

PREPARATION OF VINYL CHLORIDE POLYMER POWDERS

The invention is concerned with polymers of vinyl chloride capable of giving plastisols with improved rheological properties, and with their preparation.

For some applications where vinyl chloride polymers are used in the form of plastisols, e.g. coating, there is a known demand for polymers in the form of a powder appropriate to the preparation of plastisols containing very small quantities of plasticiser, down to 25 parts by weight of plasticiser per 100 parts of polymer, and having the lowest possible viscosity both at low and high velocity gradients.

Homopolymers and copolymers of vinyl chloride suitable for giving plastisols are prepared by polymerising vinyl chloride in emulsion or microsuspension, optionally with at least one other monomer that can be copolymerised with it. On an industrial scale the polymerisation provides a latex that generally contains from 40 to 55% by weight of dry material. To obtain the polymer in a powdered state, the latex is generally treated by drying, particularly by spray drying or flaking. The greater the weight of dry material in the latex, the less onerous is the drying operation. It is therefore desirable to start with a latex containing the largest possible weight of dry material. On the other hand, for polymerisation, the higher the weight of dry material in the latex to be prepared, the more emulsifying agent required. Latices con-

taining a large weight of dry material thus contain large quantities of emulsifying agent. After the drying process these are mixed with the polymer and are detrimental to its properties, such as the transparency of the articles obtained, its thermal stability, its reaction to light and ultraviolet rays and the ability of the plastisols to lose their bubbles. In addition, it is more difficult to dissipate the heat liberated during the polymerisation reaction if the weight of water in the polymerising medium is low, i.e. if the weight of dry material in the latex to be prepared is high. What is required therefore is to prepare a latex containing a relatively low weight of dry material and, before carrying out the drying operation, to concentrate it by eliminating part of the aqueous phase in the liquid state.

In our prior U.K. Patent Specification No. 1,503,247 is disclosed a method of preparing polymers of vinyl chloride comprising polymerising the corresponding monomer or monomers in microsuspension in the presence of two seeding substances in the form of dispersions of polymer particles with a different average diameter, the particles of at least one of the seeding substances containing the initiator necessary for polymerisation.

This process gives a latex containing two populations of particles with respective average diameters ranging from 0.4 to 2.5 μm and from 0.08 to

1 μm , in a ratio of average diameters in the range 1:1 to 20:1 and a weight ratio in the range 0.1:1 to 10:1.

The latex obtained by this process contains polymers which, after the separation of the polymerising medium, are in the form of a powder particularly appropriate for the preparation of plastisols with a Newtonian or pseudoplastic action, containing very small quantities of plasticiser, down to 25 parts per 100 parts by weight of polymer, and with a low viscosity, both at low and high velocity gradients, thus allowing for very high speed coating.

The present invention is based on the discovery that, by concentrating a latex of a polymer of vinyl chloride containing from 30 to 60% by weight of dry material and comprising two populations of particles with specific granulometric properties, by eliminating a large enough fraction of the aqueous phase in the liquid state, it is possible, after drying out the residual water, to obtain a powdered polymer appropriate to the preparation of plastisols with rheological properties still better than those prepared from the polymer obtained by direct drying of the latex. By doing this it is possible to obtain a polymer containing only a small quantity of emulsifier, which has very little effect on its other properties.

In accordance with the invention, there is provided a method of preparing polymers of vinyl chloride in the form of a powder capable of giving plastisols with

improved rheological properties, comprising concentrating a latex of homopolymer or copolymer of vinyl chloride containing from 30 to 60% by weight of dry material and two populations of particles by eliminating a fraction of the aqueous phase in the liquid state and then drying out the residual water, in which the weight of dry material contained in the latex after its concentration is from 50 to 80%, the difference between the weight per cent of dry material contained in the latex before and after its concentration is over 10%, preferably 15 to 25%, and the two populations of particles in the latex have mean diameters within the respective ranges 0.7 to 1.5 μm and 0.12 to 0.3 μm , at least 90% by weight of the particles of each population having a diameter within the range from 0.7 to 1.6 times the mean diameter of the said population, 5 to 45% by weight of the particles of the latex having a diameter less than 0.4 μm .

The vinyl chloride polymers referred to, as well as homopolymers, are copolymers containing at least 50% by weight of vinyl chloride and at least one monomer copolymerisable with vinyl chloride. The copolymerisable monomers are those generally used in conventional methods of copolymerising vinyl chloride. Some examples are vinyl esters of monocarboxylic and polycarboxylic acids, such as vinyl acetate, propionate, and benzoate; unsaturated monocarboxylic and polycarboxylic acids, such as acrylic, methacrylic, maleic,

fumaric, and itaconic acids, their aliphatic, cyclo-aliphatic and aromatic esters, their amides and their nitriles; alkyl, vinyl and vinylidene halides; alkyl vinyl ethers; and olefins.

The latex to be concentrated may be prepared directly by polymerising vinyl chloride in emulsion, in the presence of two seeding substances prepared by polymerisation in emulsion. It may equally be prepared directly by polymerising vinyl chloride in seeded micro-suspension, particularly by the process described in our said prior U.K. Patent Specification. Again, it may be prepared by mixing two latices, each containing one of the two populations of particles.

The latices containing one population of particles may be prepared by polymerising vinyl chloride in emulsion, possibly in the presence of a seeding substance prepared by emulsion polymerisation. They may equally be prepared by polymerising vinyl chloride in micro-suspension, possibly in the presence of a seeding substance, particularly by the method described in French Patent No. 1,485,547, the seeding substance having been prepared by polymerisation in micro-suspension.

The latex containing two populations of particles is concentrated by eliminating a fraction of the aqueous phase in the liquid state. This can be done by any known process such as filtration or centrifugal decantation and is preferably done by ultra-filtration of the latex through a semi-permeable membrane.

(17) The ultrafiltration may be carried out in a conventional installation such as is found in industry.

An installation of the type is shown in the single figure of the accompanying drawing, which is a view in vertical section. It essentially comprises a tank 1 containing the latex to be treated, an ultrafilter 2 and a pump 3, which makes the latex flow through pipe 4 to the ultrafilter 2. A pipe 5 has flow-meter 6 mounted on it, and the concentrate discharged by the ultrafilter 2 is recycled through the pipe 5 to the tank 1. A coil 7 for circulating heat-exchange fluid is submerged in the latex contained in the tank 1 and keeps it at constant temperature. A pipe 8 is used to start up the installation.

The installation further comprises stop valves 9, 10, 11, 12 and 13 and manometers 14 and 15.

The apparatus is started up and the operation carried out as follows: with the valve 10 closed and the valve 9 open, the pump 3 is set in motion, then the valves 10 and 11 are opened and the valve 9 closed. The opening of the valves 10 and 11 is adjusted by successive approximations, until the desired flow of latex is obtained at the desired pressure. The difference between the pressures indicated by the manometers 14 and 15 represents the drop in pressure in the ultrafilter 2.

For satisfactory performance of the ultrafiltration, it is advantageous, according to the invention, to observe the following conditions:

- 15 - the semi-permeable membrane must have a high cutting threshold, generally of from 10 000 to 50 000, expressed as the value of the molecular weight of standard proteins in a neutralised medium,
- 20 - the speed at which the latex passes onto the membrane must be over 0.5 m/s and preferably from 2 to 3 m/s, to avoid any clogging of the membrane and also to limit the pressure drop in the ultrafilter and the shearing to which the latex is subjected,
- 25 - the difference between the pressures at each side of the membrane must be from 0.3 to 6 bars and preferably from 0.5 to 3 bars,
- the temperature of the latex must be from 10 to 50°C and preferably from 30 to 50°C,

- (19)
- stoppage of the installation must be followed by a cycle of adequate rinsing with an aqueous solution of emulsifying agent, to avoid irreversible plugging and consequent destruction of the membrane.

5 All other things otherwise being equal, the time taken for ultrafiltering increases commensurately with the weight of dry material to be contained in the desired latex. As an illustration, for 100 kg of latex containing 48% by weight of dry material and with an ultrafiltration area of 10 m², the ultrafiltering time taken to obtain 63% by weight of dry material is generally from 5 to 90 minutes.

When the latex has been concentrated the residual water is eliminated by any known drying process, such as spraying or flaking.

15 The invention also covers the polymers thus obtained. These are in the form of a powder particularly adapted to the preparation of plastisols with a Newtonian or pseudoplastic action, containing very small quantities of plasticiser, which may be as little as 25 parts by weight of plasticiser per 100 parts of polymer, and with a low viscosity, thus permitting very high speed coating.

20 The polymers of the invention may be applied to the manufacture of sheets, films, threads, hollow bodies, cellular materials, or articles shaped by calendering, extrusion, extrusion with blowing, injection or moulding, as well as to the production of coated claddings, cellular materials, or articles shaped by any known methods of using plastisols: coating, moulding by rotation, or soaking.

Some examples of the invention will now be given, purely as an illustration and without imposing any restrictions. For all the examples the ultrafiltering conditions are the same as those described in example 1.

5 For latices containing two populations of particles, the granulometric properties taken into consideration, according to the invention, are as follows:

- D_C is the average diameter of the population of coarse particles,
- 10 - D_F is the average diameter of the population of fine particles,
- P_C is the proportion by weight of those particles in the population of coarse particles which have a diameter ranging from 0.7 to 1.6 times the
- 15 average diameter of the said population,
- P_F is the proportion by weight of those particles of the population of fine particles which have a diameter ranging from 0.7 to 1.6 times the average diameter of the said population, and
- 20 - P_W is the proportion by weight of the particles smaller in diameter than $0.4 \mu m$ in the latex.

Examples 1, 3, 4, 5, 6, 11, 13 and 15 are in accordance with the invention. They show that the vinyl chloride polymers which are obtained by drying a latex

25 after its concentration and which are prepared by the method of the invention, give plastisols of a lower viscosity than plastisols obtained, all other things being equal, from polymers obtained by drying the same latex before it is concentrated.

Examples 2, 7, 8, 9, 10, 12, 14 and 16 are given as a comparison. They show that the vinyl chloride polymers, which were obtained by drying a latex after its concentration and which are prepared by a method not in accordance with the invention, give plastisols of a viscosity the same as or even higher than that of the plastisols obtained, all other things being equal, from polymers obtained by drying the same latex before it is concentrated. At the beginning of each comparative example an explanation is given of where the method used departs from the invention.

EXAMPLE 1

Preparation of latex 1 A

A 1000 litre autoclave is used to prepare a latex of vinyl chloride homopolymer by the process described in our said prior U.K. patent specification.

For this purpose the following are placed in the autoclave:

- 255 kg of deionised water,
- 400 kg of vinyl chloride,
- 65 kg of a polyvinyl chloride seeding latex, containing 31.5% by weight of dry material, which has previously been prepared in microsuspension, its particles having an average diameter of 0.507 μ m and containing 1.92% by weight of lauroyl peroxide relative to the polymer,
- 23 kg of a polyvinyl chloride seeding latex, containing 43.5% by weight of dry material, which has previously been prepared in emulsion, the

particles having an average diameter of 0.130 μm
and not containing any lauroyl peroxide,

- 2.8 kg of sodium dodecyl benzene sulphonate,
- 15 g of copper sulphate of the formula $\text{SO}_4\text{Cu} \cdot 5\text{H}_2\text{O}$,
- 15 g of ascorbic acid.

The reaction mixture is agitated and heated to 52°C
under autogenous pressure, and this temperature is maintained
throughout the polymerising operation. After 10.5 hours
of polymerisation and degassing of the non-reacted vinyl
chloride, latex 1A is obtained, containing 2 populations of
particles and having the following granulometric properties:

$$D_C (\mu\text{m}) = 1.07 ; D_F (\mu\text{m}) = 0.19;$$

$$P_C (\%) = 92 ; P_F (\%) = 92 ;$$

$$P_W (\%) = 27.$$

Two portions of latex 1 A are concentrated by
ultrafiltration in an installation developing an ultra-
filtration area of 10 m^2 . The installation is equipped
with a membrane with a cutting threshold of 20 000,
marketed by Applicants under the trade name "IRIS 3038"
and supplied by a pump adapted to discharge $30 \text{ m}^3/\text{h}$ at
a pressure of 5 bars. Latex 1 B and latex 1 C are
obtained. When the ultrafiltering process has been
completed the installation is emptied and thoroughly
rinsed with an aqueous solution of emulsifying agent.

There is found to be no plugging of the membrane.

Table 1 sets out the weight of dry material in each
latex and the viscosity of each latex, determined by a
rotational instrument for measuring rheological properties
of the Brookfield RVT type (spindle no. 1, 20 rpm, conditioning

and reading at 23⁰C).

Table 1

Reference of latex	Content of dry material by weight %	Brookfield RVT viscosity centipoises
1 A	54.2	10.3
1 B	70.5	125
1 C	77.3	1380

Latices 1 B and 1 C have excellent mechanical resistance to shearing.

Latices 1 A, 1 B and 1 C are treated by spraying; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer and 40 parts by weight of dioctyl phthalate. The rheological properties of the plastisol are determined:

- firstly with a rotational instrument for measuring such properties, of the Brookfield RVT type (conditioning and reading at 25⁰C)
- and secondly with an instrument to measure such properties by extrusion, of the Severs type (conditioning 2 hours at 25⁰C).

The rheological properties of the three plastisols obtained are given in Table 2.

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Table 2

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
1 A	0.5	210	600	450
	24	420		
1 B	0.5	190	600	372
	24	400		
1 C	0.5	150	600	300
	24	300		

EXAMPLE 2

This example is given as a comparison: the absolute difference between the weight of dry material in the latex before and after concentration is not in accordance with the invention.

A portion of latex 1 A described in example 1 is concentrated by ultrafiltration to give latex 2 B.

Table 3 sets out the weight of dry material contained in each latex and the Brookfield RVT viscosity of each latex (spindle no. 1, 20 rpm, conditioning and reading at 23°C).

Table 3

Reference of latex	Content of dry material%by weight	Brookfield RVT viscosity centipoises
1 A	54.2	10.3
2 B	62	32

Latices 1 A and 2 B are treated by spraying; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer and 40 parts by weight of dioctyl phthalate.

The rheological properties of the two plastisols obtained are given in Table 4.

Table 4

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
1 A	0.5	210	600	450
	24	420		
2 B	0.5	210	600	450
	24	420		

EXAMPLE 3

A latex of vinyl chloride homo polymer is prepared in a 1000 litre autoclave by the method described in our said prior U.K. patent specification.

For this purpose the following are placed in the autoclave:

- 255 kg of deionised water,
- 400 kg of vinyl chloride,
- 55.6 kg of a polyvinyl chloride seeding latex containing 36% by weight of dry material, which has previously been prepared in micro suspension, the particles having an average diameter of 0.54 μ m and

containing 1.72% of lauroyl peroxide relative to the polymer,

- 23.2 kg of a polyvinyl chloride seeding latex containing 38.8% by weight of dry material, which has previously been prepared in emulsion, the particles having a mean diameter of 0.13 μm and not containing any lauroyl peroxide,
- 2.8 kg of sodium dodecyl benzene sulphonate,
- 15 g of copper sulphate of the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$,
- 15 g of ascorbic acid.

After 10.75 hours of polymerisation at 52°C and degassing of unreacted vinyl chloride, latex 3 A is obtained, containing two populations of particles and having the following granulometric properties:

$$\begin{aligned} D_C (\mu\text{m}) &= 1.2 ; D_F (\mu\text{m}) = 0.19 ; \\ P_C (\%) &= 92 ; P_F (\%) = 92 ; \\ P_W (\%) &= 28. \end{aligned}$$

Two portions of latex 3 A are concentrated by ultra-filtration to give latex 3 B and latex 3 C.

Table 5 sets out the weight of dry material in each latex and the Brookfield RVT viscosity of each latex (spindle no. 1, 20 rpm, conditioning and reading as 23°C).

Table 5

Reference of latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
3 A	54.7	9.5
3 B	70.6	96
3 C	76.2	1130

Latices 3 B and 3 C have excellent mechanical resistance to shearing.

Latices 3 A, 3 B and 3 C are treated by flaking, the flaking equipment being formed by two drums, each 0.6 m² in area; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer and 40 parts by weight of dioctyl phthalate.

The rheological properties of the three plastisols obtained are summarised in Table 6.

Table 6

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
3 A	0.5	260	400	625
	24	890		
3 B	0.5	250	400	250
	24	820		
3 C	0.5	170	400	168
	24	500		

EXAMPLE 4

Preparation of latex 41

Using a 1000 litre autoclave, a latex of vinyl chloride homo polymer is prepared in emulsion, in the presence of a seeding substance. For this purpose the following are placed in the autoclave:

- 340 kg of deionised water,
- 0.45 kg of lauric acid ,
- 0.6 kg of a 12 N aqueous ammonia,

- 5 - 13 kg of a polyvinyl chloride seeding latex containing 40.2% by weight of dry material, which has previously been prepared in emulsion, the particles having a mean diameter of 0.195 μm ,
- 300 kg of vinyl chloride.

- 10 The reaction mixture is agitated and heated to 52°C under autogenous pressure, and this temperature is maintained throughout the polymerising operation. As soon as the mixture reaches 52°C 0.15 kg of potassium persulphate is introduced. 30 minutes later 20 litres
- 15 of a 10% by weight aqueous solution of sodium tetradecyl sulphonate is added continuously at 2 litres per hour. After 10.5 hours of polymerisation the unreacted vinyl chloride is degassed to give latex 41. This contains one population of particles, with 41.5% by weight
- 20 of dry material and a mean particle diameter of 0.730 μm .

Preparation of latex 42

- A latex of vinyl chloride homo polymer is prepared in emulsion in a 1000 litre autoclave. The following
- 25 are placed in the autoclave:

- 350 kg deionised water,
- 1.06 kg of lauric acid,
- 0.6 kg of a 50% by weight aqueous solution of KOH
- 300 kg of vinyl chloride.

The reaction mixture is agitated and heated to 52°C under autogenous pressure; this temperature is then maintained throughout the polymerising operation. As soon as the mixture reaches 52°C 0.15 kg of potassium persulphate is introduced. 15 minutes later 22 litres of a 10% by weight aqueous solution of sodium tetradecyl sulphonate is added continuously at 2.5 litres per hour. After 12.7 hours of polymerisation the unreacted vinyl chloride is degassed to give latex 42. This contains one population of particles, with a dry material content of 41.8% by weight and a mean particle diameter of 0.180 µm.

Preparation of latex 4 A

By mixing 202 parts by weight of latex 41 and 60 parts by weight of latex 42, latex 4 A is obtained, containing two populations of particles and having the following granulometric properties:

$$D_C (\mu\text{m}) = 0.730 ; D_F (\mu\text{m}) = 0.180 ;$$

$$P_C (\%) = 94 ; P_F (\%) = 94 ;$$

$$P_W (\%) = 25.2.$$

A portion of latex 4 A is concentrated by ultra-filtration to give latex 4 B.

Table 7 sets out the weight of dry material in each latex and the Brookfield RVT viscosity (spindle no. 1, 50 rpm, conditioning and reading at 23°C).

Table 7

Reference of latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
4 A	41.6	6
4 B	65.5	88

Latex 4 B has excellent mechanical resistance to shearing.

Latices 4 A and 4 B are treated by spraying; the powder obtained is ground, and a plastisol is prepared by mixing 100 parts by weight of polymer and 45 parts by weight of dioctyl phthalate.

The rheological properties of the two plastisols obtained are summarised in Table 8.

Table 8

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
4 A	0.5	310	600	400
	24	600		
4 B	0.5	260	600	350
	24	530		

EXAMPLE 5

Preparation of latex 51

Using a 1000 litre autoclave, a latex of vinyl chloride homo polymer is prepared in emulsion, in the presence of a seeding substance. The following are placed in the autoclave:

- 340 kg of deionised water,
- 0.45 kg of lauric acid,
- 0.6 kg of a 12 times normal aqueous ammoniacal solution,

- (31)
- 13 kg of a polyvinyl chloride seeding latex containing 40.2% of dry material by weight, which has previously been prepared in emulsion, the particles having a mean diameter of 0.195 μm ,
 - 300 kg of vinyl chloride.

5

The reaction mixture is agitated and heated to 57°C under autogenous pressure; this temperature is maintained throughout the polymerising operation. As soon as the mixture reaches 57°C 0.10 kg of potassium persulphate is introduced. 30 minutes later 20 litres of a 10% by weight aqueous solution of sodium lauryl sulphate is added continuously at 3 litres per hour. After 10.5 hours of polymerisation the unreacted vinyl chloride is degassed to give latex 51. This contains one population of particles, with 41.6% by weight of dry material and a mean particle diameter of 0.760 μm .

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Preparation of latex 52

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A latex of vinyl chloride homo polymer is prepared in emulsion in a 1000 litre autoclave. The following are placed in the autoclave:

25

- 350 kg of deionised water,
- 1.06 kg of lauric acid,
- 0.6 kg of a 50% by weight aqueous solution of potash,
- 300 kg of vinyl chloride.

The reaction mixture is agitated and heated to 57°C under autogenous pressure; this temperature is maintained throughout the polymerising operation. As soon as the mixture reaches 57°C 0.10 kg of potassium persulphate is

introduced. 15 minutes later 22 litres of a 10% by weight aqueous solution of sodium lauryl sulphate is added continuously at 2.5 litres per hour. After 8.5 hours of polymerisation the unreacted vinyl chloride is degassed to give latex 52. This contains one population of particles with a dry material content of 41.2% by weight and a mean particle diameter of 0.170 μm .

Preparation of latex 5 A

By mixing 171 parts by weight of latex 51 and 94 parts by weight of latex 52 latex 5 A is obtained. This contains two populations of particles and has the following granulometric properties:

$$D_C (\mu\text{m}) = 0.760 ; D_F (\mu\text{m}) = 0.170 ;$$

$$P_C (\%) = 94 ; P_F (\%) = 94 ;$$

$$P_W (\%) = 35.$$

A portion of latex 5 A is concentrated by ultrafiltration to give latex 5 B.

Table 9 sets out the weight of dry material contained in each latex and the Brookfield RVT viscosity (spindle no. 1, 50 rpm, conditioning and reading at 23°C).

Table 9

Reference of Latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
5 A	41.4	7
5 B	68.2	97

Latex 5 B has excellent mechanical resistance to shearing.

Latices 5 A and 5 B are treated by spraying; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer and 50 parts by weight of dioctyl phthalate.

The rheological properties of the two plastisols obtained are summarised in Table 10.

Table 10

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
5 A	0.5	900	200	160
	24	1330		
5 B	0.5	530	200	122
	24	810		

EXAMPLE 6

Preparation of latex 6 A

A latex of vinyl chloride and vinyl acetate co-polymer is prepared in a 1000 litre autoclave by the method described in our said prior U.K. patent specification.

The following are placed in the autoclave:

- 330 kg of deionised water,
- 475 kg of vinyl chloride ,
- 25 kg of vinyl acetate ,
- 86 kg of a polyvinyl chloride seeding latex containing



- 10

After 11 hours of polymerisation at 52°C,

15

20

A portion of latex 6 A is concentrated by ultra-filtration to give latex 6 B.

25

Table 11

Reference of latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
6 A	52.8	23
6 B	69.3	65

Latex 6 B has excellent mechanical resistance to shearing.

Latices 6 A and 6 B are treated by spraying; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer and 50 parts by weight of dioctyl phthalate.

The rheological properties of the two plastisols obtained are summarised in Table 12.

Table 12

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
6 A	0.5	110	400	118
	24	200		
6 B	0.5	100	400	101
	24	190		

EXAMPLE 7

This example is given as a comparison: the latex to be concentrated contains only one population of particles.

Preparation of latex 7 A

Using a 1000 litre autoclave, a latex of vinyl chloride homo polymer is prepared in micro-suspension, in the presence of a seeding substance. The following are placed in the autoclave:

- 385 kg of deionised water ,
- 300 kg of vinyl chloride ,
- 30.5 kg of a polyvinyl chloride seeding latex containing 35.4% of dry material, which has previously been prepared in micro-suspension, the particles having a mean diameter of 0.490 μm and containing 1.47% by weight of lauroyl peroxide relative to the polymer, ,
- 2.1 kg of sodium dodecyl benzene sulphonate ,
- 12 g of copper sulphate of the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$,
- 12 g of ascorbic acid.

After 12 hours of polymerisation at 52°C and degassing of the unreacted vinyl chloride, latex 7 A is obtained.

This contains one population of particles with an average diameter of 1.12 μm .

A portion of latex 7 A is concentrated by ultrafiltration to give latex 7 B.

Table 13 sets out the weight of dry material contained in each latex and the Brookfield RVT viscosity (spindle no. 1, 20 rpm, conditioning and reading at 23°C).

Table 13

Reference of latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
7 A	40.6	5
7 B	53	52

Latices 7 A and 7 B are treated by spraying; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer and 45 parts by weight of dioctyl phthalate.

The rheological properties of the two plastisols obtained are summarised in Table 14.

Table 14

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
7 A	0.5	160	350	890
	24	270		
7 B	0.5	160	350	245
	24	270		

EXAMPLE 8

This example is given as a comparison: the latex to be concentrated contains only one population of particles.

A portion of each of latices 41 and 42 described in example 4 and latices 51 and 52 described in example 5 are concentrated by ultra filtration, to give latices 8 B₄₁, 8 B₄₂, 8 B₅₁ and 8 B₅₂ respectively.

Table 15 gives the weight of dry material in each latex and the Brookfield RVT viscosity (spindle no. 1, 50 rpm, conditioning and reading at 23°C).

Table 15

Reference of latex	Content of dry material %by weight	Brookfield RVT viscosity centipoises
41	41.5	7
8 B ₄₁	52.6	43
42	41.8	9
8 B ₄₂	53.1	59
51	41.6	6
8 B ₅₁	52.7	40
52	41.2	9
8 B ₅₂	53.3	64

Latices 41, 42, 51, 52, 8 B₄₁, 8 B₄₂, 8 B₅₁ and 8 B₅₂ are treated by spraying; the powder obtained is ground and a plastisol is obtained by mixing 100 parts by weight of polymer and the number of parts by weight of dioctyl phthalate given in Table 16.

Table 16

Reference of latex	Number of parts by weight of dioctyl phthalate per 100 parts by weight of polymer
41 8 B ₄₁	50
42 8 B ₄₂	70
51 8 B ₅₁	55
52 8 B ₅₂	70

The rheological properties of the eight plastisols obtained are given in Tables 17 and 18.

Table 17

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
41	0.5	700	500	608
	24	1300		
8 B ₄₁	0.5	700	500	953
	24	1300		
51	0.5	400	170	1400
	24	1000		
8 B ₅₁	0.5	400	170	1450
	24	1000		

Table 18

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
42	0.5	1900	500	118
	24	3000		
8 B ₄₂	0.5	1900	500	129
	24	3000		
52	0.5	2200	150	210
	24	6500		
8 B ₅₂	0.5	2200	150	210
	24	6500		

EXAMPLE 9

This example is given as a comparison: D_C and D_F are not in accordance with the invention.

Preparation of latex 91

The method of preparing latex 41 described in example 4 is followed, but with 25 kg of the seeding latex placed in the autoclave instead of 13 kg, to prepare latex 91 of vinyl chloride homo polymer. This contains one population of particles, the content of dry material being 42.8% by weight and the mean diameter of the particles 0.590 μm .

Preparation of latex 92

The method of preparing latex 42 described in example 4 is followed, except that 2.04 kg of lauric acid instead of 1.06 kg and 1.15 kg of 50% by weight aqueous KOH solution instead of 0.6 kg are placed in the autoclave, to prepare latex 92 of vinyl chloride homo polymer. This contains one population of particles, the content of dry material being 40.6% by weight and the mean diameter of the particles 0.098 μm .

Preparation of latex 9 A

290 parts by weight of latex 91 and 102 parts by weight of latex 92 are mixed to give latex 9 A, which contains two populations of particles and has the following granulometric properties:

$$D_C (\mu\text{m}) = 0.590 ; D_F (\mu\text{m}) = 0.098 ;$$

$$P_C (\%) = 93 ; P_F (\%) = 93 ;$$

$$P_W (\%) = 26.$$

A portion of latex 9 A is concentrated by ultrafiltration to give latex 9 B.

Table 19 sets out the weight of dry material in each latex and the Brookfield RVT viscosity (spindle no. 1, 50 rpm, conditioning and reading at 23°C).

Table 19

Reference of Latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
9 A	42.1	6
9 B	61.7	72

Latices 9 A and 9 B are treated by spraying; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer and 50 parts by weight of dioctyl phthalate.

The rheological properties of the two plastisols are summarised in Table 20.

Table 20

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 5 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
9 A	0.5	390	600	310
	24	800		
9 B	0.5	390	600	310
	24	800		

EXAMPLE 10

This example is given as a comparison: P_C is not in accordance with the invention.

Preparation of latex 10 A

A latex of vinyl chloride homo polymer is prepared in a 1000 litre autoclave by the method described in our said prior U.K. patent specification.

5 For this purpose the following are placed in the autoclave:

- 255 kg of deionised water,
- 400 kg of vinyl chloride,
- 44.5 kg of a polyvinyl chloride seeding latex
- 10 containing 35.2% by weight of dry material, which has previously been prepared in micro-suspension, the particles having a mean diameter of $0.482 \mu\text{m}$ and containing 1.88% by weight of lauroyl peroxide relative to the polymer ,
- 15 - 19.3 kg of a polyvinyl chloride seeding latex containing 41.5% by weight of dry material, which has previously been prepared in emulsion, the particles having a mean diameter of $0.112 \mu\text{m}$ and not containing any lauroyl peroxide,
- 20 - 2.8 kg of sodium dodecyl benzene sulphonate,
- 15 g of copper sulphate of the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$,
- 15 g of ascorbic acid.

After 12.5 hours of polymerisation at 52°C and degassing of the unreacted vinyl chloride, latex 10 A is

25 obtained, containing two populations of particles and with the following granulometric properties:

$$D_C (\mu\text{m}) = 1.08 ; D_F (\mu\text{m}) = 0.197 ;$$

$$P_C (\%) = 78 ; P_F (\%) = 92 ;$$

$$P_W (\%) = 33.$$

A portion of latex 10 A is concentrated by ultra-filtration to give latex 10 B.

Table 21 sets out the weight of dry material contained in each latex and the Brookfield RVT viscosity (spindle no. 1, 20 rpm, conditioning and reading at 23°C).

Table 21

Reference of Latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
10 A	54.3	9
10 B	71.2	140

Latex 10 B has good mechanical resistance to shearing.

Latices 10 A and 10 B are treated by spraying; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer and 40 parts by weight of dioctyl phthalate.

The rheological properties of the two plastisols obtained are summarised in Table 22.

Table 22

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
10 A	0.5	370	200	250
	24	710		
10 B	0.5	370	200	250
	24	710		

EXAMPLE 11

Preparation of latices 11 A₁, 11 A₂, 11 A₃, 11 A₄,
11 A₅, 11 A₆ and 11 A₇

By mixing latex 7 A described in example 7 with latex 42 described in example 4 in the proportions indicated in Table 23, latices 11 A₁, 11 A₂, 11 A₃, 11 A₄, 11 A₅, 11 A₆ and 11 A₇ of vinyl chloride homo polymer are obtained, containing two populations of particles.

Table 23

Reference of Latex	Parts by weight	
	Latex 7 A	Latex 42
11 A ₁	98	7
11 A ₂	90	10
11 A ₃	87	13
11 A ₄	80	20
11 A ₅	70	30
11 A ₆	60	40
11 A ₇	56	44

Latices 11 A₁ to 11 A₇ have the granulometric properties summarised in Table 24.

Table 24

	Latex						
	11 A ₁	11 A ₂	11 A ₃	11 A ₄	11 A ₅	11 A ₆	11 A ₇
D _C (μm)	1.12	1.12	1.12	1.12	1.12	1.12	1.12
D _F (μm)	0.18	0.18	0.18	0.18	0.18	0.18	0.18
P _C (%)	92	92	92	92	92	92	92
P _F (%)	94	94	94	94	94	94	94
P _W (%)	7.1	10.3	13.3	20.5	30.6	40.7	44.7

A portion of each of latices 11 A₁, 11 A₂, 11 A₃, 11 A₄, 11 A₅, 11 A₆ and 11 A₇ is concentrated by ultrafiltration to give latices 11 B₁, 11 B₂, 11 B₃, 11 B₄, 11 B₅, 11 B₆ and 11 B₇ respectively.

Table 25 summarises the weight of dry material contained in each latex and the Brookfield RVT viscosity (spindle no. 1, 20 rpm, conditioning and reading at 23°C).

Table 25

Reference of Latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
11 A ₁ 11 B ₁	40.7 53	6 12
11 A ₂ 11 B ₂	40.7 55	6 12
11 A ₃ 11 B ₃	40.7 56	6, 5 12
11 A ₄ 11 B ₄	40.8 60	6 11
11 A ₅ 11 B ₅	41.0 61.2	6 11
11 A ₆ 11 B ₆	41.1 62.1	6 11
11 A ₇ 11 B ₇	41.1 63	6 11

Latices 11 A₁ to 11 A₇ and 11 B₁ to 11 B₇ are treated by spraying; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer with the number of parts by weight of dioctyl phthalate given in Table 26.

Table 26

Reference of Latex	Number of parts by weight of dioctyl phthalate per 100 parts by weight of polymer
11 A ₁ 11 B ₁	45
11 A ₂ 11 B ₂	40
11 A ₃ 11 B ₃	40
11 A ₄ 11 B ₄	40
11 A ₅ 11 B ₅	40
11 A ₆ 11 B ₆	45
11 A ₇ 11 B ₇	45

The rheological properties of the fourteen plastisols obtained are summarised in Table 27.

Table 27

Reference	Brookfield RVT rheometer (spindle No. 7/20 rpm)	Severs Rheometer		
of Latex	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
11 A ₁	0.5	130	350	690
	24	250		
11 B ₁	0.5	125	350	680
	24	240		
11 A ₂	0.5	250	400	660
	24	490		
11 B ₂	0.5	230	400	630
	24	450		

Table 27 Cont.

Reference of Latex	Brookfield RVT rheometer (spindle No. 7/20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
11 A ₃	0.5	230	500	690
	24	470		
11 B ₃	0.5	210	500	640
	24	420		
11 A ₄	0.5	200	600	450
	24	410		
11 B ₄	0.5	180	600	340
	24	360		
11 A ₅	0.5	210	600	440
	24	400		
11 B ₅	0.5	170	600	330
	24	350		
11 A ₆	0.5	150	400	370
	24	300		
11 B ₆	0.5	140	400	340
	24	270		
11 A ₇	0.5	190	400	380
	24	400		
11 B ₇	0.5	180	400	360
	24	390		

EXAMPLE 12

This example is given as a comparison: P_w is not in accordance with the invention.

Preparation of latices 12 A₁ and 12 A₂

- 5 By mixing latex 7 A described in example 7 with latex 42 described in example 4, in the proportions indicated in Table 28, latices 12 A₁ and 12 A₂ of vinyl chloride homo polymer are obtained, containing two populations of particles.

Table 28

Reference of Latex	Parts by weight	
	Latex 7 A	Latex 42
12 A ₁	97	3
12 A ₂	50	50

Latices 12 A₁ and 12 A₂ have the granulometric properties summarised in Table 29.

Table 29

	Latex	
	12 A ₁	12 A ₂
D _C (μm)	1.12	1.12
D _F (μm)	0.18	0.18
P _C (%)	92	92
P _C (%)	94	94
P _W (%)	3	49.3

A portion of each of latices 12 A₁ and 12 A₂ is concentrated by ultrafiltration to give latices 12 B₁ and 12 B₂ respectively.

Table 30 sets out the weight of dry material in each latex and the Brookfield RVT viscosity (spindle no. 1, 20 rpm, conditioning and reading at 20°C).

Table 30

Reference of Latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
12 A ₁	40.6	6
12 B ₁	52	12
12 A ₂	41.2	6
12 B ₂	62	11

Latices 12 A₁, 12 A₂, 12 B₁ and 12 B₂ are treated by spraying; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer with 45 parts by weight of dioctyl phthalate.

The rheological properties of the four plastisols obtained are summarised in Table 31.

Table 31

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
12 A ₁	0.5	155	350	820
	24	260		
12 B ₁	0.5	155	350	2100
	24	260		
12 A ₂	0.5	350	300	740
	24	820		
12 B ₂	0.5	350	300	740
	24	820		

EXAMPLE 13Preparation of latices 131, 132, 133 and 134

The method of preparing latex 42 described in example 4 is followed, except that the quantities of lauric acid and potash placed in the autoclave are those given in Table 32, to prepare four latices 131, 132, 133 and 134 of vinyl chloride homo polymer. These contain only one population of particles, and the content of dry material by weight and the average diameter of the particles are also given in Table 32.

Table 32

Reference of Latex	Lauric Acid kg	50% by weight aqueous solution of potash kg	Content of dry material by weight %	Mean diameter of particles μm
131	1.57	0.880	40.1	0.121
132	1.23	0.690	40.3	0.149
133	0.45	0.252	40.7	0.252
134	0.19	0.106	40.6	0.295

Preparation of latices 13 A₁, 13 A₂, 13 A₃ and 13 A₄

Latex 13 A₁ is obtained by mixing 75 parts by weight of latex 41 described in example 4 with 25 parts by weight of latex 131. Similarly latices 13 A₂, 13 A₃ and 13 A₄ are obtained respectively by mixing latices 41 with 132, 41 with 133 and 41 with 134 in the same proportions. Latices 13 A₁, 13 A₂, 13 A₃ and 13 A₄ contain two populations of particles and have the granulometric properties summarised in Table 33.

Table 33

	Latex			
	13 A ₁	13 A ₂	13 A ₃	13 A ₄
D _C (μm)	0.730	0.730	0.730	0.730
D _F (μm)	0.121	0.149	0.252	0.295
P _C (%)	90	90	90	90
P _F (%)	90	90	92	93
P _W (%)	24.4	24.4	24.6	24.6

A portion of each of latices 13 A₁, 13 A₂, 13 A₃ and 13 A₄ is concentrated by ultrafiltration to give latices 13 B₁, 13 B₂, 13 B₃ and 13 B₄ respectively.

Table 34 sets out the weight of dry material contained in each latex and the Brookfield RVT viscosity (spindle no. 1, 20rpm, conditioning and reading at 23).

Table 34

Reference of Latex	Content of dry material by weight %	Brookfield RVT viscosity centipoises
13 A ₁	41.1	7
13 B ₁	63.7	88
13 A ₂	41.2	7
13 B ₂	64	87
13 A ₃	41.3	7
13 B ₃	63.9	86
13 A ₄	41.3	7
13 B ₄	62.1	85

Latices 13 A₁ to 13 A₄ and 13 B₁ to 13 B₄ are treated by spraying; the powder obtained is ground and a plastisol is

prepared by mixing 100 parts by weight of polymer with 45 parts by weight of dioctyl phthalate.

The rheological properties of the eight plastisols obtained are summarised in Table 35.

Table 35

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
13 A ₁	0.5	620	600	270
	24	1210		
13 B ₁	0.5	610	600	260
	24	1200		
13 A ₂	0.5	400	400	470
	24	810		
13 B ₂	0.5	360	400	420
	24	710		
13 A ₃	0.5	380	400	490
	24	740		
13 B ₃	0.5	350	400	410
	24	690		
13 A ₄	0.5	350	400	600
	24	710		
13 B ₄	0.5	340	400	575
	24	700		

EXAMPLE 14

This example is given as a comparison: D_p is not in accordance with the invention.

Preparation of latices 141 and 142

The method of preparing latex 42 described in example 4 is followed, except that the quantities of lauric acid and KOH placed in the autoclave are those given in Table 36, to prepare two latices 141 and 142 of vinyl chloride homo polymer. They contain one population of particles, and the weight content of dry material and mean diameter of the particles are given in

Table 36.

Table 36

Reference of Latex	Lauric Acid kg	50% by weight aqueous solu- tion of KOH. kg	Content of dry material by weight %	Mean diameter of particles μm
141	1.77	0.991	40.1	0.098
142	0.09	0.051	40.5	0.332

Preparation of latices 14 A₁ and 14 A₂

Latex 14 A₁ is obtained by mixing 75 parts by weight of latex 41 described in example 4 with 25 parts by weight of latex 141.

Similarly latex 14 A₂ is obtained by mixing latices 41 and 142 in the same proportions. Latices 14 A₁ and 14 A₂ contain two populations of particles and have the granulometric properties summarised in Table 37.

Table 37

	Latex	
	14 A ₁	14 A ₂
D _C (μm)	0.730	0.730
D _F (μm)	0.098	0.332
P _C (%)	90	90
P _F (%)	90	95
P _W (%)	24.3	24.5

A portion of each of latices 14 A₁ and 14 A₂ is

concentrated by ultrafiltration to give latices 14 B₁ and 14 B₂ respectively.

Table 38 sets out the weight of dry material contained in each latex and the Brookfield RVT viscosity (spindle no. 1, 20 rpm, conditioning and reading at 23°C).

Table 38

Reference of Latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
14 A ₁	41.1	7
14 B ₁	63.1	88
14 A ₂	41.2	7
14 B ₂	62.8	86

Latices 14 A₁, 14 A₂, 14 B₁ and 14 B₂ are treated by spraying; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer with 45 parts by weight of dioctyl phthalate.

The rheological properties of the four plastisols obtained are summarised in Table 39.

Table 39

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
14 A ₁	0.5	930	600	250
	24	2000		
14 B ₁	0.5	930	600	275
	24	2000		
14 A ₂	0.5	300	200	760
	24	680		
14 B ₂	0.5	300	200	830
	24	680		

EXAMPLE 15Preparation of latex 151

Using a 1000 litre autoclave, a latex of vinyl chloride homo polymer is prepared in micro-suspension, in the presence of a seeding substance. For this purpose the following are placed in the autoclave:

- 540 kg of deionised water,
- 300 kg of vinyl chloride,
- 69.2 kg of a polyvinyl chloride seeding latex containing 21.7% by weight of dry material, which has previously been prepared in micro-suspension, the particles having a mean diameter of 0.602 μm and containing 1.63% by weight of lauroyl peroxide relative to the polymer,
- 2.1 kg of sodium dodecyl benzene sulphonate,
- 12 g of copper sulphate of the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$,
- 12 g of ascorbic acid.

After 11.5 hours of polymerisation at 52°C and degassing of the unreacted vinyl chloride, latex 151 is obtained. This contains one population of particles; the content of dry material is 32.8% by weight and the mean diameter of the particles 1.47 μm .

Preparation of latex 15 A

Latex 15 A is obtained by mixing 75 parts by weight of latex 52 described in example 5 with 25 parts by weight of latex 151.

It contains two populations of particles and has the following granulometric properties:

$$D_C (\mu\text{m}) = 1.47 ; D_F (\mu\text{m}) = 0.170 ;$$

$$P_C (\%) = 92 ; P_F (\%) = 93 ;$$

$$P_W (\%) = 29.5.$$

A portion of latex 15 A is concentrated by ultra-filtration to give latex 15 B.

Table 40 sets out the weight of dry material contained in each latex and the Brookfield RVT viscosity (spindle no. 1, 20 rpm, conditioning and reading at 23°C).

Table 40

Reference of Latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
15 A	34.9	4
15 B	55.1	10

Latices 15 A and 15 B are treated by spraying; the powder obtained is ground and a plasticol is prepared by mixing 100 parts by weight of polymer with 45 parts by weight of dioctyl phthalate.

The rheological properties of the two plastisols are summarised in Table 41.

Table 41

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time Hours	Viscosity poises	Speed gradient seconds ⁻¹	Viscosity poises
15 A	0.5	90	500	195
	24	170		
15 B	0.5	80	500	170
	24	140		

EXAMPLE 16

This example is given as a comparison: D_C is not in accordance with the invention.

Preparation of latex 161

Using a 1000 litre autoclave a latex of vinyl chloride homo polymer is prepared in micro-suspension, in the presence of a seeding substance. For this purpose the following are placed in the autoclave:

- 540 kg of deionised water,
- 300 kg of vinyl chloride,
- 76.9 kg of a polyvinyl chloride seeding latex containing 27.3% by weight of dry material, which has previously been prepared in micro-suspension, the particles having a mean diameter of $0.640 \mu\text{m}$ and containing 1.57% by weight of lauroyl peroxide relative to the polymer,
- 3 kg of sodium dodecyl benzene sulphonate,
- 12 g of copper sulphate of the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$,
- 12 g of ascorbic acid.

After 10.25 hours' polymerisation at 52°C and degassing of the unreacted vinyl chloride, latex 161 is obtained. This contains one population of particles; the content of dry material is 33.1% by weight and the mean particle diameter is $1.55 \mu\text{m}$.

Preparation of latex 16 A

Latex 16 A is obtained by mixing 75 parts by weight of latex 52 described in example 5 with 25 parts by weight of latex 161.

It contains two populations of particles and has the following granulometric properties:

$$D_C (\mu\text{m}) = 1.55 ; D_F (\mu\text{m}) = 0.170 ;$$

$$P_C (\%) = 92 ; P_F (\%) = 93 ;$$

$$P_W (\%) = 29.3.$$

A portion of latex 16 A is concentrated by ultra-filtration to give latex 16 B.

Table 42 sets out the weight of dry material contained in each latex and the Brookfield RVT viscosity (spindle no. 1, 20 rpm, conditioning and reading at 23°C).

Table 42

Reference of Latex	Content of dry material % by weight	Brookfield RVT viscosity centipoises
16 A	35.1	4
16 B	55.2	10

Latices 16 A and 16 B are treated by spraying; the powder obtained is ground and a plastisol is prepared by mixing 100 parts by weight of polymer with 45 parts by weight of dioctyl phthalate.

The rheological properties of the two plastisols are summarised in Table 43.

Table 43

Reference of Latex	Brookfield RVT rheometer (spindle no. 7, 20 rpm)		Severs Rheometer	
	Conditioning time hours	Viscosity poises	Speed gradient seconds	Viscosity poises
16 A	0.5 24	100 180	350	330
16 B	0.5 24	100 180	350	350

(67)



CLAIMS

1. A method of preparing polymers of vinyl chloride in the form of a powder capable of giving plastisols with improved rheological properties, comprising concentrating a latex of a homopolymer or copolymer of vinyl chloride containing from 30 to 60% by weight of dry material and two populations of particles by eliminating a fraction of the aqueous phase in the liquid state and then drying out the residual water, in which the weight of dry material contained in the latex after its concentration is from 50 to 80%, the difference between the weight per cent of dry material contained in the latex before and after its concentration is over 10% and the two populations of particles in the latex have mean diameters within the respective ranges 0.7 to 1.5 μ m and 0.12 to 0.3 μ m, at least 90% by weight of the particles of each population having a diameter within the range from 0.7 to 1.6 times the mean diameter of the said population, 5 to 45% by weight of the particles of the latex having a diameter less than 0.4 μ m.
2. A method as claimed in Claim 1, in which the difference between the weight per cent of dry material contained in the latex before and after its concentration is in the range 15 to 25%.



3. A method as claimed in Claim 1 or 2, in which the latex is concentrated by ultrafiltration through a semi-permeable membrane.
4. A method as claimed in any one of Claims 1 to 3, in which drying is effected by spraying.
5. A method as claimed in any one of Claims 1 to 3, in which drying is effected by flaking.
6. A method of preparing polymers of vinyl chloride in the form of a powder capable of giving plastisols with improved rheological properties substantially as hereinbefore described in any one of Examples 1, 3 to 6, 11, 13 and 15.
7. Polymers of vinyl chloride in the form of a powder adapted to the preparation of plastisols, when prepared by a method as claimed in any one of Claims 1 to 6.

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