% by weight, based on the total weight of the monomers.

The incorporation of one or more amides of α, β -unsaturated carboxylic acids, preferably monocarboxylic acids, especially acrylamide and/or methacrylamide, promotes the formation of finely distributed dispersions, when the or each amide is added to the batch in conjunction with the other monomers. Preferably, the quantity of the amide in the monomer mixture is in the range of from 1.5 to 3.5% by weight.

The incorporation of one or more α, β -unsaturated monocarboxylic acids into the copolymer increases the stability of the dispersion during its manufacture, storage and application. Acrylic and methacrylic acid in amounts of from 0.1% to 5% by weight, relative to the total amount of monomers, are preferred examples.

It should, however, be noted that the amides and the carboxylic acids are themselves hydrophilic monomers which tend to increase the hydrophilic nature of the total molecule. In order not to reduce the water resistance of the primer coats and coatings obtained with the use of the dispersions of the invention to a too great an extent, the total amount of these monomers is preferably in the range of from 0.2 to 8.5% by weight. The higher the content of hydrophobic monomers in the hardening and plasticising components and other α, β -unsaturated compounds (if present) the higher may be the content of the amides and carboxylic acids. The total content of amide and carboxylic acid monomers may approach the preferred upper limit of 8.5 per cent by weight when the other monomers are especially hydrophobic, such as styrene, butylacrylate, 2-ethylhexylacrylate or 2-ethylhexylmethacrylate, and should approach the lower limit of 0.2 percent when the other monomers are less hydrophobic such as methylmethacrylate, ethylacrylate, acrylonitrile or the hydroxy-alkylacrylates.

When α, β -unsaturated compounds are used in preparing the dispersion, the quantity and choice of compounds used should be such that the resistance to water and saponification of the resulting copolymer are not materially reduced.

Examples of suitable monomer combinations are the following (parts being given by weight):

Butylacrylate/styrene/acrylic acid and/or methacrylic acid/acrylamide and/or methacrylamide (40 to 80/60 to 15/0.1 to 4/0.1 to 4).

2-Ethylhexylacrylate/styrene/acrylic acid and/or methacrylic acid/acrylamide and/or methacrylamide (30 to 80/65 to 15/0.1 to 4/0.1 to 4).

2-Ethylhexylacrylate/methylmethacrylate/acrylic acid and/or methacrylic acid/acrylamide and/or methacrylamide (30 to 80/65 to 15/0.1 to 4/0.1 to 4).

Butylacrylate/methylmethacrylate/acrylic acid and/or methacrylic acid/acrylamide and/or methacrylamide (40 to 80/55 to 15/0.1 to 3/0.1 to 3).

The polymerization must be performed in the presence of an anionic emulsifier, for example, alkali metal salts of sulphuric acid semi-esters of alkylphenols or alcohols, which may be oxethylated; or alkyl or aryl sulphonates.

Preferred anionic emulsifiers are alkali metal salts of sulphuric acid semi-esters of a nonyl phenol reacted with from 4 to 5 moles of ethylene oxide; sodium lauryl sulphate, sodium lauryl ethoxylate sulphate containing from 2 to 5 moles of ethylene oxide; sodium dodecylbenzene sulphonate and secondary sodium alkane sulphonates having from 8 to 20 carbon atoms in the carbon chain.

The amount of anionic emulsifier may be from 0.5 to 10% by weight, preferably from 2 to 8% by weight, relative to the total weight of the monomers. Generally, an increase of the amount of anionic emulsifier used reduces the particle size.

In order to increase the stability of the dispersions, non-ionic emulsifiers, such as ethoxylated alkylphenols or ethoxylated fatty alcohols, and particularly nonylphenols having from 4 to 30 mols of ethylene oxide may be employed in addition and in admixture with the anionic emulsifier. When selecting the emulsifiers and monomers to be used and also the reaction conditions of the process, care should be taken that dispersions are obtained which do not form aggregates after manufacture or after dilution with water, since formation of larger aggregates may decrease the penetrating power when the finely distributed plastics dispersions are used for impregnation and in primer coatings.

As initiators to be used in the process, there may be mentioned the usual inorganic peroxy-compounds such as ammonium persulphate, potassium persulphate, sodium persulphate, or organic peroxides such as benzoyl peroxide, organic peresters such as perisopivalate. Advantageously the initiators also comprise a reducing agent such as sodium bisulphite, hydrazine or hydroxylamide. It is preferable to use, in addition to the initiators, catalytic quantities of accelerators such as salts of iron, cobalt, cerium and/or vanadium; preference is given to the use of alkali metal or ammonium peroxydisulphates.

The polymerization temperature varies generally in the range of from 10° to 100°C, preferably from 30° to 90°C.

The solids content of the final dispersion is preferably in the range of from 20 to 45%, by weight.

It is advantageous for the preparation of the dispersions having an especially fine particle size distribution for the polymerization to be carried out at low solids contents, since reduction of the solids contents generally gives finely distributed dispersions. As is shown in Table 1, dispersions containing coarser particles have less penetrating power and less solidifying effect than the finely distributed dispersions. In the case where finely distributed dispersions contain a proportion of coarser particles due to a broad distribution of particle sizes, these coarser particles do not contribute to the solidifying effect and penetrating power of the dispersion. Therefore, plastics dispersions having a narrow distribution of particle sizes are preferred.

After polymerization, the pH of the finely distributed dispersions is established at a value in the range of from 7 to 10, preferably from 7.5 to 9 and by means of alkali, ammonia or amines.

When dispersions having a low solids content are obtained, the solids content may be increased by vacuum distillation without retracting from the very fine distribution of the dispersions.

In a preferred process according to the invention the polymerization is carried out as follows:

30—50% of the water and from 20—50% of the anionic emulsifier are recharged together with from 10—50% of a non-ionic emulsifier. A preliminary emulsion is prepared from the monomers the remaining part of the water and the emulsifiers, and is metered over a period of from 1 to 3 hours into the liquor formed from the water and emulsifier which has been heated to 50—90°C. The ratio of monomers to water is chosen so that the resulting dispersion contains from 20 to 45% of solids.

The amount of anionic emulsifier is in the range of from 2 to 8%, relative to the monomers, depending on the solids content intended.

The reaction batch is then stirred, and, after termination of the feed, the whole

batch is stirred for another 1—3 hours at a temperature of from 70 to 90°C. The initiator is preferably added as a 1 to 5 per cent aqueous solution during the addition of the emulsion. Subsequently, the pH is adjusted to 7.5 to 9 by means of ammonia, aliphatic amines or alkali metal hydroxides.

The addition of the monomers in the form of a preliminary emulsion is not essential for preparing the plastics dispersions: they may also be obtained by metering the monomer mixture into a liquor containing all the water and the emulsifiers.

When plastics dispersions are to be used for priming and impregnation, the solids content of the dispersions has a decisive influence on the penetrating depth, the solidifying effect and the absorption of the treated substrates.

Dilute dispersions penetrate deeper into the substrate pores than concentrated dispersions. When using concentrated dispersions, only some of the particles penetrate into the substrate pores, the others forming a film on the substrate surface.

Therefore, on application, concentrated dispersions reduce the absorption of the substrate to a very high degree, while dilute dispersions only reduce the absorption of the substrate by a small degree.

The solidifying effect depends both on the nature of the polymer and on the amount of polymer per unit area of the treated surface. Although dilute dispersions penetrate deeply into the substrate, the amount of plastics material per unit area is relatively low. In the case of concentrated dispersions, that part of the polymer which remains on the surface after drying does not contribute to the solidification of deeper layers.

It is therefore possible to adjust the ratio of penetrating depth, solidification and sealing of the surface, and to adapt these parameters to the various substrates encountered in practice by a corresponding choice of the solids content. Using the dispersions of the invention, good results are obtained at solids contents of from 5 to 25% by weight, preferably from 10 to 20% by weight. One advantage of the dispersions of the invention resides in the fact that within a relatively wide concentration range an especially favorable ratio of good penetrating depth and good solidification can be obtained by a high specific plastics amount in the treated surface, when the mean particle size is in the range of from 0.01 to 0.06 μm (the mean particle size being determined by the light scattering method and electron microscopy).

As is current practice for dispersion paints, auxiliaries may be added. Examples of such auxiliaries are solvents for improving film formation and for lowering the film-forming temperature, plasticizers, defoamers, preservatives, surface-active agents for improving wetting, and pigments or soluble dyestuffs.

The degree of penetration may be tested by different methods. The material to be submitted to such a test may be applied to the chosen substrate, for example, by brushing, pouring or dropping. After drying, the penetrated material may then be identified by means of its cross-section. If dissolved resins are used, they may be coloured by soluble dyestuffs. This method can however lead to spurious results, as the aqueous phase may be coloured simultaneously. Since the aqueous phase of most dispersions penetrates deeper than the particles, the coloured zone of the cross-section may not correspond to the actual penetration of the particles.

In order to demonstrate the improved penetration of the dispersions of the invention copolymer dispersions containing optical brighteners were prepared by copolymerization with vinyl-sulphonyl-pyrazoline-brighteners at concentration rates of from 0.01—0.05% (based on the monomers). The polymers so prepared contained a random distribution of brightener molecules as structural units, all over the macromolecule which forms the particle and so the optical brightener could not be extracted from the polymer. The polymer is therefore located in the substrate exactly where the optical brightener shows the characteristic fluorescence under UV radiation. The finely distributed copolymer dispersions containing optical brighteners were applied onto a number of substrates such as wooden plates, calcareous sandstone, plaster plates, plastering lime, plastering concrete, filler coating, unglazed clay plates, gas concrete, brick etc. The dry specimens were checked under UV radiation and the depth of their penetration measured on the planes of section.

Other methods for determining the penetration of polymer dispersions are also known. One suitable method consists, for example, of burning off a plane section of coated or impregnated substrate with a bunsen burner, the polymer then being distinguished by a grey discoloration. Sections of acid-resistant substrates may also

be coated with concentrated sulphuric acid in order to identify the penetration of the polymer. These experiments showed that the finely distributed plastics dispersions of the invention, at the same solids content, penetrate to the same depth and solidify as well as known binders in solvent-containing systems, and that the penetration depth and degree of solidification was much greater than that of dispersions with comparable polymer structure and average particle size diameters of more than $0.06 \mu\text{m}$.

The superiority of dispersions having particle sizes of less than $0.06 \mu\text{m}$ (which are preferred products of the invention) can be seen by the fact that at relatively high solids contents of, for example, from 15 to 20 per cent by weight which allow the application of a large amount of plastics material per unit area in one single operation, the finely distributed dispersions still penetrate almost completely into the substrate, where they contribute to solidification and improved anchorage for subsequent coats of paint. Dispersions having larger particle sizes do not penetrate into the substrate to a substantial extent, but merely from a film on the surface.

A further test allows one to study not only the penetration of the dispersion but also the degree of solidification obtained from a certain quantity of binder, by reacting the dispersion with fine-grained, loose material. This method also has the advantage that the material produces a compound of the grained material in the penetration zone after drying. The solidified core can be easily removed and weighed. Its weight is a reference for measuring the penetrating ability and the solidifying effect. This test simulates, for example, the solidification of surfaces of old, weather-beaten construction parts.

For performing the test, flat receptacles were filled with quartz powder (average analysis $50\% < 40 \mu\text{m}$). Where the material was to be submitted to the test, a hemispherical groove having a diameter of 2.5 cm was formed by using a stamp. 2 ml of the dispersion was dropped into this groove, and after having allowed the filling layer to dry at room temperature for four hours, it was placed in a drying cabinet at 50°C for another 15 hours. The results of these tests are shown in Table 1. The tests were carried out on plastics dispersions according to the invention having particle sizes from 0.01 to $0.06 \mu\text{m}$, which were prepared according to the Examples 1 to 6.

Dispersions having particle size $D > 0.08 \mu\text{m}$ were tested for comparison, these dispersions being based on various monomer systems and commercial polymers in organic solvents which are recommended for penetrative primer coatings.

The results of the tests show that the highest core weight and thus the best penetrating ability combined with a high degree of solidification is obtained with dispersions according to the invention and with the polymer solutions in organic solvents (Table 1); the results obtained from aqueous plastics dispersions having larger average particle diameters ($D > 0.1 \mu\text{m}$) being clearly inferior to those achieved with the dispersions according to the invention.

A further requirement to be met by primers having a penetrative effect is their ability to ensure good adhesion to paints subsequently applied onto the coated substrate and to provide a good anchorage between the paint and the substrate. This requirement must still be met even in the case where the paint is applied to primer layers of uneven thickness which may be due to irregular absorption of the substrate after many application of the primer.

This requirement was tested by applying about 12% dispersions according to the invention three times, separated by intermediate drying, on asbestos cement plates as the substrate. After drying in air for three days, the coat of primer was painted with a dispersion paint containing a styrene/butyl acrylate dispersion as binder and having a ratio of dispersion to pigment filler mixture of 1:1.6. A reinforcing cloth strip of polyethylene terephthalate was imbedded in the fresh paint and then painted with the same paint after drying of the first coat of paint.

The adhesion between the primer coat and the substrate, and between the primer coat and the dispersion paint coat was tested by trying to remove the cloth strip. Good adhesion was found regardless of whether it was peeled off dry or wetted by storing under water and re-drying. The same results were obtained from tests performed according to Examples 1 to 6 with soft binder films which had adjustable monomer ratios, or with hard binder films of polymers. Without exception, the cloth strips could be pulled off the dispersion paint coating, leaving the lattice-type fabric structure embossed on the paint layer; however, no paint was taken off the substrate or the primer coat in this operation. The same results were obtained by cross-cutting the dried dispersion paint coating and trying to pull the

dispersion paint film off the cross-cut squares by means of an adhesive tape. The paint layer did not come off either.

The following Examples illustrate the preparation of dispersions according to the invention.

5 EXAMPLE 1 5
A stable monomer emulsion is prepared from

		parts by weight	
10	styrene	134	
	butylacrylate	200	10
	acrylamide	4.5	
	methacrylic acid	12.0	
	sodium salt of a secondary		
15	alkyl-sulfonate (C ₁₂ —C ₁₆)	10	
	reaction product of nonyl-phenol		15
	with 10—12 moles of ethylene oxide	5.0	
	water	400	

20 The emulsion is metered into a liquor comprising 230 parts by weight of water, 2 parts by weight of a non-ionic emulsifier and 8 parts by weight of an ionic emulsifier. Simultaneously with the dosing in of the emulsion, a solution of 2 parts by weight of ammonium persulfate in 40 parts by weight of water is added.

The mean particle size of the dispersion adjusted to a pH of 8—9 is 0.036 μm .

25 EXAMPLE 2 25
Copolymer dispersions containing an optical brightener and having fine particles are obtained by dissolving additionally 0.1 part by weight of a vinyl-sulfonyl-pyrazoline brightener (cf. German Offenlegungsschrift No. 2,011,552) in the monomer mixture of Example 1, and subsequently preparing the plastics dispersions as before.

30 Both the aqueous plastics dispersion and the dry polymer film exhibit a characteristic blue fluorescence under UV radiation which allows detection of even very small polymer amounts in the different substrates. Fractionating by gel permeation chromatography shows that the optical brightener is incorporated uniformly in the polymer, i.e. no accumulations are formed in certain ranges of molecular weight. The average particle size of the copolymer dispersion containing the optical brightener is 0.038 μm .

35 EXAMPLE 3 35
A monomer mixture comprising

		parts by weight	
40	styrene	170	40
	butylacrylate	170	
	acrylamide	4	
	methacrylic acid	10	

45 is metered into a liquor comprising 680 parts by weight of water, 25 parts by weight of a secondary sodium alkyl sulfonate (C₁₂—C₁₆) and 10 parts by weight of the reaction product of nonyl-phenol and from 8—12 moles of ethylene oxide.

A solution of 2 parts by weight of ammonium persulfate in 40 parts by weight of water is used as initiator. The average particle size diameter is 0.038 μm .

50 EXAMPLE 4 50
A stable monomer emulsion is prepared from

		parts by weight	
55	styrene	3600	
	butyl acrylate	3600	
	acrylamide	100	55
	methacrylic acid	250	
	sodium lauryl sulfate	340	
	reaction product of nonyl-phenol with 8—12 moles of		
60	ethylene oxide	180	
	water	10,000	60

The emulsion is metered into a liquor comprising 5000 parts by weight of water, 80 parts by weight of the non-ionic emulsifier and 280 parts by weight of the anionic emulsifier. A solution of 40 parts by weight of ammonium persulfate in 900 parts by weight of water is metered in simultaneously. The average particle diameter of the dispersion adjusted to a pH of 8—9 is 0.042 μm .

The dispersion can be concentrated in the same reaction vessel, under water jet vacuum, to a solids content of about 45%. The average particle size remains 0.042 μm .

EXAMPLE 5

10	A monomer mixture of	parts by weight	10
	methylmethacrylate	130	
	butylacrylate	200	
15	acrylic acid	12	15
	acrylamide	4	

is metered into a liquor comprising 660 parts by weight of water, 20 parts by weight of sodium lauryl ethoxylate-sulfate (with 2—5 moles of ethylene oxide) and 8 parts by weight of a reaction product of nonyl-phenol and 6—10 moles of ethylene oxide. A solution of 3 parts by weight of potassium persulfate in 30 parts by weight of water is used as initiator. The average particle size is 0.041 μm .

EXAMPLE 6

The composition of the liquor is as in Example 5.
The monomer mixture comprises

25	The monomer mixture comprises	parts by weight	25
	methylmethacrylate	100	
	butylacrylate	230	
	acrylic acid	13	
30	acrylamide	5	30

2 parts by weight of potassium persulfate dissolved in 20 parts by weight of water are employed as initiator. The average particle diameter is 0.045 μm .

EXAMPLE 7

A stable monomer emulsion is prepared from

35	A stable monomer emulsion is prepared from	parts by weight	35
	styrene	170	
	butylacrylate	170	
	sodium lauryl sulfate	15	
40	reaction product of nonyl-phenol with 8—12 moles of ethylene oxide	5	40
	water	450	

The emulsion is metered into a liquor comprising 200 parts by weight of water, 3 parts by weight of the non-ionic emulsifier and 8 parts by weight of the ionic emulsifier. A solution of 3 parts by weight of ammonium persulfate in 30 parts by weight of water is simultaneously metered in.

The average particle size of the dispersion being adjusted to pH 8—9 is 0.060 μm .

COMPARATIVE EXAMPLE A

50	A copolymer dispersion is prepared comprising vinyl acetate	parts by weight	50
	vinyl acetate	70	
	Versatic ^(R) -10C-acid vinyl ester	25	
55	crotonic acid	5	55

with an anionic emulsifier and an inorganic per-compound and containing from 40—50% of solids.

The average particle size is 0.620 μm .

COMPARATIVE EXAMPLE B

5 A copolymer dispersion is prepared according to Example A, consisting of 5

	parts by weight
vinyl acetate	70
butylacrylate	30

10 The average particle size is 0.270 μm . 10

COMPARATIVE EXAMPLE C

A copolymer dispersion is prepared, comprising

	parts by weight
styrene	50
butylacrylate	50
acrylic acid	2
methacrylic acid	5
acrylamide	3

20 with a mixture of anionic and non-ionic emulsifiers and an inorganic per- 20
compound.

The average particle size is 0.150 μm .

COMPARATIVE EXAMPLE D

25 A copolymer composed of 25

	parts by weight
vinyl acetate	70
maleic acid dibutyl ester	30

30 is dissolved in ethyl acetate to yield a 60% solution. The viscosity at 20°C according 30
to Höppler (DIN 53 015) is 80 P. a primer having a penetrative effect is prepared
from this solution in the following manner:

	parts by weight
60% copolymer solution in ethyl acetate	28
Shellsol A (trade mark)	62
Ethylglycol acetate	10

COMPARATIVE EXAMPLE E

From a copolymer comprising

	parts by weight
vinyl toluene	85
acrylic acid-2-ethyl-hexyl ester	15

having a viscosity of about 60 cP at 20°C according to Höppler in a 30% solution in xylene, a primer coating solution is prepared in the following manner:

	parts by weight
copolymer	170
white spirit	545
Shellsol A (trade mark)	285

TABLE I
Penetration Test in Quartz Sand Fillings

	Example	Average particle size (μm) (according to light scattering method)	core weight (g) after application of 2 ml of a 17% and 11% dispersion		
5	1	0.036	12.3	13.6	5
	2	0.038	11.8	12.5	
	3	0.038	12.1	12.8	
	4	0.042	10.5	11.9	
10	5	0.041	11.3	11.9	10
	6	0.045	11.1	11.5	
	7	0.060	10.5	11.0	
	Comparative Examples				
15	A	0.620	0.6	1.1	15
	B	0.270	3.4	3.8	
	C	0.150	6.0	6.4	
	D	—	10.8	11.0	
	E	—	10.4	11.2	

WHAT WE CLAIM IS:—

1. A process for the preparation of a finely distributed plastics dispersion, which comprises incorporating a monomer mixture comprising:

I from 20 to 80% by weight of a hardening component comprising styrene or methyl methacrylate or a styrene/methyl methacrylate mixture,

II from 20 to 80% by weight of a plasticising component comprising an ester of one or more linear or branched alcohols having from 2 to 8 carbon atoms and acrylic acid and/or an ester of one or more linear or branched alcohols having from 4 to 8 carbon atoms and methacrylic acid,

III from 0.1 to 5% by weight of an amide of an α,β -unsaturated carboxylic acid, and

IV from 0.1 to 5% by weight of an α,β -unsaturated monocarboxylic acid, in the form of the pure monomer mixture or a preliminary emulsion, simultaneously with an initiator, with an aqueous liquor containing an anionic emulsifier, said monomers being used in such an amount that the solids content of the final dispersion does not exceed 45% by weight, polymerising said monomers in said aqueous liquor to form said dispersion, and causing the dispersion so formed to have a pH in the range of from 7 to 10.

2. A process as claimed in Claim 1, wherein the quantity of the amide in the mixture is in the range of from 1.5 to 3.5 percent by weight.

3. A process as claimed in Claim 1 or Claim 2, wherein the amide is acrylamide or methacrylamide.

4. A process as claimed in any one of Claims 1 to 3, wherein the α,β -unsaturated monocarboxylic acid is acrylic acid or methacrylic acid.

5. A process as claimed in any one of Claims 1 to 4, wherein the total quantity of α,β -unsaturated monocarboxylic acids and amides of α,β -unsaturated carboxylic acids in the mixture is in the range of from 0.2 to 8.5 percent by weight, based on the total weight of the monomers.

6. A process as claimed in any one of Claims 1 to 5, wherein the mixture further comprises one or more α,β -unsaturated compounds which are copolymerisable with the hardening component and the plasticising component.

7. A process as claimed in Claim 6, wherein the said α,β -unsaturated compounds are any of those specifically mentioned herein.

8. A process as claimed in Claim 6 or Claim 7, wherein the quantity of the said α,β -unsaturated compounds in the mixture is not more than 10 percent by weight, based on total weight of the monomers.

9. A process as claimed in Claim 8, wherein the quantity of the said α,β -unsaturated compounds in the mixture is not more than 5 percent by weight.

10. A process as claimed in any one of Claims 1 to 9, wherein the hardening component consists wholly of styrene.

11. A process as claimed in any one of Claims 1 to 9, wherein the hardening component comprises a styrene/methyl methacrylate mixture containing not more than 15 percent by weight of methyl methacrylate.

12. A process as claimed in Claim 1, wherein the composition of the monomer mixture is any one of those specifically mentioned herein.

13. A process as claimed in any one of Claims 1 to 12, wherein the initiator comprises any one or more of the following: an inorganic peroxy compound, an organic peroxide, or an organic perester.
- 5 14. A process as claimed in Claim 13, wherein the initiator further comprises a reducing agent. 5
15. A process as claimed in Claim 14, wherein the reducing agent is sodium bisulphite, hydrazine or hydroxylamine.
16. A process as claimed in any one of Claims 1 to 15, wherein the anionic emulsifier is any one of those specifically mentioned herein.
- 10 17. A process as claimed in any one of Claims 1 to 16, wherein the quantity of the anionic emulsifier present is in the range of from 0.5 to 10 percent by weight, based on the total weight of the monomers. 10
18. A process as claimed in Claim 17, wherein the said quantity of anionic emulsifier is in the range of from 2 to 8 percent by weight.
- 15 19. A process as claimed in any one of Claims 1 to 17, wherein a non-ionic emulsifier is present in the aqueous medium. 15
20. A process as claimed in Claim 19, wherein the non-ionic emulsifier comprises an ethoxylated alkylphenol or an ethoxylated fatty alcohol.
21. A process as claimed in any one of Claims 1 to 20, wherein the solids content of the final dispersion is in the range of from 20 to 45 percent by weight. 20
22. A process as claimed in any one of Claims 1 to 21, wherein an accelerator is present.
23. A process as claimed in Claim 22, wherein the accelerator comprises one or more salts of iron, cobalt, cerium or vanadium or an alkali metal or ammonium peroxydisulphate. 25
24. A process as claimed in any one of Claims 1 to 23, wherein the polymerisation is conducted at a temperature in the range of from 10 to 100°C.
25. A process as claimed in Claim 24, wherein the said temperature is in the range of from 30 to 90°C.
- 30 26. A process as claimed in any one of Claims 1 to 25, wherein the resulting dispersion has a mean particle size in the range of from 0.01 to 0.06 μm . 30
27. A process as claimed in any one of Claims 1 to 26, wherein the pH of the resulting dispersion is caused to be in the range of from 7.5 to 9.
28. A process as claimed in any one of Claims 1 to 27, wherein the solids content of the resulting dispersion is increased by vacuum distillation. 35
29. A process for the preparation of an aqueous plastics dispersion substantially as hereinbefore described in any one of Examples 1 to 7.
30. An aqueous polymer dispersion prepared by a process as claimed in any one of Claims 1 to 29.
- 40 31. A material which has been treated with an aqueous polymer dispersion as claimed in Claim 30. 40

ABEL & IMRAY,
Chartered Patent Agents,
Northumberland House,
303—306 High Holborn,
London, WC1V 7LH.