

SPECIFICATION

Process of polymerising vinyl chloride in seeded microsuspension

The present invention concerns the preparation of homopolymers and copolymers of vinyl chloride by polymerisation in seeded microsuspension.

It is known from U.K. Patent No. 1 170 963 that polymerisation in microsuspension of vinyl chloride in the presence of a seeding material containing all the initiator required for polymerisation enjoys the advantages, in comparison with polymerisation in simple microsuspension, of minimum initiator consumption, greater regularity of reaction, a lower degree of crusting in the reaction zone and a higher level of concentration of polymer in the latex formed.

It is also known from U.K. Patent No. 1 503 247 that the use, in polymerisation of vinyl chloride in microsuspension, of at least two seeding substances comprising different particle sizes, of which at least one contains all the initiator required for polymerisation, makes it possible to further increase the concentration of polymer in the latex formed, to reduce its viscosity, to improve the granulometry of the particles and to produce substances having properties that make them particularly suitable for the preparation of plastisols.

Moreover, it is known from U.K. Patent No. 1 435 425 that it is possible to reduce the amount of initiator used, increase the polymerisation speed, and reduce the formation of crusting in the reaction zone, by activating the initiator, throughout the polymerisation operation, by means of an organo-soluble metal complex that has been prepared beforehand or that is formed *in situ* by reaction between a water-soluble metal salt and a complexing agent.

Although the above-described processes enable vinyl chloride polymers to be produced by seeded microsuspension polymerisation on an industrial scale, it is essential to try to make improvement, either (a) in the reaction process, in order to increase the profitability by reducing the polymerisation time and the amount of crusting formed or to reduce the dangers of pollution by the monomer, with higher rates of conversion; or (b) in the substances to be produced, for example by reducing the amounts of water-soluble metal salts, the residues of which can cause degradation of the stability to heat and ultra-violet rays of the vinyl chloride polymer.

The present invention makes it possible to achieve such improvements. The process of the present invention comprises polymerising the vinyl chloride monomer or a mixture of at least 50% by weight of vinyl chloride monomer and at least one copolymerisable monomer in microsuspension in the presence of one or more seeding substances in the form of dispersions of particles of vinyl polymers that have been prepared beforehand and that have particle sizes different from each other and of which at least one, whose particles have a mean diameter of from 0.05 to 1.5 μm , is produced by polymerisation in microsuspension and contains all the organo-soluble initiator required for polymerisation, the amount of seeding substance(s) used being such that the amount of polymer that they contain represents from 1 to 50% by weight of the sum of the amounts of monomer(s) to be polymerised and of seeding polymer(s), the amount of water used being such that the sum of the initial amounts of monomer(s) to be polymerised and of seeding polymer(s) represents from 20 to 80% by weight with respect to the reaction mixture, the said organo-soluble initiator included in the seeding polymer particles representing from 0.05 to 5% by weight of the polymer and throughout polymerisation being activated by a nitric-acid-associated organo-soluble metal complex that has been prepared before hand or formed *in situ* by reaction between a water-soluble metal salt and a complexing agent capable of causing the metal to pass from its water-soluble form to a form that is soluble in vinyl chloride, the metal salt:initiator molar ratio being from 0.05:1 to 8:1, the complexing agent: metal salt molar ratio being from 0.5:1 to 4.5:1, and the nitric acid: metal salt molar ratio being from 0.1:1 to 5:1.

The copolymerisable monomers are those generally used in conventional processes for the copolymerisation of vinyl chloride, in particular 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 and their aliphatic, cyclo-aliphatic and aromatic esters, their amides and their nitriles; vinyl and vinylidene halides; alkyl vinyl ethers; and olefins.

The vinyl polymers that form seeding substances are represented by polyvinyl chloride, copolymers of vinyl chloride and the copolymerisable monomers as defined above, homopolymers of such monomers, and copolymers of such monomers with one another. Polymers of the different seeding substances in a single operation may be identical or different.

The seeding substance that contains the initiator (hereinafter referred to as the first seeding substance) is prepared by conventional methods of polymerisation in microsuspension, that is to say, polymerisation in the presence of organo-soluble initiators of at least one monomer dispersed by forcible mechanical means (homogenised) in an aqueous medium containing an emulsifying agent as a stabilising agent. It is in the form of an aqueous dispersion of particles of polymer, whose diameter is from 0.05 to 1.5 μm and preferably from 0.2 to 1 μm .

The organo-soluble initiators required for polymerisation and that are included in the polymer particles are generally organic peroxides, such as diacylperoxides, among which we may mention

lauroyl, decanoyl and caproyl peroxides, tert-butyl diethyl-peracetate, diethylhexyl percarbonate and diacetyl peroxide.

The choice of initiator depends on its speed of decomposition at the reaction temperature adopted. Two or more organo-soluble initiators can be used; in this case, they are preferably so selected as to be of different reactivity.

The organo-soluble initiators included in the seeding polymer particles represent from 0.05 to 5% by weight of the polymer.

The other seeding substance or substances, where appropriate, are in the form of dispersions of particles of vinyl polymer which may or may not contain an initiator and whose mean diameters, which are different from each other and different from that of the first seeding substance, are from 0.02 to 1.5 μm and preferably from 0.02 to 0.8 μm . These dispersions of particles may be produced by conventional processes of polymerisation in micro-suspension or in emulsion.

In the polymerisation according to the invention, the amount of seeding substance or substances to be used must be such that the amount of polymer that it contains or they contain represents from 1 to 50% by weight with respect to the sum of vinyl chloride with or without comonomers to be polymerised + seeding polymer(s).

When two or more seeding polymers are used, the proportion by weight of the first with respect to the other or others, which depends on the composition of the polymer to be produced, is from 95:5 to 5:95. In addition, the proportions of the seeding substances relative to each other and the total amount of the seeding substances are so selected that the amount of organo-soluble initiator included in the polymer particles is sufficient to effect polymerisation or copolymerisation without the supplementary addition of initiator.

The amount of water present during polymerisation, including the water content of the seeding substance or substances, must be such that the initial concentration of all polymers present, i.e. the polymer(s) in the seeding substance or substances, the vinyl chloride and any copolymerisable monomer that may be present, is from 20 to 80% and preferably from 45 to 75% by weight with respect to the reaction mixture.

The substance or substances for seeding in the micro-suspension mode, which is or are present in the polymerisation medium, is or are sufficient to ensure dispersion of the monomer, without its being necessary to have recourse to fresh homogenisation of the medium.

In order to improve the stability of the micro-suspension, it may be advantageous for at least one anionic emulsifying agent, possibly in association with at least one non-ionic emulsifying agent, to be added before and/or in the course of polymerisation, in successive fractions or continuously. The anionic emulsifying agents are preferably represented by fatty acid soaps; alkyl sulphates, alkyl sulphonates, alkylaryl sulphonates, alkyl phenoxybenzene sulphonates, vinyl sulphonates, allyl sulphonates, alkyl sulphosuccinates and alkyl phosphates of alkali metals. The non-ionic emulsifying agents are preferably represented by polycondensates of ethylene oxide or propylene oxide on various hydroxylated organic compounds.

The amounts of emulsifying agent may represent up to 3% by weight of the vinyl chloride or the mixture of it with polymerisable monomer. These are the amounts generally used in order to achieve a useful effect in the reaction. However, it is not a departure from the scope of the present invention to use amounts outside the above-indicated limits, the emulsifying agents acting only as a stabilising agent for the micro-suspension and having no action on the granulometry of the particles.

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

In order to accelerate the speed of polymerisation, the initiator included in the particles of the seeding substance or substances is activated throughout polymerisation by an organo-soluble metal complex, which is formed beforehand or *in situ* by reaction between a water-soluble metal salt and a complexing agent.

The metal salt is used in an amount such that the metal salt:initiator molar ratio is from 0.05:1 to 8:1. The metal is preferably iron, copper, cobalt, nickel, zinc, tin, titanium, vanadium, manganese, chromium or silver and is used in the form of water-soluble salts such as sulphates, chlorides, nitrates or acetates.

The complexing agents to be used are compounds capable of causing the metal to pass from its water-soluble form to a form that is soluble in vinyl chloride, and that do not have any inhibiting action on polymerisation and on activation of the initiator by the metal. Compounds that comply with these requirements may be represented by monocarboxylic acids that are weakly soluble in water such as perfluorobutyric acid, α -bromolauric acid, sulphosalicylic acid, naphthenic acid, and octoic acid; polycarboxylic acids such as succinic, tartaric, maleic, and dihydroxymaleic acids and corresponding anhydrides; alkylphosphoric acids such as di-(2-ethylhexyl)-phosphoric acid; lactones such as ascorbic acid and its esters and butyrolactone; ketones having, in α or β position, groups activating the carbonyl function such as acetylacetone, 1,3-dihydroxyacetone, and benzoin; and carbazones, such as diphenylthiocarbazone.

The amounts of complexing agent to be used depend on the polymerisation temperature, the

cooling capacity of the reactor and the level of purity of the reagents. They are such that the complexing agent:metal salt molar ratio is from 0.5:1 to 4.5:1.

The metal salts may be introduced into the reaction medium before polymerisation or in the course of polymerisation, in successive fractions or continuously, either alone in aqueous solution or in admixture with a solution of emulsifying agent when it is added in the course of polymerisation, or in aqueous solution with the complexing agent to give the complex before the introduction operation is performed.

The complexing agent is introduced continuously, either alone or with a solution of emulsifying agent, or with the metal salt.

In order to achieve a better level of use of the activator system, nitric acid is added to it, in amounts such that the nitric acid:metal salt molar ratio is from 0.1:1 to 5:1 and preferably from 0.2:1 to 3:1.

The nitric acid is introduced into the reaction medium in aqueous solution, either alone, or with the metal salt, or with the complexing agent, or with the complex.

Activation of the initiator by the complex may be interrupted at any moment by terminating the operation of introducing the complexing agent or the complex and/or causing the metal ion to return from its organo-soluble form to its water-soluble form; this is easily achieved by adding to the reaction medium, as sequestering agent, an alkali metal salt of an acid of the ethylenediaminetetraacetic acid group, e.g. ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid and N-(2-hydroxyethyl)-ethylenediaminetriacetic acid. The sequestering agent is used in proportions ranging up to molar stoichiometry with respect to the metal salt.

The present invention also provides homopolymers and copolymers of vinyl chloride prepared by the above-described process after separation of the said polymers and copolymers from the polymerisation medium by any known method such as filtering, coagulation and draining, scaling, centrifugal decantation and atomisation.

The polymers and copolymers can be used for the production of sheets, films, threads, hollow bodies, cellular materials and moulded articles produced by calendering, extrusion, extrusion-blowing, injection and casting; and for the production of coated coverings, cellular materials, and articles moulded by any known processes for using plastisols, such as coating, rotary casting, or soaking.

Illustrative embodiments of the invention follow in the Examples.

EXAMPLE 1

The following are introduced into a 25-litre autoclave;
5000 g of water;

1170 g of a seeding substance prepared by polymerisation in micro-suspension, with a concentration of 34.2% by weight, that is, 400 g of polyvinyl chloride containing 7.5 g of lauroyl peroxide, in which the mean diameter of the particles is 0.494 μm ;

482 g of a seeding substance prepared by polymerisation in emulsion, having a concentration of 41.5% by weight, that is, 200 g of polyvinyl chloride containing no initiator, in which the mean particle diameter is 0.112 μm ;

354 g of an aqueous 19.8% by weight solution of sodium dodecylbenzene sulphonate;
0.3 g of copper sulphate;
10000 g of vinyl chloride.

The reaction mixture is then heated at a temperature of 52°C under autogenous pressure and maintained at that temperature throughout the reaction.

As soon as the medium reaches 52°C, an aqueous solution containing 0.4 g/l of ascorbic acid and 0.16 g/l of nitric acid (specific gravity = 1.38) is introduced at a rate of 0.12 l/h of solution for a period of three hours, then 0.08 l/h for a period of three hours and finally 0.04 l/h until the end of the reaction.

When the pressure in the autoclave has dropped by two bars, that is to say, after ten and a half hours, the introduction of the acid solution is stopped and the unreacted monomer is degassed.

17000 g of a dispersion of polymer in which the concentration in respect of polymer is 57% by weight is obtained, that is to say, a real conversion rate of 91% with respect to the vinyl chloride used.

The weight of crusts in the autoclave is 122 g, that is to say, 1.22% by weight of the vinyl chloride used.

The polymer produced is formed by two populations of particles, which are respectively of mean diameters of 1.12 μm and 0.2 μm .

Example 1 is repeated, by way of comparison, without nitric acid.

The polymerisation time is ten hours forty minutes.

The result obtained is 16500 g of a dispersion of polymer, wherein the concentration in respect of polymer is 55.7% by weight, which is a real conversion rate of 86% by weight with respect to the vinyl chloride used.

The weight of crusts is 1.75 g, which is 1.75% by weight of the vinyl chloride used.

The mean diameters of the two populations of particles are respectively 1.12 μm and 0.195 μm .

It is noted that the presence of nitric acid makes it possible to achieve a higher conversion rate while producing a smaller amount of crust formation.

EXAMPLE 2

Operation is carried out as in Example 1, but using 0.150 g of copper sulphate instead of 0.3 g. The results and those of the comparative test are as follows:

		Example 2	Comparative test	
5	Polymerisation time	hours	11.40	12
	Conversion rate	% by weight	90.5	87
	Crusting rate	% by weight	1.62	2.20
	Size particles 1	μm	1.14	1.13
	Size particles 2	μm	0.20	0.19

10 The influence of nitric acid on the results obtained can be observed.

EXAMPLE 3

The mode of operation in this Example is the same as that in Example 2, except that the copper sulphate is not in the reaction vessel but in the same aqueous solution as the ascorbic acid and the nitric acid, in a proportion of 0.25 g/l.

The polymerisation time is ten hours.

The resulting product is 17200 g of a dispersion of polymer wherein the polymer concentration is 57.8% by weight, giving a real conversion rate of 93.5% by weight with respect to the vinyl chloride used.

The degree of crust formation in the reaction vessel is 0.33% by weight of the vinyl chloride used.

The polymer is formed by two populations of particles which are respectively 1.12 μm and 0.194 μm in diameter.

The same test, when carried out without nitric acid, gives the following result:

- a polymerisation time of ten hours fifty minutes;
- a conversion rate of 86.6% by weight;
- a crusting rate of 1.25% by weight of the vinyl chloride;
- particle diameters of 1.11 μm and 0.191 μm .

EXAMPLES 4 TO 9

Example 3 is repeated, with the copper sulphate being replaced by the same amount of another metal salt, or with the ascorbic acid being replaced by the same amount of another complexing agent, with the corresponding comparative tests.

The operating conditions and the results, together with those of Example 3, are set forth in Table I.

EXAMPLE 10

The following are introduced into a 25 litre autoclave:

- 6400 g of water
- 1386 g of a seeding substance prepared by polymerisation in micro-suspension, in a concentration of 32.5% by weight, that is to say, 450 g of polyvinyl chloride containing 7.70 g of lauroyl peroxide, wherein the mean diameter of the particles is 0.521 μm ; and
- 9000 g of vinyl chloride.

The reaction mixture is then heated at a temperature of 52°C under autogenous pressure and held at that temperature throughout the reaction.

As soon as the reaction medium has reached a temperature of 52°C, there is begun the operation of simultaneously introducing:

- an aqueous solution containing 58 g/l of sodium dodecylbenzene sulphonate, at a rate of 0.135 l/h, for a period of eight hours;
- an aqueous solution containing 0.25 g/l of copper sulphate, 0.4 g/l of ascorbic acid and 0.16 g/l of nitric acid ($d = 1.38$), at a rate of 0.09 l/h.

When the pressure in the autoclave has dropped by two bars, the operation of introducing the solution of complex and nitric acid is stopped and the unreacted monomer is degassed.

By way of comparison, the same test is repeated without nitric acid.

The results obtained are as follows:

		Example 10	Comparative test	
Polymerisation time	hours	10.50	15	
Weight of dispersion	g	18 400	17 830	
Polymer concentration	% by weight	45.4	44.5	
5 Conversion rate	% by weight	88	83	5
Crusting rate	% by weight	1.92	2.35	
Particle size	μm	1.11	1.11	

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TABLE I

Ex.	Metal salt	Complexing agent		Polymerisation time Hours	Conversion rate % by weight	Crusting % by weight	Size of particles μm	
							1	2
3	Copper sulphate	Ascorbic acid	ex. test	10 10.50	92 86.6	0.33 1.25	1.12 1.11	0.194 0.191
4	Cobalt nitrate	Ascorbic acid	ex. test	11.50 12	92 90	0.77 1.35	1.06 1.03	0.20 0.195
5	Copper nitrate	Ascorbic acid	ex. test	10.50 11.20	91 89	1.05 1.42	1.10 1.08	0.188 0.185
6	Copper sulphate	Citric acid	ex. test	17.55 20	86 76.5	0.3 1.27	1.10 1.08	0.184 0.184
7	Copper sulphate	Tartaric acid	ex. test	18.30 20	89 88	2.20 3.25	1.13 1.12	0.187 0.187
8	Copper sulphate	Naphthenic acid	ex. test	20.10 20.30	92.5 91	0.25 0.45	1.12 1.11	0.182 0.182
9	Copper sulphate	Sulphosalicylic acid	ex. test	19.45 20	89 87	2.51 3	1.20 1.18	0.186 0.186

EXAMPLE 11

The following are introduced into a 25 litre autoclave:

- 4000 g of water;
 - 5 — 1170 g of a seeding substance prepared by polymerisation in micro-suspension, with a concentration of 34.2% by weight, that is to say, 400 g of polyvinyl chloride containing 7.5 g of lauroyl peroxide and wherein the mean diameter of the particles is 0.494 μm ;
 - 482 g of a seeding substance prepared by polymerisation in emulsion, with a concentration of 41.5% by weight, that is to say, 200 g of polyvinyl chloride which does not contain any initiator and wherein the mean diameter of the particles is 0.112 μm ; and
 - 10 — 10000 g of vinyl chloride.
- The reaction mixture is then heated at a temperature of 52°C under autogenous pressure and maintained at that temperature throughout the reaction.
- As soon as the reaction medium has reached a temperature of 52°C, there is begun the operation of simultaneously introducing:
- 15 — an aqueous solution containing 58 g/l of sodium dodecylbenzene sulphonate, at a rate of 0.15 l/h for a period of eight hours;
 - an aqueous solution containing 0.25 g/l of copper sulphate, 0.4 g/l of ascorbic acid and 0.16 g/l of nitric acid, at a rate of 0.10 l/h, for a period of ten hours thirty minutes.
- When the pressure in the autoclave has dropped by two bars, the operation of introducing the solution of complex and nitric acid is stopped and the unreacted monomer is degassed.
- By way of comparison:
- the same test is repeated without nitric acid (comparative test A);
 - a test is carried out without nitric acid, but with amounts of activating system such that the products obtained are substantially the same as those of Example 11 (comparative test B).
- 25 The operating conditions and the results obtained are indicated below:

		Ex. 11	Comparative test	Comparative test	
	Activating system				
	— copper sulphate	g/l	0.25	0.25	0.5
30	— ascorbic acid	g/l	0.4	0.4	0.8
	— nitric acid	g/l	0.16	0	0
	Polymerisation time	hours	10.40	12	10.50
	Weight of dispersion	g	17000	16470	16820
	Polymer concentration	% by weight	56.9	56.3	57.2
35	Conversion rate	% by weight	90.5	86.5	90.2
	Crusting rate	% by weight	1.2	2.34	1.5
	Size particles 1	μm	1.10	1.08	1.10
	Size particles 2	μm	0.195	0.194	0.195

- 40 It will be noted that, in order to achieve the same result with a copper sulphate-ascorbic acid activating system, the addition of nitric acid makes it possible to reduce by half the amounts of copper sulphate and ascorbic acid, thereby avoiding degradation in respect of the thermal stability of the polyvinyl chloride produced.

EXAMPLE 12

- 45 Operation is as in Example 11, except that the copper sulphate is in solution in the solution of emulsifying agent, in a proportion of 0.22 g/l, and not with the ascorbic acid and nitric acid.
- By way of comparison, the same test is repeated without nitric acid.

The results obtained are as follows:

		Example 12	Comparative test	
	Polymerisation time	hours	11	11.25
	Weight of dispersion	g	16800	16400
5	Concentration of polymer	% by weight	55.5	56.6
	Conversion rate	% by weight	87.25	86.5
	Crusting rate	% by weight	1.4	1.78
	Size particles 1	μm	1.11	1.10
	Size particles 2	μm	0.180	0.180

10 EXAMPLE 13

Operation is as in Example 11 but the ascorbic acid is in the emulsifying agent solution in a proportion of 0.35 g/l and not with the copper sulphate and nitric acid.
The results are as follows:

		Example 13	Comparative test	
15	Polymerisation time	hours	10.30	10.40
	Weight of dispersion	g	17400	16900
	Concentration of polymer	% by weight	56.9	57
	Conversion rate	% by weight	93	90.5
	Crusting rate	% by weight	0.55	1.3
20	Size particles 1	μm	1.12	1.11
	Size particles 2	μm	0.182	0.180

EXAMPLE 14

Example is as in Example 3, but with the 10000 g of vinyl chloride being replaced by 9550 g of vinyl chloride and 450 g of vinyl acetate.

The results obtained are as follows:

		Example 14	Comparative test	
	Polymerisation time	hours	10.55	11.25
	Weight of dispersion	g	17100	16700
	Concentration of polymer	% by weight	57	55.9
30	Conversion rate	% by weight	91.5	87
	Crusting rate	% by weight	1.17	1.38
	Size particles 1	μm	1.14	1.13
	Size particles 2	μm	0.198	0.189

EXAMPLE 15

The following are introduced into an 800 litre autoclave:

— 265 kg of de-ionized water;

— 68.5 kg of a seeding substance produced by polymerisation in microsuspension, with a

concentration of 36.8% by weight, that is to say, 25.2 kg polyvinyl chloride, containing 0.3 kg of lauroyl peroxide, and wherein the mean particle diameter is 0.55 μm ;

— 29.7 kg of a seeding substance produced by polymerisation in emulsion, with a concentration of 40.5% by weight, that is to say, 12 kg of polyvinyl chloride which does not contain initiator and wherein the mean particle diameter is 0.13 μm ;

— 17.3 kg of an aqueous 20.3% by weight solution of sodium dodecylbenzene sulphonate; and
— 500 kg of vinyl chloride.

The reaction mixture produced is then heated at a temperature of 52°C under autogenous pressure and maintained at that temperature throughout the reaction.

As soon as the medium has reached the temperature of 52°C, there is begun the operation of introducing an aqueous solution containing 0.65 g/l of copper sulphate, 1 g/l of ascorbic acid and 0.83 g/l of nitric acid, at a rate of 2 l/h for a period of four hours, then 1.4 l/h for three hours and finally 0.7 l/h until the end of the reaction.

When the pressure in the autoclave is dropped three bars, the operation of introducing the solution of complex and nitric acid is stopped and the unreacted monomer is degassed.

By way of comparison, Example 15 is repeated, but without nitric acid.

The results obtained are as follows:

		Example 15	Comparative test	
	Polymerisation time	hours	12	14.10
20	Weight of dispersion	kg	879.5	852.7
	Polymer concentration	% by weight	60.1	59.9
	Conversion rate	% by weight	98	94.7
	Crusting rate	% by weight	0.3	0.62
	Size particles 1	μm	1.15	1.15
25	Size particles 2	μm	0.2	0.195

CLAIMS

1. A process for the preparation of homopolymers and copolymers of vinyl chloride by polymerisation in seeded microsuspension, that comprises polymerising the vinyl chloride monomer or a mixture of at least 50% by weight of vinyl chloride monomer and at least one copolymerisable monomer in microsuspension in the presence of one or more seeding substances in the form of dispersions of particles of vinyl polymers that have been prepared beforehand and that have particle sizes different from each other and of which at least one, whose particles have a mean diameter of from 0.05 to 1.5 μm , is produced by polymerisation in microsuspension and contains all the organo-soluble initiator required for polymerisation, the amount of seeding substance(s) used being such that the amount of polymer that they contain represents from 1 to 50% by weight of the sum of the amounts of monomer(s) to be polymerised and of seeding polymer(s), the amount of water used being such that the sum of the initial amounts of monomer(s) to be polymerised and of seeding polymer(s) represents from 20 to 80% by weight with respect to the reaction mixture, the said organo-soluble initiator included in the seeding polymer particles representing from 0.05 to 5% by weight of the polymer and throughout polymerisation being activated by a nitric-acid-associated organo-soluble metal complex that has been prepared beforehand or formed *in situ* by reaction between a water-soluble metal salt and a complexing agent capable of causing the metal to pass from its water-soluble form to a form that is soluble in vinyl chloride, the metal salt: initiator molar ratio being from 0.05:1 to 8:1, the complexing agent: metal salt molar ratio being from 0.5:1 to 4.5:1, and the nitric acid: metal salt molar ratio being from 0.1:1 to 5:1.

2. A process according to Claim 1, substantially as hereinbefore described in any one of Examples 1 to 15.

3. Polymers and copolymers of vinyl chloride produced in accordance with the process of Claim 1 or 2.



concentration of 36.8% by weight, that is to say, 25.2 kg polyvinyl chloride, containing 0.3 kg of lauroyl peroxide, and wherein the mean particle diameter is 0.55 μm ;

— 29.7 kg of a seeding substance produced by polymerisation in emulsion, with a concentration of 40.5% by weight, that is to say, 12 kg of polyvinyl chloride which does not contain initiator and wherein the mean particle diameter is 0.13 μm ;

— 17.3 kg of an aqueous 20.3% by weight solution of sodium dodecylbenzene sulphonate; and

— 500 kg of vinyl chloride.

The reaction mixture produced is then heated at a temperature of 52°C under autogenous pressure and maintained at that temperature throughout the reaction.

As soon as the medium has reached the temperature of 52°C, there is begun the operation of introducing an aqueous solution containing 0.65 g/l of copper sulphate, 1 g/l of ascorbic acid and 0.83 g/l of nitric acid, at a rate of 2 l/h for a period of four hours, then 1.4 l/h for three hours and finally 0.7 l/h until the end of the reaction.

When the pressure in the autoclave is dropped three bars, the operation of introducing the solution of complex and nitric acid is stopped and the unreacted monomer is degassed.

By way of comparison, Example 15 is repeated, but without nitric acid.

The results obtained are as follows:

		Example 15	Comparative test	
Polymerisation time	hours	12	14.10	
20 Weight of dispersion	kg	879.5	852.7	20
Polymer concentration	% by weight	60.1	59.9	
Conversion rate	% by weight	98	94.7	
Crusting rate	% by weight	0.3	0.62	
Size particles 1	μm	1.15	1.15	
25 Size particles 2	μm	0.2	0.195	25

CLAIMS

1. A process for the preparation of homopolymers and copolymers of vinyl chloride by polymerisation in seeded microsuspension, that comprises polymerising the vinyl chloride monomer or a mixture of at least 50% by weight of vinyl chloride monomer and at least one copolymerisable monomer in microsuspension in the presence of one or more seeding substances in the form of dispersions of particles of vinyl polymers that have been prepared beforehand and that have particle sizes different from each other and of which at least one, whose particles have a mean diameter of from 0.05 to 1.5 μm , is produced by polymerisation in microsuspension and contains all the organo-soluble initiator required for polymerisation, the amount of seeding substance(s) used being such that the amount of polymer that they contain represents from 1 to 50% by weight of the sum of the amounts of monomer(s) to be polymerised and of seeding polymer(s), the amount of water used being such that the sum of the initial amounts of monomer(s) to be polymerised and of seeding polymer(s) represents from 20 to 80% by weight with respect to the reaction mixture, the said organo-soluble initiator included in the seeding polymer particles representing from 0.05 to 5% by weight of the polymer and throughout polymerisation being activated by a nitric-acid-associated organo-soluble metal complex that has been prepared beforehand or formed *in situ* by reaction between a water-soluble metal salt and a complexing agent capable of causing the metal to pass from its water-soluble form to a form that is soluble in vinyl chloride, the metal salt: initiator molar ratio being from 0.05:1 to 8:1, the complexing agent: metal salt molar ratio being from 0.5:1 to 4.5:1, and the nitric acid: metal salt molar ratio being from 0.1:1 to 5:1.

2. A process according to Claim 1, substantially as hereinbefore described in any one of Examples 1 to 15.

3. Polymers and copolymers of vinyl chloride produced in accordance with the process of Claim 1 or 2.