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(54) PREPARATION OF VINYL CHLORIDE POLYMERS

(71) We, RHONE-POULENC INDUSTRIES, a French body corporate, of 22 avenue Montaigne, 75 Paris (8th), France, 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:—

The invention is concerned with the preparation of vinyl chloride homopolymers and copolymers by polymerisation in seeded microsuspension, and with the resultant polymers.

Polymerization in microsuspension, also called "fine suspension", is understood as being polymerisation, in the presence of initiators soluble in organic material, of at least one monomer dispersed by powerful mechanical means in an aqueous medium containing an emulsifier as stabiliser, in order to obtain a dispersion of particles of an average diameter less than 5 microns.

It is known from U.K. Patent No. 1,170,963 that polymers of vinyl chloride can be prepared in microsuspension in the presence of a seeding product containing all the initiator necessary for polymerisation. However, when polymerisation is carried out so as to obtain a latex with a polymer concentration of over 45%, the high viscosity of the medium necessitates slower agitation, owing to the mechanical instability of the latex formed. This slow agitation leads to a decrease in the exchange coefficients, which necessitates an increase in the polymerisation time.

Moreover, it is difficult to use plastisols prepared from such polymers because of their dilatance, i.e. the increase in their viscosity with the speed gradient, and because the minimum proportion of plasticiser that can be used is 50 parts per 100 of polymer.

It is also known that, in the case of polymers of vinyl chloride prepared by polymerisation in emulsion, the use of a plastisol is improved if the polymer comprises elementary particles forming at least two sets that have particles of different sizes. This plurality of sets can be

obtained by mixing two or more latices consisting of particles of different sizes, but the mixture cannot be made at a high concentration. It is also known that plastisols can be improved by simultaneously preparing the various populations (herein called sets) of particles by polymerisation in emulsion of at least one monomer in the presence of two or more seeding products prepared by polymerisation in emulsion. However, this operation is very tricky, for the quantity of emulsifier used has to be stipulated and limited and its introduction requires special care, that is to say, a specific rate of introduction all the time, in order to avoid nucleation of new particles, which would limit the polymer concentration of the latex obtained. Moreover, it is difficult to make seeding products with particles of very small sizes that are measured and homogeneous, since the slightest variation in particle size results in variation in the ratios of the dimensions and in the proportions of the various sets of particles obtained after polymerisation.

According to the invention, poly(vinyl chloride) or a copolymer containing at least 50% by weight of vinyl chloride and at least one copolymerisable monomer is prepared by polymerising the corresponding monomer or monomers in microsuspension in the presence of a seeding product in the form of a first dispersion of particles of a vinyl polymer previously prepared by polymerisation in microsuspension, and in the presence of one or more other seeding products in the form of dispersions of particles of a vinyl polymer, the average diameters of which differ from the particle average diameter of the first seeding product and, when more than one such other seeding product is used, from one another, in which the particles of the first dispersion contain at least one initiator soluble in organic material and no supplementary addition of free initiator (as herein defined) is made to the reaction mixture. The term 'free initiator' means initiator not contained in particles of vinyl polymer.

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2 By proceeding in accordance with the present invention, it is possible to avoid drawbacks of the prior methods, and to prepare latices having a polymer concentration well over 45% by weight, a low viscosity and a perfectly reproducible particle size by polymerisation in micro-suspension, without any limitations, precautions or difficulties. Furthermore, it is easy to convert the polymers thus obtained, more particularly to form plastisols, which may contain very little plasticiser but that are nevertheless easy to use.

5 The term "polymers of vinyl chloride" means the homopolymer, i.e. poly(vinyl-chloride), or a copolymer containing at least 50% by weight of vinyl chloride and at least one monomer that is copolymerisable with vinyl chloride. The copolymerisable monomers are those generally used in conventional methods of copolymerising vinyl chloride. Some examples are vinyl esters of mono- and poly-carboxylic acids, such as vinyl acetate, propionate and benzoate; unsaturated mono-carboxylic and polycarboxylic acids such as acrylic, methacrylic, maleic, fumaric and itaconic acids as well as their aliphatic, cyclo-aliphatic and aromatic esters, their amides and their nitriles; vinyl and vinylidene halides; alkyl vinyl ethers and olefins.

10 The vinyl polymers that constitute seeding products may be polymers of vinyl chloride as defined above or homopolymers of one of the above-mentioned copolymerisable monomers, or a copolymer of two or more such monomers.

15 The polymers of the various seeding products in one and the same operation may be identical or different.

20 The use of a vinyl polymer other than vinyl chloride as a seeding product may make it possible to improve certain mechanical properties or the suitability of the resultant polymers for processing, such as extrusion or calendering.

25 The first seeding product necessary for polymerisation is prepared by conventional methods of polymerisation in micro-suspension. It is in the form of a dispersion of particles of polymer with an average diameter in the range 0.05 to 1.5 μm , preferably 0.2 to 1 μm .

30 The first seeding product may be prepared by finely dispersing a vinyl monomer or a mixture of vinyl monomers in water with the aid of a powerful mechanical means such as a colloid mill, a high speed pump, a vibrating agitator or an ultrasonic machine, in the presence of an initiator soluble in organic material and an anionic emulsifier, possibly associated with a non-ionic emulsifier. The micro-suspension obtained is then heated under autogenous pressure and with moderate agitation to a temperature generally from 30 to 65°C. When the pressure has dropped the reaction is stopped and the non-converted monomer or

monomers are degassed.

The initiator to be used in preparing the seeding product may be an organic peroxide such as diacyl peroxide, e.g. lauroyl, decanoyl or caproyl peroxide, *t*-butyl diethylperacetate, diethylhexyl percarbonate or diacetyl peroxide.

35 The choice of the initiator soluble in organic material depends on the speed at which it decomposes at the temperature used for the reaction. The initiator must in fact be reactive enough for normal quantities, say 0.1 to 3% by weight relative to the monomer or mixture of monomers, to enable the seeding product to be prepared within periods of 4 to 20 hours. However, the rate of decomposition of the initiator must not be too high, so that the quantity of initiator decomposed in preparing the seeding product is not more than half the quantity of initiator originally added. It is therefore necessary to select an initiator with a half life such that the proportion of initiator destroyed in preparing the seeding product is from 5 to 50% by weight of all the initiator used.

40 In cases where two or more such initiators are used it is advantageous to choose initiators of different reactivity; the most reactive initiators are active chiefly during the preparation of the seeding product, whereas the less reactive initiators are active mainly during the subsequent seeded polymerisation of the vinyl chloride or of the mixture of vinyl chloride and copolymerisable monomer.

45 The other seeding product or products are in the form of dispersions of particles of polymer, which may or may not contain an initiator; their average diameters, which differ from one another and from that of the first seeding product, are from 0.02 to 1.5 μm , preferably from 0.02 to 0.8 μm . For example, in cases where there are only two seeding products, the average diameter of the particles of the second seeding product is from 0.05 to 1.5 μm , preferably from 0.05 to 0.8 μm ; and in cases where there are three seeding products, the average diameter of the particles of the second seeding product is from 0.05 to 1.5 μm , preferably from 0.05 to 0.8 μm , and the average diameter of the particles of the third seeding product is from 0.02 to 0.8 μm , preferably from 0.02 to 0.5 μm .

50 These dispersions of particles may be obtained by conventional methods of polymerisation in micro-suspension or in emulsion.

55 The preparation of the seeding product or products, other than the first one, when carried out by polymerisation in micro-suspension, takes place as described above, but there is a greater degree of homogenisation if the particles to be obtained are very small. In the method of the invention it is generally more advantageous to use one or more seeding products, other than the first, that do not contain any initiator. They are then polymerised with a quantity of initiator such that at least 80% by weight

of the initiator is destroyed during the reaction.

Preparation of the seeding product or products, other than the first one, when carried out by polymerisation in emulsion, comprises using water, a vinyl monomer, either alone or associated with a copolymerisable monomer, a water-soluble initiator and an anionic emulsifier, possibly associated with a non-ionic emulsifier.

The size of the particles is regulated by the usual methods suitable for polymerisation in emulsion, e.g. by carefully choosing the nature and quantity of emulsifier used, by using seeds and by adjusting the agitating speed.

The reaction mixture is heated under auto-genous pressure and with moderate agitation to a temperature from 30 to 65°C. When the pressure has dropped the reaction is stopped and the non-converted monomer or monomers are degassed.

The water-soluble initiators required for preparing these seeding products are generally represented by hydrogen peroxide and persulphates of alkali metals or of ammonium, possibly associated with water-soluble reducing agents, such as sulphites or bisulphites of alkali metals. The quantities used vary greatly, depend on the initiating system chosen, and are just sufficient to ensure polymerisation within periods of 4 to 10 hours.

In polymerisation according to the invention, the total quantity of the various seeding products used is preferably such that the quantity of polymers contained therein is 1 to 50% by weight of the sum of vinyl chloride (with or without comonomer to be polymerised) and seeding polymers. A quantity of over 50% of seeding polymers can be used but is of little interest, for it is then very large relative to the vinyl chloride or mixture of vinyl chloride and copolymerisable monomer, and the advantages of the invention are thus minimised. A quantity of less than 1% of seeding polymers is also of very little interest, for the quantity of reactive initiator contained in the first seeding polymer or in two or more seeding polymers is then very small and does not in practice enable the vinyl chloride or mixture of vinyl chloride and copolymerisable monomer to be polymerised. It is in fact the excess of organo soluble initiator in the first seeding polymer or in two or more seeding polymers that very effectively initiates polymerisation of the vinyl chloride or mixture of vinyl chloride and copolymerisable monomer, by setting up a constant reaction speed, as is shown in U.K. Patent No. 1170963.

The proportion of the first seeding polymer to the other seeding polymer or polymers, which depends on the composition of the polymer to be obtained, is in the range from 95:5 to 5:95.

Thus there are several possible ways of carrying out seeded polymerisation. Some examples of these are set forth below, in which

polymers that contain an initiator are prepared by polymerisation in micro-suspension; polymers that do not contain an initiator by polymerisation in emulsion or micro-suspension, and the initiator is in all cases soluble in organic material:—

1. A first seeding product containing an initiator is used in conjunction with a second seeding product having finer particles and also containing an initiator.

2. A first seeding product containing an initiator is used in conjunction with a second seeding product having finer particles and not containing an initiator.

3. A first seeding product containing an initiator is used in conjunction with a second seeding product having finer particles and not containing an initiator, and a third seeding product having finer particles than the second and not containing an initiator.

4. A first seeding product containing an initiator is used in conjunction with a second seeding product having finer particles and not containing an initiator and a third seeding product having finer particles than the second and containing an initiator.

5. A first seeding product containing an initiator is used in conjunction with a second seeding product having finer particles and also containing an initiator, and a third seeding product having finer particles than the second and not containing an initiator.

6. A first seeding product containing an initiator is used in conjunction with a second seeding product having finer particles and also containing an initiator, and a third seeding product having finer particles than the second and also containing an initiator.

7. A first seeding product containing an initiator is used in conjunction with a second seeding product having coarser particles and not containing an initiator, and a third seeding product having coarser particles than the second and not containing an initiator.

8. A first seeding product containing an initiator is used in conjunction with a second seeding product having coarser particles and also containing an initiator, and a third seeding product having coarser particles than the second and not containing an initiator.

9. A first seeding product containing an initiator is used in conjunction with a second seeding product having finer particles and not containing an initiator, and a third seeding product having coarser particles than the first and not containing an initiator.

10. A first seeding product containing an initiator is used in conjunction with a second seeding product having coarser particles and not containing an initiator.

In a preferred embodiment of the invention a first seeding product prepared by polymerisation in micro-suspension, in which the polymer particles contain an initiator, is used with a seeding product prepared by polymerisation

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in emulsion, in which the polymer particles, which are finer than those of the first seeding product, do not contain any initiator.

The proportions of seeding products relative to one another and the total quantity of seeding products are selected so that the quantity of organosoluble initiator present in the particles of polymer is sufficient to effect polymerisation or copolymerisation without any supplementary addition of initiator.

The quantity of water required for polymerisation according to the invention is such that the initial polymer concentration of the seeding products plus the vinyl chloride with or without copolymerisable monomer is from 20 to 80%, and preferably 45 to 75% by weight of the reaction mixture.

In order to improve the stability of the micro-suspension it may be advantageous to add, before and/or during the polymerisation in the presence of the seeding products, at least one anionic emulsifier, possibly associated with at least one non-ionic emulsifier. The anionic emulsifier is preferably a soap of a fatty acid or an alkyl sulphate, alkylsulphonate, alkylarylsulphonate, vinylsulphonate, allylsulphonate, alkyl sulphosuccinate or alkali metal alkyl phosphate; the non-ionic emulsifiers are preferably polycondensates of ethylene or propylene oxide on various hydroxylated organic compounds. The emulsifier(s) may be the same as that or those used in the preparation of the seeding products.

The quantity of emulsifier may be up to 3% by weight of the vinyl chloride or mixture of vinyl chloride and copolymerisable monomer. These are the quantities generally used to obtain a useful effect in the reaction. However, quantities outside the above limits can be used without going beyond the scope of the invention, since the only function of the emulsifiers is to stabilise the micro-suspension and they have no effect on the size of the particles.

The reaction medium is heated under autogenous pressure to the polymerisation temperature determined by the properties of the desired vinyl chloride polymer, depending on the molecular weights. The temperature is usually from 10 to 85°C and preferably from 30 to 70°C.

In order to accelerate polymerisation it is recommended that the initiator be activated with a metal complex that is soluble in organic material and that is formed throughout the polymerisation process by reaction between a water-soluble metal salt and a complexing agent which is introduced gradually, as described in the specification of our copending Application No. 1435425. The metal salt is used in quantities such that the molar ratio of metal salt to initiator is from 0.1:1 to 10:1. The metal is represented by iron, copper, cobalt, nickel, zinc, tin, titanium, vanadium, manganese, chromium or silver. The complexing agent is represented by a

monocarboxylic, polycarboxylic or alkylphosphoric acid, a lactone, a ketone or a carbazone. It is used in proportions that may reach molar stoichiometry relative to the metal salt.

The process of polymerisation in micro-suspension, as described above, may obviously be carried out continuously.

Apart from the important advantages of the invention, such as minimal consumption of initiator, a reaction which is more regular and possibly shorter than in conventional processes, and virtually no incrustation of the reaction zone, thus facilitates the heat exchanges necessary to obtain uniform polymerisation, there are also more particular advantages, viz. that the invention gives a micro-suspension with great fluidity a polymer concentration that may be as high as 75% by weight and in practice is 20 to 75% by weight, resulting in better exploitation of the polymerising and separating means, and that the invention leads to exceptional reproducibility of the sizes of particles contained in the latex obtained.

Latices thus prepared contain at least two sets of particles of different average diameters. Thus, when two seeding products are used, the two sets obtained have average diameters which, in the case of the coarser particles, range from 0.4 to 2.5 μm and, in the case of the finer particles, from 0.08 to 1 μm , in an average diameter ratio in the range of 1:1 to 20:1 and a weight ratio of 0.1:1 to 10:1. Similarly, when three seeding products are used, three sets are obtained, with average diameters ranging from 0.4 to 2.5 μm for the coarser particles, from 0.15 to 1 μm for the medium ones and from 0.05 to 0.4 μm for the finer ones. The diameter ratios of coarse particles to medium particles and of medium particles to fine particles, which may be similar or different, range from 1:1 to 20:1, and the weight ratios of coarse particles to medium particles and of medium particles to fine particles, which may be similar or different, range from 0.1:1 to 20:1.

The diameters and weight ratios, within the above limits, are selected according to the conditions of use for the polymers formed, such as rheological properties of plastisols or suitability for extrusion.

The particles of different average diameters result from enlargement of the particles of seeding products. By application of present-day knowledge, the particles of seeding products containing initiator should undergo an enlargement as defined in U.K. Patent No. 1170963; on the other hand enlargement should be zero for particles of seeding products not containing any initiator. One of the discoveries that the invention is based on is that the enlargement of particles containing an initiator is less than expected, whereas particles not containing any initiator undergo an

enlargement that is not negligible yet is proportionally less than that of particles containing an initiator; this enlargement complies neither with the law of enlargement covering polymerisation in micro-suspension nor with the law covering polymerisation in emulsion.

The vinyl chloride polymers prepared by the method of the invention are separated from the polymerising medium by any known methods such as filtration; coagulation and draining; scaling; centrifugal decantation; and atomisation.

The invention also concerns the polymers thus obtained, which are in the form of powders particularly suitable for preparing plastisols having Newtonian or pseudoplastic behaviour with a very low plasticiser content of up to 25 parts by weight of plasticiser per 100 parts by weight of polymer, and a low viscosity, which enables coatings to be applied at very high speed.

The polymers and copolymers of the invention are applicable to the manufacture of sheets, films, threads, hollow bodies, cellular materials or articles moulded by calendering, extrusion, blow extrusion, injection or casting; they may also be used to obtain coated coverings; cellular materials or articles moulded by any known methods of using plastisols: coating, rotation moulding or dipping.

Some examples will now be given to illustrate the invention.

Example 1.

Preparation of seeding latex 1 in micro-suspension.

The following are mixed:

- 40 kg of vinyl chloride;
- 0.6 kg of lauroyl peroxide,
- 4 kg of a 10% by weight aqueous solution of sodium dodecylbenzenesulphonate,
- enough water to bring the vinyl chloride concentration to 43% by weight.

The mixture is homogenised to form a micro-suspension which is then placed in a 120-litre autoclave. It is heated to 52°C under autogenous pressure.

When the pressure has dropped, i.e. after 9 hours, the unreacted vinyl chloride is degassed. The latex is obtained with a poly(vinyl chloride) concentration of 40% by weight; its particles have an average diameter of 0.4 μm and contain 1.5% by weight of lauroyl peroxide relative to the polymer.

Preparation of seeding latex 2 in emulsion.

The following are placed in a 120-litre autoclave:

- 60.6 kg of water,
- 2.60 kg of a 10% by weight solution of sodium tetradecylsulphonate,
- 0.053 kg of ammonia at 22° Beaume,
- 52 kg of vinyl chloride.

The mixture is heated to 52°C under autogenous pressure and this temperature is maintained throughout the operation. As soon as the mixture is at 52°C 0.035 kg of potassium persulphate is introduced. 15 minutes later 4.75 litres of a 10% aqueous solution of sodium tetradecylsulphonate is added continuously at a rate of 0.5 litre/hour. After 9 hours 30 minutes at 52°C the unreacted vinyl chloride is degassed. The latex obtained has a polymer concentration of 40.2% by weight and a particle diameter of 0.12 μm . The particles do not contain any initiator.

Polymerisation in the presence of seeding products.

The following are placed in a 120-litre autoclave:

- 33.2 kg of water,
- 5.7 kg of latex 1, i.e. 2.3 kg of poly(vinyl chloride) containing 34.5 g of lauroyl peroxide,
- 3.5 kg of latex 2, i.e. 1.4 kg of poly(vinyl chloride),
- 1.5 kg of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate,
- 55 kg of vinyl chloride.

The mixture is agitated, with the agitator at 50 revolutions/min, and heated to 52°C. 3 hours later 2.5 kg of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate is added.

After 18 hours' reaction a drop in pressure is observed. When the pressure has dropped 2 bars the non reacted vinyl chloride is degassed. A latex is obtained with a polymer concentration of 54% by weight and a viscosity of 38 cp.

The weight of crusts in the autoclave is only 300 g.

Particle size analysis of the latex obtained shows the polymer to be made up of two sets of particles with average diameters of 0.20 μm and 0.98 μm respectively. An increase in the size of the particles of latex 2 is noted, although they do not contain any initiator. The fine particles represent 29% by weight of the polymer.

The latex obtained is atomised, the powder obtained crushed, and a plastisol prepared by mixing 100 parts by weight of polymer and 40 parts by weight of dioctyl phthalate. The rheological properties of the plastisol are measured:

— firstly with the aid of a rotary rheometer of the Brookfield RTV type (needle n° 6, 20 revs/minute, measuring and conditioning at 25°C); the results are given in table 1;

— secondly with the aid of a Severs extrusion-type rheometer (conditioning 2 hours at 25°C); the results are set out in table 2.

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TABLE 1
Brookfield Viscosity

Conditioning at 25°C hours	Viscosity poises
0.5	210
24	440

The table shows that, although the plastisol contains little plasticiser, its viscosity is low and it develops slowly with the passage of time.

TABLE 2
Severs Viscosity

Speed gradient sec ⁻¹	Viscosity poises
235	308
480	280
820	260

A study of the table reveals the surprising fact that the viscosity of the plastisol diminishes as the speed gradient increases; this is characteristic of a slight pseudo-plasticity of the plastisol, which makes it easier to use.

A plastisol consisting of 50 parts by weight of dioctyl phthalate per 100 parts by weight of poly(vinyl chloride) also has pseudoplastic behaviour, that is to say, viscosity diminishes as the speed gradient increases.

For purposes of comparison three tests are carried out, with one seeding latex, according to prior art.

Test A in which the procedure is as above, but with proportions of reagents such that a latex of similar concentration is obtained.

The following are placed in the reactor:

- 32.4 kg of water,
- 6.9 kg of latex 1, i.e. 2.75 kg of poly(vinyl chloride),
- 1.5 kg of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate,
- 55 kg of vinyl chloride.

The reaction is carried out under the same conditions. The drop in pressure is observed after 18 hours. After degassing, a precipitated polymer is obtained in the reactor; it is impossible to recover this by conventional separating processes.

Test B carried out like test A but with an agitator speed of 30 revs/min. The drop in pressure is observed after 22 hours. The latex obtained has a polymer concentration of 54.5% by weight and a viscosity of 500 cp. The weight of crusts in the reactor is 2 kg.

Particle size analysis of the latex shows there to be only one set of particles, with an average diameter of 1.05 μ m.

Atomisation of the latex is difficult. The product obtained is crushed and two plastisols are prepared. The results are given in table 3.

TABLE 3

PLASTISOL		Rheology	
PVC parts by weight	DOP parts by weight		
100	40	Impossible to put into paste form. A greatly dilatant heterogeneous mastic is obtained.	
100	50	Severs Viscosity Gradient sec ⁻¹	Viscosity poises
		138	520
		187	770
		255	860

Comparison of tests A and B and example 1 show the improvement provided by the method of the invention in obtaining latex with a high polymer concentration and low viscosity. It also shows that the products of the process gives plastisols of greater fluidity for a low plasticiser content, enabling coatings to be applied at high speed.

Test C. If in test B, at high concentration, the proportion of initiator in the seed polymer is increased or an activating system added in order to increase the speed of the reaction, the reaction mixture becomes thermally unstable due to the poor coefficient of thermal exchange of the reactor under the conditions of agitation of the viscous medium. Control of the temperature of the reactor is thereby lost and the reaction races, giving a latex which is useless, the polymer not having the required molecular weight.

Example 2.

Seeding latices 1 and 2 from example 1 are used in polymerisation.

Polymerisation.

The following are charged into a 120-litre autoclave:

- 28.6 kg of water,
- 5.7 kg of latex 1, i.e. 2.3 kg of poly(vinyl chloride),
- 3.5 kg of latex 2, i.e. 1.4 kg of poly(vinyl chloride),
- 1.5 kg of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate,
- 2.7 g of copper sulphate,
- 55 kg of vinyl chloride.

The reaction mixture is agitated, with the agitator at a speed of 50 revs/min, and heated to 52°C.

Continuous introduction of 0.4 litre/hour of a 0.68 g/litre aqueous solution of ascorbic acid is heated as soon as the temperature reaches 52°C.

After 3 hours at 52°C 2.5 kg of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate is added.

After 9 hours' reaction a drop in pressure is observed. When pressure has dropped 2 bars the addition of ascorbic acid is stopped and the non reacted vinyl chloride is degassed. A latex is obtained with a polymer concentration of 55% by weight and a viscosity of 40 cp.

The weight of crusts in the reactor is only 120 g.

Particle size analysis of the latex obtained shows the polymer to be made up of 2 sets of particles. One constitutes 30% by weight of the polymer and the average diameter of the particles is 0.20 μm ; the other has an average particle diameter of 1 μm and constitutes 70% by weight. The growth of the particles of latex 2 is noted, although they did not contain any initiator.

The latex is atomised and the polymer ob-

tained is converted into 2 plastisols, respectively containing 40 and 50% by weight of dioctyl phthalate per 100 parts by weight of polymer.

The rheological properties of the first plastisol are set out in tables 4 and 5 and those of the second plastisol in table 6.

TABLE 4
Brookfield Viscosity

Conditioning at 25°C hours	Viscosity poises
0.5	180
24	300

TABLE 5
Severs Viscosity

Speed Gradient sec^{-1}	Viscosity poises
215	360
400	350
670	340

This plastisol has very slightly pseudoplastic behaviour, as indicated by the decrease in viscosity with the speed gradient.

Comparison between tables 2 and 5, i.e. examples 1 and 2, shows that activation of the initiator has virtually no effect on rheological properties; it influences only the reaction speed.

TABLE 6
Severs Viscosity

Speed Gradient sec^{-1}	Viscosity poises
90	112
220	100
540	80

Comparative test D. Polymerisation in emulsion.

Preparation of seeding latex 1 in emulsion. The following are placed in a 120-litre autoclave:

- 61 kg of water,
- 0.053 kg of ammonia at 22° Beaumé,

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- 2.6 kg of seeding latex 2 from example 1, i.e. 1.150 kg of poly(vinyl chloride),
 — 50 kg of vinyl chloride.
- The mixture is then heated to 52°C under autogenous pressure and this temperature is maintained throughout the operation. As soon as the mixture is at 52°C 0.035 kg of potassium persulphate is introduced and 15 mins later a 10% by weight aqueous solution of sodium tetradecylsulphonate is added continuously at a rate of 0.55 litre/hour. After 9 hours 30 minutes the non-reacted vinyl chloride is degassed. The latex obtained has a polymer concentration of 40.5% by weight with a particle diameter of 0.40 μm .

Polymerisation.

- The following are placed in a 120-litre autoclave:
- 45 kg of water,
 — 0.053 kg of ammonia at 22°C Beaumé,
 — 4.10 kg of latex 1, i.e. 1.67 kg of poly(vinyl chloride),
 — 2.55 kg of latex 2 from example 1, i.e. 1.02 kg of poly(vinyl chloride),
 — 40 kg of vinyl chloride.
- The mixture is then heated to 52°C under autogenous pressure and this temperature is maintained throughout the reaction. As soon as the mixture is at 52°C 0.025 kg of potassium persulphate is introduced. 15 mins later 5 litres of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate is added continuously at a rate of 0.5 litre/hour.
- After 10 hours' reaction the non reacted vinyl chloride is degassed. The latex obtained has a polymer concentration of 42% by weight. The weight of crusts in the reactor is 500 g. Particle size analysis of the latex obtained shows the polymer to be made up of 2 sets of particles. One constitutes 39% by weight of the polymer, and the average diameter of its particles is 0.83 μm ; the other has an average particle diameter of 0.34 μm and constitutes 61% by weight.
- The latex is atomised then converted into plastisol as in example 1.
- The rheological properties are as follows:

TABLE 7

Brookfield Viscosity

Conditioning at 25°C hours	Viscosity poises
0.5	1800
24	>2000

TABLE 8

Severs Viscosity

Speed Gradient sec ⁻¹	Viscosity poises
105	2050
160	3100
190	4200

Comparison between example 2 and test D shows the very great difference in particle size between the latices obtained by polymerisation in micro-suspension and in emulsion, and consequently the difference between the rheological properties of plastisols formed from the polymers obtained from these latices.

Examples 3 to 9.

Polymerisation.

In each of the examples a 120-litre autoclave is used, in which there are placed:

— a variable quantity of water,
 — 5.7 kg of latex 1 from example 1, i.e. 2.3 kg of poly(vinyl chloride),
 — a variable quantity of latex 2, the average diameters of the particles being different in each of the examples; the difference between the average diameters of the particles is obtained by varying the quantity of emulsifier used at the beginning of the preparation of latex 2 from example 1,
 — 0.55 kg of a 10% by weight aqueous solution of sodium tetradecylsulphonate,
 — 4 g of copper sulphate,
 — 55 kg of vinyl chloride.

The procedure is the same as in example 2, except that 3.5 kg of the same solution of sodium tetradecylsulphonate is added during polymerisation instead of the sodium dodecylbenzene sulphonate solution.

The variable data of the reaction and the results obtained are set out in table 9.

A study of the table shows the effect of the total quantity of seeding latices, the effect of the proportion of one of the seeding latices relative to the other, and the effect of the particle diameter of the latices on the formation of crusts during polymerisation, and on the particle size of the latices obtained.

Example 10.

Example 2 is repeated, except that the quantity of water used for polymerisation is 11.7 kg instead of 28.6 kg.

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At the end of the reaction the polymer concentration of the latex is 67% by weight and its viscosity is 60 cp. The weight of crusts in the autoclave is 240 g.

The latex contains particles, 29% by weight of which have an average diameter of 0.19 μm and 71% by weight of which have an average diameter of 1 μm .

The latex thus obtained is divided into two portions.

The first portion is atomised under normal conditions at low temperature. The powder obtained is crushed and converted into plastisol by mixing in 40 parts of dioctyl phthalate per 100 parts of powder.

The rheological properties of the plastisol, measured as in example 1, are summarised in tables 10 and 11.

TABLE 9

Examples	3	4	5	6	7	8	9
Polymerisation:							
— Water	kg	20.3	22.2	21.8	21.9	21.7	22.1
— Latex 2 40%	kg	20.65	6.9	10.35	3.45	3.45	3.45
i.e. PVC	kg	8.25	2.75	4.125	1.37	1.37	1.37
particle size	μm	0.18	0.18	0.14	0.14	0.13	0.105
— Crusts	g	350	300	300	250	300	250
Properties of latex obtained:							
— Concentration	%	55.7	60.8	55.3	60	56.9	56.6
— Viscosity	cp	31	30	28	31	29	27
— Average diameter of particle							
Particles 1	μm	0.98	1	0.98	1.01	0.95	1.02
Particles 2	μm	0.26	0.306	0.24	0.26	0.19	0.15
Content of particles 2	%	50	35	46	25	27	30

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TABLE 10.
Brookfield Viscosity

Conditioning at 25°C hours	Viscosity poises
0.5	220
24	460

TABLE 11
Severs Viscosity

Speed gradient sec ⁻¹	Viscosity poises
243	313
500	302
830	272

This example shows the surprising fact that latices with a very high concentration and with low viscosity can be obtained without any crust formation.

— The second portion of the latex is atomised at a higher temperature. The powder obtained has poly(vinyl chloride) particles with an average density of 113 μm , an apparent mass per unit volume of 0.69 g/ml and a viscosity index of 117.

100 parts by weight of the polymer thus obtained are mixed with 0.5 part by weight of calcium stearate, 4 parts by weight of a lead stabiliser and 4 parts by weight of titanium oxide. The composition is then studied with the aid of a BRABENDER extrusion recorder and a BRABENDER plastograph and compared with an identical composition prepared with a poly(vinyl chloride) obtained by mass polymerisation, with a viscosity index of 101.

The results are set out in table 12.

TABLE 12

POLYMER	BRABENDER PLASTOGRAPH		BRABENDER EXTRUSION RECORDER		
	Gellation time sec.	Gellation torque m/g	Flow rate kg/h.	Power consumed by machine w	Diameter of extruded product mm
PVC in example	60	3,900	1.73	273	2.31
Mass PVC	600	2,350	1.62	233	2.53 swelling

The poly(vinyl chloride) obtained by the method of the invention is found to gel more quickly, to be extruded slightly more quickly and to show less swelling on emerging from the die than a poly(vinyl chloride) prepared by mass polymerisation.

Example 11.

— Seeding latex 1 in micro-suspension is that prepared in example 1.

— Preparation of seeding latex 2 in micro-suspension.

The procedure is the same as in example 1, preparation of seeding latex 1, except that 8 kg of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate is used instead of 4 kg and 0.04 kg of lauroyl peroxide instead of 0.6 kg. There is very fine homogenisation.

The particles of latex obtained have an average diameter of 0.12 μm and contain only 0.07% by weight of initiator.

— Polymerisation.

The following are placed in a 120-litre autoclave:

- 28.6 kg of water,
- 5.7 kg of latex 1, i.e. 2.3 kg of poly(vinyl chloride),
- 3.5 kg of latex 2, i.e. 1.4 kg of poly(vinyl chloride) containing only very little initiator, corresponding to 0.002% by weight of the monomer present,
- 2.7 g of copper sulphate,
- 1.5 kg of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate,
- 55 kg of vinyl chloride.

The reaction is carried out as in example 2. The polymer concentration of the latex ob-

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tained is 54% by weight and its viscosity is 60 cp. The weight of crusts is approximately 100 g.

The polymer is made up of two sets of particles with respective average diameters of 0.19 μm and 1 μm , the fine particles constituting 29% by weight.

An enlargement of the particles of latex 2 was noted although its initiator content was virtually zero.

Example 12.

— Preparation of seeding latex 1 in micro-suspension.

The preparation of seeding latex 1 in example 1 is repeated, but with homogenisation such that the particle size of the latex is 0.48 μm . The polymer concentration is 39.5% by weight and the particles contain 1.5% by weight, relative to the polymer, of lauroyl peroxide.

— Preparation of seeding latex 2 in micro-suspension.

The preparation of seeding latex 1 in example 1 is repeated, with homogenisation such that the particle size of the latex is 0.1 μm . The polymer concentration is 40% and the particles contain 1.5% by weight, relative to the polymer, of lauroyl peroxide.

— Polymerisation.

The following are placed in a 120-litre reactor:

— 31.2 kg of water,

— 1.5 kg of a 10% aqueous solution of sodium dodecylbenzene sulphonate,

— 9.9 kg of latex 1, i.e. 3.9 kg of poly(vinyl chloride),

— 6.35 kg of seeding latex 2, i.e. 2.5 kg of poly(vinyl chloride),

— 55 kg of vinyl chloride.

The reaction mixture is agitated, heated to 52°C under autogenous pressure and kept at that temperature throughout the reaction.

After 3 hours' reaction 2.5 kg of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate is added to the mixture. The drop in pressure takes place after 12 hours' reaction. When it has dropped 2 bars the non-reacted vinyl chloride is degassed.

The polymer concentration of the latex obtained is 54% by weight. The weight of crusts is 500 g.

The two sets of particles forming the polymer have respective average diameters of 0.18 μm and 0.99 μm which constitute 29 and 71% of the weight.

Example 13.

Example 8 is repeated except that the following are used for polymerisation:

— 16.4 kg of water,

— 52.25 kg of vinyl chloride and

— 2.75 kg of vinyl acetate.

The latex obtained has a concentration of 58.1% by weight and a viscosity of 40 cp. The weight of crusts is low at 150 g. The polymer is made up of 22% by weight of particles with an average diameter of 0.22 μm and 78% by weight of particles with an average diameter of 1.05 μm .

The latex is atomised; the product obtained is a copolymer containing 3.6% by weight of vinyl acetate. The rheological properties of plastisols containing different quantities of dioctyl phthalate are given in table 13.

TABLE 13

DOP parts/100 of polymer	Brookfield		Severs	
	Viscosity ½ hour	(poises) 1 day	Speed gradient (sec ⁻¹)	Viscosity (poises)
40	280	660	100	700
50	100	220	(390 ((940	(390 ((240
60	30	35	(1000 ((2600	(70 ((58

A low viscosity plastisol, containing 40 parts by weight of dioctyl phthalate per 100 parts by weight of vinyl chloride/vinyl acetate co-

polymer is found to be obtained; this is impossible with previous processes.

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Example 14.

—Seeding latex 1 used is that from example

1. — *Preparation of seeding latex 2 in emulsion.*

5 The procedure is exactly the same as in example 1. The average diameter of the particles obtained is $0.115\text{ }\mu\text{m}$.

—*Polymerisation.*

Example 2 is repeated.

10 At the end of the reaction the concentration of the latex is 54.9% by weight and its viscosity is 40 cp. The weight of crusts in the autoclave is 150 g.

15 The polymer of the latex is made up of 69% by weight of particles with an average diameter of $0.98\text{ }\mu\text{m}$ and 31% by weight of particles with an average diameter of $0.19\text{ }\mu\text{m}$.

Comparative tests E and F in emulsion with two seeding latices of the emulsion type.

20 — *Preparation of seeding latex 1 in emulsion.*

The procedure is like that followed in preparing the seeding latex in comparative test D of example 2.

25 — *Preparation of seeding latex 2 in emulsion.*

30 e) The preparation of seeding latex 2 from example 1 is repeated, except that 1.04 kg of a 10% by weight aqueous solution of sodium tetradecylsulphonate is used instead of 2.6 kg thereof, and no sodium tetradecylsulphonate is introduced during polymerisation. The average particle diameter of the latex obtained is $0.031\text{ }\mu\text{m}$.

35 f) The procedure is exactly the same as in e). The average particle diameter of the latex obtained is $0.025\text{ }\mu\text{m}$.

2 polymerisations are carried out as follows,

one with latex 2e and the other with latex 2f. The proportions are such that the weight ratio of the two sets of particles and the diameter of the coarsest particles in the latex to be obtained are close to those of the latex in example 14.

The following are charged into 25-litre autoclave:

—8000 g of deionised water,

— seeding latices 1 and 2 in varying quantities,

— vinyl chloride in a quantity such that the weight of monomer and seeding polymer is 7000 g.

The mixture is agitated and heated to 52°C . As soon as the mixture reaches that temperature 4 g of ammonium persulphate is introduced. 1 hour later 2 litres of a 1.75% by weight aqueous solution of sodium dodecylbenzene sulphonate is introduced continuously at a rate of 0.23 litre/hour.

When pressure is at 5 bars the non-reacted monomer is degassed.

The operating data and results of tests E and F are summarised in table 14 and compared with examples 2 and 14.

A study of this table shows that a slight difference in the average particle diameters of seeding latices 2 in polymerisation in micro-suspension results in virtually no differences in the average particle size of the products obtained or in the rheological properties. On the other hand, an identical difference between the average particle diameters of seeding latices 2 in polymerisation in emulsion leads to significant differences in the particle size of the products obtained and consequently in their rheological properties. In this case there is no reproducibility of the process.

TABLE 14

	TESTS			EXAMPLES		
	E	F		2		14
Polymerisation.						
Latex 1 [- average particle diameter [- ratio Polymer Monomer+Polymer % weight	0.40 4.4	0.40 4.4		0.40 3.92		0.40 3.92
Latex 2 [- average particle diameter [- ratio Polymer Monomer+Polymer % weight	0.031 0.20	0.025 0.20		0.12 2.4		0.115 2.4
Products obtained						
Particle set 1 [- average diameter [- quantity %	0.96 68	0.96 68		1.00 70		0.98 69
Particle set 2 [- average diameter [- quantity %	0.16 32	0.131 32		0.20 30		0.19 31
Plastisols PVC/DOP-100/40 - Rheology						
Brookfield Viscosity [½ hour [1 day	200 450	280 800		180 300		200 310
Servers Viscosity [Speed gradient sec ⁻¹ [Viscosity	240-520-810 320-315-297	260-410-620 410-430-462		215-400-670 360-350-340		200-410-660 380-360-340

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Example 15.

— Preparation of seeding latex 1 in micro-suspension.

5. The preparation of seeding latex 1 from example 1 is repeated with homogenisation such that the average particle diameter of the latex is 0.25 μm . The polymer concentration of the latex obtained is 40% by weight and the particles contain 1.5% by weight, relative to the polymer, of lauroyl peroxide.

10 — Preparation of seeding latex 2 in emulsion.

- 15 Procedure is the same as in comparative test D in example 2, but with 0.43 kg, instead of 2.6 kg, of seeding latex 2 from example 1, i.e. 0.190 kg of poly(vinyl chloride).

The latex obtained has a polymer concentration of 40% by weight, and the average diameter of its particles is 0.74 μm .

20 — Polymerisation.

The following are placed in a 120 litre autoclave:

- 25 — 52 kg of water,
— 4.95 kg of latex 1, i.e. 2 kg of poly(vinyl chloride),
— 3.15 kg of latex 2, i.e. 1.25 kg of poly(vinyl chloride),
— 1.5 kg of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate,
30 — 2.7 g of copper sulphate,
— 50 kg of vinyl chloride.

Polymerisation is carried out in the same way as in example 2.

- 35 The latex obtained has a polymer concentration of 43% by weight. Particle size analysis shows it to contain two sets of elementary particles with respective average diameters of 0.88 μm and 0.52 μm , constituting 10 and 90% by weight of the polymer. This confirms
40 the growth of the particles of the two seeding latices.

Example 16.

— Preparation of seeding latex 1 in micro-suspension.

- 45 Preparation is the same as that of latex 1 in example 1.

— Preparation of seeding latex 2 in emulsion.

- 50 The preparation of seeding latex 2 from example 1 is repeated.

— Preparation of seeding latex 3 in emulsion.

The following are placed in a 120-litre autoclave:

- 55 — 65 kg of water,
— 2 kg of a 5% by weight aqueous solution of potassium laurate,
— 0.053 kg of ammonia at 22° Beaumé,
— 52 kg of vinyl chloride.

- 60 The mixture is then heated to 52°C under autogenous pressure and this temperature is maintained throughout the operation. As soon as the mixture is at 52°C 0.035 kg of potassium persulphate is introduced. After 9 hours
65 30 at 52°C the non-reacted vinyl chloride

is degassed. The latex obtained has a polymer concentration of 40.2% by weight and an average particle diameter of 0.2 μm . The particles do not contain any initiator.

— Polymerisation.

The following are placed in a 120-litre autoclave:

- 32.2 kg of water,
— 5.7 kg of latex 1, i.e. 2.3 kg of poly(vinyl chloride) containing 34.5 g of lauroyl peroxide, 75
— 1.75 kg of latex 2, i.e. 0.7 kg of poly(vinyl chloride),
— 1.75 kg of latex 3, i.e. 0.7 kg of poly(vinyl chloride), 80
— 1.5 kg of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate,
— 55 kg of vinyl chloride.

The reaction mixture is agitated, at an agitator speed of 50 revs/min, and heated to 52°C. After 3 hours 2.5 kg of a 10% by weight aqueous solution of sodium dodecylbenzene sulphonate is added. 85

After 18 hours' reaction a drop in pressure is observed. When the pressure has dropped 2 bars the non-reacted vinyl chloride is degassed. The latex obtained has a polymer concentration of 54% by weight and a viscosity of 25 cp. 90

The weight of crusts in the autoclave is only 300 g. 95

Particle size analysis of the latex obtained shows the polymer to be made up of three sets of particles, with respective average diameters of 0.16 μm , 0.40 μm and 0.97 μm , constituting respectively 16%, 20% and 64% of the weight of polymer. 100

Comparison between the latex of example 16 and the latex of example 1 shows that, for a same polymer concentration, the viscosities are different. 105

Example 17.

The seeding latex 1 used is that from example 1.

— Preparation of seeding latex 2 in emulsion. 110

The preparation of seeding latex 3 from example 16 is repeated.

— Preparation of seeding latex 3 in emulsion. 115

This is prepared like the seeding latex in comparative test D of example 2.

— Polymerisation.

The following are placed in a 120-litre autoclave: 120

- 33.2 kg of water,
— 5.7 kg of latex 1, i.e. 2.3 kg of poly(vinyl chloride) containing 34.5 g of lauroyl peroxide, 125
— 10.5 kg of latex 2, i.e. 4.2 kg of poly(vinyl chloride),
— 10.5 kg of latex 3, i.e. 4.2 kg of poly(vinyl chloride),
— 1.5 kg of a 10% by weight aqueous

solution of sodium dodecylbenzene sulphonate,
— 55 kg of vinyl chloride.

Polymerisation is carried out as in example 16 and the latex obtained has a polymer concentration of 53% by weight and a viscosity of 45 cp.

The weight of crusts in the autoclave is only 320 g.

Particle size analysis shows the latex to contain three sets of particles with respective average diameters of 0.26 μm , 0.54 μm and 0.92 μm , constituting 22, 32 and 46% by weight of the polymer.

Example 18.

Seeding latices 1 and 2 from example 16 are used in polymerisation.

— *Preparation of seeding latex 3 in emulsion.*

The preparation of seeding latex 2 from example 1 is repeated, but with 1.04 of a 10% by weight aqueous solution of sodium tetradecylsulphonate instead of 2.6 kg and without the introduction of sodium tetradecylsulphonate during polymerisation. The average particle diameter of the latex obtained is 0.031 μm .

— *Polymerisation.*

This is done under the same conditions as in example 16.

The latex obtained has a viscosity of 22 cp and contains three sets of particles constituting 13, 22 and 65% by weight of the polymer, with respective average diameters of 0.067 μm , 0.19 μm and 0.97 μm .

Example 19.

— *Preparation of seeding latex 1 in micro-suspension.*

The preparation of seeding latex 1 from example 1 is repeated.

— *Preparation of seeding latex 2 in emulsion.*

The following are placed in a 25-litre autoclave:

— 9.1 kg of water,

— 0.75 kg of seeding latex 3 from Example 18, i.e. 0.3 kg of poly(vinyl chloride).

These are agitated and heated to 75°C, and this temperature is maintained throughout the operation. As soon as the mixture is at 75°C, 12 g of potassium persulphate in solution in 100 g of water is introduced. 6 kg of butyl acrylate and one litre of an aqueous solution containing 30 g of sodium pyrophosphate and 60 g of sodium dodecylbenzene sulphonate are then added simultaneously and continuously over three hours. After 8 hours the reaction is stopped; the latex obtained has a polymer concentration of 33% by weight and an average particle diameter of 0.09 μm .

— *Polymerisation.*

The procedure is as in example 1 but using 4.25 kg of latex 2 above, i.e. 1.4 kg of polymer.

The latex obtained has a concentration of 52% by weight and a viscosity of 40 cp.

The weight of crusts in the autoclave is only 400 g.

Particle size analysis of the latex obtained shows the polymer to be made up of two sets of particles with respective average diameters of 0.18 μm and 0.96 μm , the fine particles constituting 30% by weight.

WHAT WE CLAIM IS:—

1. A method of preparing poly(vinyl chloride) or a copolymer containing at least 50% by weight of vinyl chloride and at least one copolymerisable monomer, comprising polymerising the corresponding monomer or monomers in micro-suspension in the presence of a seeding product in the form of a first dispersion of particles of a vinyl polymer previously prepared by polymerisation in micro-suspension, and in the presence of one or more other seeding products in the form of dispersions of particles of a vinyl polymer, the average diameters of which differ from the particle average diameter of the first seeding product and, when more than one such other seeding product is used, from one another, in which the particles of the first dispersion contain at least one initiator soluble in organic material and no supplementary addition of free initiator (as herein defined) is made to the reaction mixture.

2. A method as claimed in Claim 1, in which the vinyl polymer used as each seeding product is a poly(vinyl chloride) or a copolymer containing at least 50% by weight of vinyl chloride and at least one copolymerisable monomer, or a homopolymer of a monomer copolymerisable with vinyl chloride, or a copolymer of one or more monomers copolymerisable with vinyl chloride.

3. A method as claimed in Claim 1 or 2, in which the average diameter of the polymer particles of the first seeding product is in the range from 0.05 to 1.5 μm .

4. A method as claimed in Claim 3, in which the average diameter of the polymer particles of the seeding product(s) other than the first lies in the range from 0.02 to 1.5 μm .

5. A method as claimed in any preceding claim, in which the particles of at least one seeding product other than the first also contain at least one initiator.

6. A method as claimed in any one of Claims 1 to 4, in which the seeding product(s) other than the first are also prepared by polymerisation in micro-suspension in the presence of an initiator soluble in organic material.

7. A method as claimed in any one of Claims 1 to 4, in which the seeding product or products other than the first are prepared by polymerisation in emulsion, in the presence of a water-soluble initiator.

8. A method as claimed in any preceding



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solution of sodium dodecylbenzene sulphonate,
— 55 kg of vinyl chloride.

Polymerisation is carried out as in example 16 and the latex obtained has a polymer concentration of 53% by weight and a viscosity of 45 cp.

The weight of crusts in the autoclave is only 320 g.

10 Particle size analysis shows the latex to contain three sets of particles with respective average diameters of 0.26 μm , 0.54 μm and 0.92 μm , constituting 22, 32 and 46% by weight of the polymer.

Example 18.

15 Seeding latices 1 and 2 from example 16 are used in polymerisation.

— Preparation of seeding latex 3 in emulsion.

20 The preparation of seeding latex 2 from example 1 is repeated, but with 1.04 of a 10% by weight aqueous solution of sodium tetradecylsulphonate instead of 2.6 kg and without the introduction of sodium tetradecylsulphonate during polymerisation. The average particle diameter of the latex obtained is 0.031 μm .

— Polymerisation.

This is done under the same conditions as in example 16.

30 The latex obtained has a viscosity of 22 cp and contains three sets of particles constituting 13, 22 and 65% by weight of the polymer, with respective average diameters of 0.067 μm , 0.19 μm and 0.97 μm .

Example 19.

35 — Preparation of seeding latex 1 in micro-suspension.

The preparation of seeding latex 1 from example 1 is repeated.

40 — Preparation of seeding latex 2 in emulsion.

The following are placed in a 25-litre autoclave:

— 9.1 kg of water,

45 — 0.75 kg of seeding latex 3 from Example 18, i.e. 0.3 kg of poly(vinyl chloride).

50 These are agitated and heated to 75°C, and this temperature is maintained throughout the operation. As soon as the mixture is at 75°C, 12 g of potassium persulphate in solution in 100 g of water is introduced. 6 kg of butyl acrylate and one litre of an aqueous solution containing 30 g of sodium pyrophosphate and 60 g of sodium dodecylbenzene sulphonate are then added simultaneously and continuously over three hours. After 8 hours the reaction is stopped; the latex obtained has a polymer concentration of 33% by weight and an average particle diameter of 0.09 μm .

60 — Polymerisation.

The procedure is as in example 1 but using 4.25 kg of latex 2 above, i.e. 1.4 kg of polymer.

The latex obtained has a concentration of 52% by weight and a viscosity of 40 cp.

The weight of crusts in the autoclave is only 400 g.

70 Particle size analysis of the latex obtained shows the polymer to be made up of two sets of particles with respective average diameters of 0.18 μm and 0.96 μm , the fine particles constituting 30% by weight.

WHAT WE CLAIM IS:—

1. A method of preparing poly(vinyl chloride) or a copolymer containing at least 50% by weight of vinyl chloride and at least one copolymerisable monomer, comprising polymerising the corresponding monomer or monomers in micro-suspension in the presence of a seeding product in the form of a first dispersion of particles of a vinyl polymer previously prepared by polymerisation in micro-suspension, and in the presence of one or more other seeding products in the form of dispersions of particles of a vinyl polymer, the average diameters of which differ from the particle average diameter of the first seeding product and, when more than one such other seeding product is used, from one another, in which the particles of the first dispersion contain at least one initiator soluble in organic material and no supplementary addition of free initiator (as herein defined) is made to the reaction mixture.

2. A method as claimed in Claim 1, in which the vinyl polymer used as each seeding product is a poly(vinyl chloride) or a copolymer containing at least 50% by weight of vinyl chloride and at least one copolymerisable monomer, or a homopolymer of a monomer copolymerisable with vinyl chloride, or a copolymer of one or more monomers copolymerisable with vinyl chloride.

3. A method as claimed in Claim 1 or 2, in which the average diameter of the polymer particles of the first seeding product is in the range from 0.05 to 1.5 μm .

4. A method as claimed in Claim 3, in which the average diameter of the polymer particles of the seeding product(s) other than the first lies in the range from 0.02 to 1.5 μm .

5. A method as claimed in any preceding claim, in which the particles of at least one seeding product other than the first also contain at least one initiator.

6. A method as claimed in any one of Claims 1 to 4, in which the seeding product(s) other than the first are also prepared by polymerisation in micro-suspension in the presence of an initiator soluble in organic material.

7. A method as claimed in any one of Claims 1 to 4, in which the seeding product or products other than the first are prepared by polymerisation in emulsion, in the presence of a water-soluble initiator.

8. A method as claimed in any preceding

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5 claim, in which the total quantity of seeding products used is such that the weight of polymer(s) contained in them represents 1 to 50% of the sum of the weight of vinyl chloride or mixture of vinyl chloride and copolymerisable monomer and the weight of the seeding polymer(s).

10 9. A method as claimed in any preceding claim, in which the ratio of the weight of the first seeding polymer to that of the other seeding polymers is in the range from 95:5 to 5:95.

15 10. A method as claimed in any preceding claim, in which the concentration of seeding polymers plus the vinyl chloride or mixture of vinyl chloride and copolymerisable monomer is from 20 to 80% by weight of the reaction mixture.

20 11. A method as claimed in any preceding claim, in which an anionic emulsifier is added before and/or during the polymerisation in the presence of the seeding products.

25 12. A method as claimed in Claim 11, in which the anionic emulsifier is associated with a non-ionic emulsifier.

30 13. A method as claimed in any preceding claim, in which the polymerisation in the presence of the seeding products is accelerated by activation of the initiator contained in the particles of the seeding products, by a metal complex, formed *in situ*, that is soluble in organic material.

35 14. A method as claimed in Claim 1, substantially as hereinbefore described in any one of the foregoing Examples.

15. Latices containing at least two sets of

particles with different average diameters, when prepared by a method as claimed in any one of Claims 1 to 14.

40 16. Latices as claimed in Claim 15 containing two sets of particles with respective average diameters from 0.4 to 2.5 μm and from 0.08 to 1 μm , in an average diameter ratio from 1:1 to 20:1 and a weight ratio from 0.1:1 to 10:1.

45 17. Latices as claimed in Claim 15 containing three sets of particles with respective average diameters of from 0.4 to 2.5 μm , from 0.15 to 1 μm and from 0.05 to 0.4 μm , in which the average diameter ratio of coarse particles to medium particles is in the range from 1:1 to 20:1, the average diameter ratio of medium particles to fine particles is in the range from 1:1 to 20:1, the average weight ratio of coarse particles to medium particles is in the range from 0.1:1 to 20:1, and the average weight ratio of medium particles to fine particles is in the range from 0.1:1 to 20:1.

50 18. Latices as claimed in any one of Claims 15 to 18 having a polymer concentration of from 20 to 75% by weight.

55 19. Polymers and copolymers in the form of powders suitable for the preparation of plastisols, separated from latices as claimed in any one of Claims 15 to 18.

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