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(54) PROCESS FOR THE PRODUCTION OF AQUEOUS
 COPOLYMER DISPERSIONS

(71) We, CHEMISCHE WERKE HÜLS AKTIENGESELLSCHAFT, a German Company, of 4370 Marl, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the production of an aqueous copolymer dispersion by emulsion polymerisation in a polymerisation vessel at elevated temperature of a mixture of from 50 to 85% by weight of a vinylaromatic compound, from 15 to 50% by weight of a conjugated diolefin, from 0 to 25% by weight of acrylonitrile and from 0 to 5% by weight of another monomer containing one or more functional groups in addition to the double bond, with shellac as the sole emulsifier and in the presence of an initiator which forms free radicals.

The use of shellac in plastics dispersions, especially when these are to be used in surface coating agents, is known from DT—PS 976,148. Shellac in this case is added to the finished polymerised dispersion.

Since this method necessitates a second working stage attempts have been made to introduce the shellac prior to the polymerisation so as to make use of its emulsifying properties. US—PS 2,961,420 describes such a process. In this case however it is necessary to use an additional nonionic emulsifier as well as shellac in order to achieve adequate stability of the dispersion.

Further industrial development has made necessary plastics dispersions having the lowest possible content of emulsifier. Accordingly attempts have been made to prepare dispersions using shellac as the sole emulsifier. DT—PS 1,495,790 (= US—PS 3,291,766) discloses such a process in which according to the invention a pH of from 7.0 to 7.8 has to be exactly maintained. It is stated in the further developed DT—PS 1,901,286 that the process of DT—PS 1,495,790 has the disadvantage that it is not suitable for large-

scale operation. In large scale batches the products are not reproducible and caking occurs on the walls of the reactor.

To avoid the said disadvantages DT—PS 1,901,286 discloses a process in which only 50% of the necessary amount of shellac is added at the beginning of the polymerisation, the remainder having to be added in the smallest possible portions with careful control of the pH.

The process of DT—PS 1,901,286 is very labour-intensive particularly when polymerisation is carried out under pressure, for example when gaseous monomers are used. In this case it is very expensive technically and in time to control the pH and to carry out the addition of a large number of portions of small amounts of shellac. If on the other hand the necessary parameters are not maintained sufficiently accurately, the rate of polymerisation reaction is too low and/or the dispersions obtained have a high proportion of coagulate.

The present invention seeks to provide a process which proceeds independently of the pH of the reaction mixture and in which all the starting materials can be added to the reactor at the beginning of the polymerisation.

According to the invention there is provided a process of the type defined at the outset wherein the total amounts of the specified monomere are placed in the polymerisation vessel prior to the commencement of the reaction, together with the shellac, and from 2 to 50% by weight (based on the monomer mixture and reckoned as solid material) of a dispersion of a copolymer of the above specified monomers in proportions within the ranges specified above, and wherein the initiator used is an azo-bis-carboxylic acid nitrile of four to seven carbon atoms in each carboxylic radical acid.

The shellac is generally used in an amount of from 1 to 10% by weight and preferably of from 3 to 7% by weight, based on the monomer mixture. All commercially available types may be used. In the case of dispersions which are to be used in surface coating agents

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the bleached types of shellac are preferred. At least 5% by weight of shellac should be used in the production of dispersions having a solids content of more than 48% by weight.

- 5 Styrene or styrene derivatives such as *α*-methylstyrene, chlorostyrene or vinyltoluene may be used, singly or mixed together, as the vinylaromatic compound in an amount of from 50 to 85% by weight of the total monomer mixture. Styrene may be partly replaced by acrylonitrile but the proportion of the latter in the monomer mixture must not be more than 25% by weight. It is preferred to use styrene in an amount of from 60 to 75% by weight.

- 10 Butadiene, isoprene, chloroprene or piperylene (penta-1, 3-diene) may be used, singly or in admixture, as the conjugated diolefin in an amount of from 15 to 50% by weight. It is preferred to use butadiene in an amount of from 25 to 40% by weight,

- 20 Comonomers having functional groups in addition to the double bond, such as acrylamide, methacrylamide, N-methylolacrylamide, N-methoxymethylacrylamide or 2-hydroxyethyl acrylate, may be used, singly or as mixtures, in amounts of up to 5% by weight,

- 25 An azo-bis-carboxylic acid nitrile of four to seven carbon atoms is used exclusively as initiator according to the invention. It is preferred to use azo-bis-isobutyronitrile. The initiator generally is added to the reaction mixture in an amount of from 0.01 to 1% by weight and preferably in an amount of from 0.1 to 0.5% by weight, in each case based on the monomer mixture. Other oil-soluble initiators, as for example dibenzoyl peroxide, do not result in usable products.

- 30 It is furthermore essential according to the invention that prior to the commencement of the polymerisation there should be present from 2 to 50% by weight and preferably from 5 to 25% by weight—based on the monomer mixture and reckoned as solid material—of a copolymer dispersion (primary latex). The primary latex may have any composition of monomers that is within the ranges quoted for the composition of the final product of the present invention. It is preferred to use as the primary latices those copolymers which have the same composition as the desired final copolymer product.

- 40 Although it would be possible in principle not to use a primary latex, dispersions devoid of coagulate are only then obtained when products having a low solids content are prepared and the polymerisation is carried out in a small vessel. It is not possible to prepare dispersions having a high solids content in a small polymerisation vessel without the proportion of coagulate increasing greatly (Examples E and F). When a primary latex is used, however, polymerisation can be carried out in a large reactor and a dispersion devoid of coagulate is obtained.

The shellac is dissolved in a base, for example ammonia, caustic soda solution or triethanolamine, so that it may be effective as an emulsifier. It is not necessary to set up any specific pH according to the invention. This is particularly advantageous because shellac as a natural product is often obtained in varying composition so that when dissolved under otherwise identical conditions different pH values are set up. The consequence of this is that in the prior art methods each new charge of shellac has to be tested to see that the critical pH is not exceeded. Setting up a pH of 7.8 or less, as is required in DT—PS 1,495,790, is particularly difficult because the amount of base necessary is so small that the time required to dissolve the shellac is inordinately long. Shellac solutions having such a low pH can only be obtained by adding an excess of base and lowering the pH with a weak acid, for example carbon dioxide, after the shellac has dissolved. The measures required by the prior art methods are therefore time-consuming and uneconomical.

The molecular weight of the copolymer produced can be regulated by adding a regulator as for example t-dodecylmercaptan in an amount of up to 1% by weight based on the monomer mixture.

Polymerisation is carried out at temperatures which are generally within the range from 50° to 85°C and preferably in the range from 60° to 75°C.

To carry out the polymerisation the desired amount of shellac is dissolved in water with the addition of an adequate amount of base. The primary latex and all the monomers and auxiliaries which are not gaseous at atmospheric pressure are added to this solution. After the polymerisation vessel has been closed airtight the gaseous monomer(s), e.g. butadiene, are introduced. The vessel is then heated. The polymerisation proceeds to completion.

One advantage of the process according to the invention is that the latices obtained can be reproducibly prepared as regards their properties. In contrast to this it is not possible to obtain a useful latex according to DT—PS 1,495,790 even when the process instructions are exactly followed.

Dispersions devoid of coagulate and having a particle size of from 100 to 300 nm are obtained by a simple procedure according to the process of the invention. The dispersions obtained may be used as binders in surface coating agents.

Examples

Production of the primary latex:
140 parts by weight of water
4 parts by weight of shellac (6% by weight solution in water)
70 parts by weight of styrene

- 0.1 part by weight of t-dodecylmercaptan and
 0.4 part by weight of azo-bis-isobutyronitrile are placed in a 12-litre polymerisation vessel. After the vessel has been rinsed three times with nitrogen and evacuated 30 parts by weight of butadiene is introduced. The reaction is over after sixteen hours at 65°C. 0.05% by weight of residual monomers is found in the dispersion. The dispersion is devoid of coagulate and specks. The pH is 8.4 and the solids content is 42.5% by weight. The same results are obtained when the polymerisation is carried out within the pH range from 7.1 to 10.3.
- To prepare the shellac solution 6 parts by weight of bleached shellac in flake form is suspended in 100 parts by weight of water and 1 part by weight of concentrated aqueous ammonia solution is added. After stirring for several hours at ambient temperature a clear brownish yellow solution is obtained having a pH of 8.3.
- Example 1**
- 105 parts by weight of water
 6 parts by weight of shellac (6% by weight solution in water, pH 8.9)
 15 parts by weight of primary latex
 70 parts by weight of styrene
 0.1 part by weight of t-dodecylmercaptan
 0.4 part by weight of azo-bis-isobutyronitrile are introduced into a 12-litre polymerisation vessel. After the vessel has been flushed three times with nitrogen and evacuated 30 parts by weight of butadiene is introduced. Polymerisation is over after twenty-four hours at 65°C. 0.3% by weight of residual monomers is found in the dispersion. The dispersion is devoid of coagulate and specks. The pH is 8.8 and the solids content is 50.9% by weight.
- Example 2**
- 120 parts by weight of water
 4 parts by weight of shellac (6% by weight solution in water, pH 8.7)
 25 parts by weight of primary latex
 70 parts by weight of styrene
 0.2 part by weight of t-dodecylmercaptan and
 0.4 part by weight of azo-bis-isobutyronitrile are introduced into a 500-litre polymerisation vessel. After the vessel has been flushed with nitrogen and evacuated 30 parts by weight of butadiene is introduced. 0.17% by weight of residual monomers is present in the dispersion. The dispersion is devoid of coagulate and specks. The pH is 8.7 and the solids content is 45.2% by weight.
- Example 3**
- 95 parts by weight of water
 5 parts by weight of shellac (6% by weight solution in water, pH 9.2)
 20 parts by weight of primary latex
 2 parts by weight of acrylamide
 68 parts by weight of styrene
 0.2 part by weight of t-dodecylmercaptan and
 0.4 part by weight of azo-bis-isobutyronitrile are introduced into a 12-litre polymerisation vessel. After the vessel has been rinsed with nitrogen and evacuated 30 parts by weight of butadiene is introduced. Polymerisation is begun at 65°C and continued after five hours at 70°C. The reaction is over after a total of twenty-two hours. 0.4% by weight of residual monomers is found. The dispersion is devoid of coagulate and specks. The pH is 7.9 and the solids content is 51.8% by weight.
- Example 4**
- 110 parts by weight of water
 6 parts by weight of shellac (6% by weight solution in water, pH 9.2)
 15 parts by weight of primary latex
 2 parts by weight of 2-hydroxyethyl acrylate
 48 parts by weight of styrene
 15 parts by weight of acrylonitrile
 0.2 part by weight of t-dodecylmercaptan and
 0.4 part by weight of azo-bis-isobutyronitrile are introduced into a 12-litre polymerisation vessel. After the vessel has been flushed three times with nitrogen and evacuated 35 parts by weight of butadiene is introduced. Polymerisation is begun at 60°C and after three hours is continued at 65°C. The reaction is over after a total of fourteen hours. 0.2% by weight of residual monomers is found in the dispersion. The dispersion is devoid of coagulate and specks. The pH is 6.5 and the solids content is 48.2% by weight.
- Example A (DT—AS 1,495,790, Example 3)**
- 150 parts by weight of water
 4 parts by weight of shellac (6% by weight aqueous solution, pH 7.8)
 70 parts by weight of styrene and
 0.1 part by weight of potassium persulphate are introduced into a 12-litre polymerisation vessel. After the vessel has been flushed three times with nitrogen and evacuated 30 parts by weight of butadiene is introduced. After twelve hours at 65°C a solids content of 35% by weight has been reached, at which the reaction subsides. After twenty-five hours the same solids content is found and there is about 8% by weight of residual styrene in the latex. The reaction is thereafter discontinued.
- Example B**
- Example B corresponds to Example A except that 0.3 part by weight of potassium persulphate is used. The reaction is over after twenty-three hours. 0.7% by weight of residual monomers is found in the latex. The content of coagulate is 10% by weight. The pH is 7.6 and the solids content is 39.6% by weight.

Example C

Example C corresponds to Example A except that 0.2 part by weight of dibenzoyl peroxide is used as initiator. The reaction hardly gets going. After twenty hours another 0.2 part by weight of dibenzoyl peroxide is added at a solids content of 7% by weight. After twenty-eight hours the solids content is unchanged and the reaction is discontinued.

Example D

This Example corresponds to the preparation of the primary latex but 0.4 part by weight of dibenzoyl peroxide is used as initiator. The reaction gets going only very slowly and remains stationary at a solids content of from 10 to 12% by weight after ten hours. The same solids content is found after twenty-three hours. The reaction is discontinued.

Example E

This Example corresponds to the preparation of the primary latex but only 107 parts by weight of water is used. The reaction is ended after fifteen hours; the product is wholly pasty.

Example F

This Example corresponds to the preparation of the primary latex but the reaction is carried out in a 500-litre vessel. The reaction becomes very violent after two hours and can scarcely be controlled. The reaction is over after twelve hours. Although the product contains little coagulate it is very viscous and becomes creamy.

All the Examples identified by letters are comparative Examples.

WHAT WE CLAIM IS:—

1. A process for the production of an aqueous copolymer dispersion by emulsion polymerisation at elevated temperature of a mixture of from 50 to 85% by weight of a vinyl-aromatic compound, from 15 to 50% by weight of a conjugated diolefin from 0 to 25% by weight of acrylonitrile and from 0 to 5% by weight of another monomer which contains one or more functional groups in addition to the double bond, in a polymerisation vessel using an initiator which forms free radicals and using shellac as the sole emulsifier, wherein the total amounts of the specified monomers are placed in the polymerisation vessel prior to the commencement of the reaction, together with the shellac, and from 2 to 50% by weight (based on the monomer mixture and reckoned as solid material) of a dispersion of a copolymer of the above-specified monomers in proportions within the ranges specified above, and wherein the initiator used is an azo-bis-carboxylic acid nitrile of four to seven carbon atoms in each carboxylic acid radical.

2. A process as claimed in claim 1 wherein the initiator is azo-bis-isobutyronitrile.

3. A process as claimed in claim 1 or 2 wherein the amount of shellac used is from 1 to 10% by weight based on the monomer mixture.

4. A process as claimed in claim 1 or 2 wherein the amount of shellac used is from 3 to 7% by weight based on the monomer mixture.

5. A process as claimed in any of claims 1 to 4 wherein a bleached type of shellac is used.

6. A process as claimed in any of claims 1 to 5 wherein the vinylaromatic compound used is styrene, α -methylstyrene, chlorostyrene, vinyltoluene or a mixture of two or more thereof.

7. A process as claimed in any of claims 1 to 5 wherein styrene is used in an amount of from 60 to 75% by weight as the vinylaromatic compound.

8. A process as claimed in any of claims 1 to 7 wherein the conjugated diolefin used is butadiene, isoprene, chloroprene or piperylene or a mixture of two or more thereof.

9. A process as claimed in any of claims 1 to 7 wherein butadiene is used in an amount of 25 to 40% by weight as the conjugated diolefin.

10. A process as claimed in any of claims 1 to 9 wherein a comonomer having one or more reactive groups is used which is acrylamide, methacrylamide, N-methylolacrylamide, N-methoxymethylacrylamide, 2-hydroxyethyl acrylate or a mixture of two or more thereof.

11. A process as claimed in any of claims 1 to 10 wherein the initiator is used in an amount of from 0.01 to 1% by weight based on the monomer mixture.

12. A process as claimed in any of claims 1 to 10 wherein the initiator is used in an amount of from 0.1 to 0.5% by weight based on the monomer mixture.

13. A process as claimed in any of claims 1 to 12 wherein the amount of copolymer dispersion present prior to the commencement of the polymerisation is from 5 to 25% by weight based on the monomer mixture and reckoned as solid material.

14. A process as claimed in any of claims 1 to 13 wherein the copolymer in the copolymer dispersion used has the same composition as that in the end product of the process.

15. A process as claimed in any of claims 1 to 14 carried out at a pH in excess of 7.8.

16. A process as claimed in any of claims 1 to 15 wherein a regulator is added in an amount of up to 1% by weight based on the monomer mixture to control the molecular weight.

17. A process as claimed in claim 16 wherein the regulator is t-dodecylmercaptan.

18. A process as claimed in any of claims 1 to 17 carried out at a temperature of from 50° to 85°C.

19. A process as claimed in any of claims

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1 to 17 carried out at a temperature of from 60° to 75°C. claims 1 to 20.

5 20. A process for the production of an aqueous copolymer dispersion carried out substantially as described in any of the foregoing Examples 1 to 4.

21. An aqueous copolymer dispersion when obtained by a process as claimed in any of

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