

PROCESS FOR PREPARING WATER-SOLUBLE STYRENE/ACRYLIC RESINS BY CONTINUOUS BULK POLYMERIZATION

Technical Field

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The present invention relates to a process for preparing water-soluble styrene/acrylic resins using continuous bulk polymerization. More particularly, the present invention relates to a process for preparing low molecular weight polymers with narrow molecular weight distributions, high acid values and low volatile contents through continuous bulk polymerization.

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Background Art

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Most of the ink, paint and coatings in current use employ organic solvents. Because the organic materials of the organic solvents are evaporated when the ink, paint and coatings are used, they are now found to produce serious air pollution. In addition, the organic solvents have a highly plausible possibility to cause a fire owing to their inflammability.

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As an alternative to avoid these problems, high solid liquid coatings based on water-soluble styrene/acrylic resins were suggested. In fact, these high solid liquid coatings are desirable in that they do not produce air pollution. Also, in contrast to organic solvent-based coatings, the high solid

liquid coatings reduce the cost required for resources, energy and work environments as well as have no possibility of catching fire or explosion.

To be useful, however, the high solid liquid coatings must be followed by the solution for the viscosity increase of inks, paints and coatings attributed to high solid contents. Even a little increase in the molecular weight of a water-soluble styrene/acrylic resin brings about a significant viscosity increase of inks, paints and coatings. In result, high molecular weight resins have a limit of being incapable of increasing solid contents. For instance, where water-soluble styrene/acrylic resins with weight average molecular weight of approximately 50,000 to 100,000 are used to prepare aqueous inks, paints or coatings, the permittable solid content is 50% at most. In contrast, water-soluble styrene/acrylic resins with weight average molecular weight of 5,000 to 15,000 enable inks, paints and coatings to have solid contents of up to 70-80% without causing problems. In this case, however, broad molecular weight distributions raise the viscosity of inks, paints and coatings on the account of the high molecular weight fraction of the resins. Thus, it is required that the molecular weight distribution be narrow to acquire aqueous ink or paint with high solid contents.

As for the water-solubility of the styrene/acrylic resins, it is provided by acid groups, typically, carboxylic groups. To recruit carboxylic groups into the resins, acrylic acids or methacrylic acids are useful. An acid value as high as or greater than 200 is necessary to provide sufficient water solubility.

A high content of volatile components in the water-soluble resins is a cause to produce a lot of foams when preparing inks or paints. And these foams are deteriorating the processability of the inks or paints. A significant quantity of antifoaming agents may be a solution for this problem, but cause depreciation in physical properties. Thus, the less volatile components the water-soluble resins contain, the better the processability is. In addition, better physical properties of the paint or ink can be obtained by virtue of less antifoaming agent used.

In summary, in order to prepare aqueous inks or paints with high solid contents, the water-soluble resins which have low average molecular weights, narrow molecular weight distributions, high acid values and low volatile contents are required.

For example, water-soluble styrene/acrylic resins with weight average molecular weights of 4,000-16,000, molecular weight distributions of 2.2 or less, acid values of 200 or more, and volatile contents of 5 %, are used to give a high solid liquid coating. The water-soluble styrene/acrylic resins which meet these conditions are impossible to produce by generally well-known solution polymerization or emulsion polymerization. In fact, solution polymerization processes are used to prepare styrene/acrylic resins with molecular weights of from about 10,000 to 100,000 while emulsion polymerization processes are applied for the resins with molecular weights of up to millions.

U.S. Pat. No. 4,414,370 discloses a continuous bulk polymerization

process for preparing water-soluble styrene/acrylic resins, teaching that monomers are continuously fed in such a way that they are polymerized at reaction temperature of 235-310 °C with a residence time of 2 minutes or more in a continuous stirred reactor, and that the polymers thus produced are transferred to a devolatilizer to remove their volatile contents. It is also written that water-soluble styrene/acrylic resins with number average molecular weight of from 1,000 to 6,000 and molecular weight distributions of less than 2.0 can be polymerized from the monomer components which comprise a mixture of styrene and alpha-methyl styrene (with a weight ratio ranging 1:2 to 2:1) and an acrylic acid (with a weight ratio of the styrene mixture to acrylic acid ranging from 60:40 to 80:20) using diethylene glycol monoethyl ether as a solvent at an amount of 1 to 10 weight parts based on the total weight of the monomer components. In order to control the reaction temperature of the reactor, it is provided with an external jacket and an internal cooling coil and heat transfer oil is allowed to flow through the jacket and the cooling coil.

However, the reaction temperature control by the combined working of the oil jacket and the cooling coil which are respectively provided outside and inside the reactor, is problematic in that, because a large temperature deviation occurs between the inside and the outside of the reactor, it is difficult to uniformly control the temperature on the inside of the reactor. Also, the high reaction temperature of the supra patent is a factor to increase the production cost. A novel process is needed by which water-soluble

styrene/acrylic resins with similar molecular weights and molecular weight distributions can be prepared at lower reaction temperatures. Diethylene glycol monoethyl ether, used as a solvent to control the viscosity of the reactant mixture, undergoes esterification with the acrylic acid, decreasing the acid value of the water-soluble resins, the products. In result, the resins are deteriorated in water solubility. Thus, there are also needed solvents which have as little influence on the products as possible and can control the viscosity of the reaction.

The devolatilization of the bulk polymerization process disclosed in the above-cited patent, by which un-reacted monomers and remaining solvent are removed from the resin produced, to our knowledge, plays an important role in determining the overall process efficiency as well as in controlling the physical properties of the product, such as volatile content. For all that, nowhere is a detailed mention.

Disclosure of the Invention

The intensive and thorough research on the development of an effective continuous bulk polymerization process, repeated by the present inventors, resulted in the finding that at relatively low temperatures, acrylic monomers and styrenic monomers can be copolymerized in a water-containing solvent to low molecular weight polymers suitable for paint, ink and coatings, by use of a cooling coil/jacket-integrated, temperature-

controllable reactor and a falling-strand type devolatilizer.

It is therefore an object of the present invention to provide a continuous bulk polymerization process for preparing a water-soluble styrene/acrylic resins with low molecular weights, narrow molecular weight
5 distributions, high acid values and low volatile contents.

The object is accomplished by a process in which approximately 5-15 parts by weight of a solvent mixture of dipropylene glycol methyl ether and water per 100 parts by weight of reactant monomers are continuously charged to a temperature-controllable reactor equipped externally with an oil
10 jacket containing a cooling coil therein, the monomers are copolymerized at 150-220 °C with a residence time of from 10 to 20 minutes in the reactor, and the polymers are transferred to a falling-strand type devolatilizer which is operated at 180-210 °C under a pressure of from -500 to -750 mmHg to remove volatile contents from the polymers.

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Brief Description of the Drawing

Fig. 1 is a schematic process view showing the continuous bulk polymerization of the present invention.

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Best Modes for Carrying Out the Invention

The present invention pertains to a process to continuously bulk

polymerize styrenic monomers and acrylic monomers (hereinafter referred to as "monomers") at lower reaction temperature than the prior arts. For this bulk polymerization, a mixture of dipropylene glycol methyl ether (DPM) and water is used as a solvent. According to the process of the present invention, water-soluble styrene/acrylic resins with narrow molecular weight distributions can be obtained at a reaction temperature of about 150-220 °C. Optionally, an alpha-methyl styrene oligomer may be added to control the molecular weights and the molecular weight distributions of the resins.

10 With reference to the drawing, there is illustrated the procedure of the continuous bulk polymerization, figured to obtain water-soluble styrene/acrylic resins. As shown, the process of the present invention is operated by use of two monomer-stirred tanks 1 and 2, a reactor 3, a falling-strand type devolatilizer 4, a distillation column 5, and a monomer
15 recycle tank 6.

From the monomer stirred tank 1 or 2 to the reactor 3, monomers are fed at a constant rate. The liquid level of the reactor 3 is controlled so as to provide a residence time of the monomers charged in the reactor 3 of about 10-20 minutes. The reactor may have a capacity of, for example, 75 liters.
20 In order to efficiently control the reaction temperature of the continuous bulk polymerization, a jacket through which heat transfer oil can flow, is provided to the reactor. Also, a cooling coil through which heat transfer oil can flow, is provided inside the jacket. By virtue of this integrated

temperature controlling means, the reaction temperature within the reactor can be easy to control. Water-soluble styrene/acrylic resins having weight average molecular weights of 3,000-10,000 and molecular weight distributions of less than 2.0 could be prepared from the monomers by bulk
5 polymerization using the equipment shown in the drawing.

While passing through the reactor, the monomers are polymerized to water-soluble resins which are, then, transferred to the falling-strand type devolatilizer 4 to remove volatile contents therefrom. The devolatilizer is maintained at a constant temperature by a jacket provided thereto, through
10 which heat transfer oil can flow, and at a constant vacuum condition with the aid of a vacuum pump 7. After passing through the devolatilizer 4, the polymer products come to have volatile contents of less than 2 %.

Comprising un-reacted monomers, high-boiling point materials, and the solvent mixture of dipropylene glycol methyl ether and water, the
15 volatile contents removed in the devolatilizer are passed to the distillation column 5 to separate the high-boiling point materials, then stored in the monomer recycle tank 6, and finally recharged to the reactor.

Diethylene glycol monoethyl ether is used as a solvent for bulk polymerization in U.S. Pat. No. 4,414,370, serving to absorb the reaction
20 heat and to control the viscosity of the reactants. As mentioned previously, this material is chemically coupled to the water-soluble resin molecules as a result of the esterification reaction between the hydroxy groups of the solvent material and the carboxyl groups of the resin produced.

Consequently, this material loses the function of the solvent itself, which causes an increase in the viscosity of the reactant mixture and makes it difficult to control the temperature of the reactor. In addition, the esterification lowers the acid value of the water-soluble resin such that its water solubility is deteriorated.

In the present invention, dipropylene glycol methyl ether is used as a solvent, but together with water. This solvent mixture is used at an amount of about 5-15 weight parts based on 100 weight parts of the monomer. In addition to being advantageous in controlling the viscosity of the reactant mixture, the co-existence of water inhibits the dipropylene glycol methyl ether's being esterified with acrylic acids. As a result, there could be prepared water-soluble styrene/acrylic resins with acid values of 200-230. The solvent mixture preferably contains water at an amount of approximately 20 to 45 % by weight. For example, if the water content is below 20 % by weight, extensive esterification occurs between the dipropylene glycol methyl ether and the acrylic acid, decreasing the acid value of the final product. On the other hand, if the water content is over 45 % by weight, the water is vaporized such a large amount, and so the viscosity of the reactant mixture cannot be efficiently controlled with a significant increase in the internal pressure of the reactor.

For best results, the monomer mixture has a weight ratio of styrenic monomer to acrylic monomer ranging from 60:40 to 80:20. The styrenic monomer comprises styrene alone or in combination with alpha-methyl

styrene with the weight ratio of styrene to alpha-methyl styrene ranging from 50:50 to 90:10. For the acrylic monomer, acrylic acid is used, alone or in combination with alkylacrylate of not more than 20 % by weight.

Optionally, an alpha-methyl styrene oligomer may be used as a
5 molecular weight controller. It is preferable that the alpha-methyl styrene oligomer is added at an amount of 2-6 weight parts based on 100 weight parts of the monomer mixture. For example, if too little alpha-methyl styrene oligomer is used, the resulting resins have high molecular weights and show broad molecular weight distributions. On the other hand, excess
10 amounts of the alpha-methyl styrene oligomer produce resins with too low molecular weights and thus, poor physical properties.

The alpha-methyl styrene monomer, serving as a modulator for the molecular weights and molecular weight distributions of the resins in the present invention, is reported to deleteriously affect the pigment dispersion
15 in resins if used in large amounts (Surface Phenomena and Latexes in Waterborne Coatings and Printing Technology, edited by M. K. Sharma, Plenum Press, New York, 1995, p139-151). Use of the alpha-methyl styrene oligomer in a small amount results in water-soluble styrene/acrylic resins superior in pigment dispersion without color and odor problems. For the
20 alpha-methyl styrene oligomer, "Techlon M21 Extra", commercially available from Tekchem Corporation, is recommended.

Since the bulk polymerization of the present invention is carried out at low temperature, a low-temperature initiator, such as t-butyl peroxy

benzoate, is desirable. Its amount preferably ranges approximately from 3 to 6 weight parts based on the total weight of the monomer mixture.

The falling-strand type devolatilizer used to remove volatile contents from the products in the present invention has advantages over the stirred tank type devolatilizer used in U.S. Pat. No. 4,414,370, in that the resin's surface area is enlarged so as to easily remove volatile contents from the resin.

Preferably, the falling-strand type devolatilizer is maintained at 180-210 °C. For example, a temperature lower than 180 °C in the devolatilizer causes a difficult problem in removing volatile contents from the resins. On the other hand, if the falling-strand type devolatilizer is heated at higher than 210 °C, the resulting resins are deteriorated in physical properties.

Upon bulk polymerization, the devolatilizer is preferably operated under pressure of -750 to -500 mmHg. For example, the resin is dramatically deteriorated in flowability under a pressure lower than -750 mmHg, so that the resin is very difficult to transfer. On the other hand, a pressure higher than -500 mmHg makes it difficult to remove the volatile contents in the resin, sufficiently.

A better understanding of the present invention may be obtained in the light of the following examples which are set forth to illustrate, but are not to be construed to limit the present invention.

EXAMPLES I TO V

To a temperature-controllable continuous stirred reactor equipped externally with an oil jacket containing a cooling coil therein were fed styrenic monomers (styrene and alpha-methyl styrene) and acrylic monomers (acrylic acid) as indicated in Table 1, below, to prepare water-soluble styrene/acrylic resins.

Polymerization was initiated in the presence of t-butyl peroxy benzoate. This polymerization initiator was used at an amount of 3.5 weight parts based on the total weight of the monomer mixture. For the polymerization, a solvent mixture of dipropylene glycol methyl ether and water with a water content amounting to 35 % by weight, was used at an amount of 15 weight parts based on 100 weight parts of the monomer mixture. At various temperature conditions from 150 to 220 °C, the polymerization was carried out. The resins polymerized were passed through a falling-strand type devolatilizer to remove volatile contents therefrom. At that time, the devolatilizer was operated at 195 °C under -750 mmHg.

TABLE 1

No. of Examples	I	II	III	IV	V
Styrene (wt. part)	35	35	35	35	35
α -Methyl Styrene (wt. part)	32	32	32	32	32
Acrylic Acid (wt. part)	33	33	33	33	33

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Rxn. Temp.(°C)	150	180	200	210	220
Number. Avg. Mw, Mn	5,000	4,800	4,400	3,600	3,100
Weight Avg. Mw, Mw	9,800	8,700	7,500	6,200	5,200
molecular weight distribution, Mw	1.9	1.8	1.7	1.7	1.7
Acid Value	223	223	225	225	226
Volatile content(%)	1.5	1.5	1.3	1.2	1.2

COMPARATIVE EXAMPLES I TO III

10 These examples were to compare the temperature control ability between the reactor of the present invention and a conventional reactor.

Water-soluble styrene/acrylic resins were prepared in similar manners to those of Examples II, IV and V, respectively, except that heat transfer oil was not allowed to flow through the cooling coil set inside the oil jacket, but
 15 allowed to flow through a cooling coil which was temporarily set inside the reactor. The physical properties of the resins prepared are given in Table 2, below.

TABLE 2

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No. of Examples	C. I	C. II	C. III
Rxn. Temp. (°C)	180	210	220
Number. Avg. Mw, Mn	4,500	3,250	2,750

Weight Avg. Mw, Mw	10,550	7,850	6,700
Molecular Weight Distribution, Mw	2.34	2.41	2.43
Acid Value	220	222	222
Volatile content(%)	1.5	1.4	1.4

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As apparent from Tables 1 and 2, the molecular weight distributions of the water-soluble styrene/acrylic resins obtained at the same temperatures by the conventional reactor are broader than those of the water-soluble styrene/acrylic resins obtained by the reactor of the present invention. This is attributed to the fact that, even under the same average reaction temperature, the reactors were different in temperature deviation, so that they had partially different temperatures. Consequently, it is difficult to control the temperature with the conventional reactor to which an oil jacket is externally provided and a cooling coil is internally provided.

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EXAMPLES VI TO IX

In order to investigate the influence that the operation condition of the devolatilizer has on the physical properties of the resins, polymerization was carried out in the same manner as that of Example IV, but under the temperature and pressure conditions for the devolatilizer, indicated in Table 3, below. The results are also given in Table 3.

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TABLE 3

	No. of Examples	IV	VI	VII	VIII	IX
	Devolatilizer Temp.(°C)	195	210	180	210	180
5	Devolatilizer Press.(mmHg)	-750	-750	-750	-500	-600
	Number. Avg. Mw, Mn	3,600	3,600	3,600	3,600	3,600
	Weight Avg. Mw, Mw	6,200	6,200	6,200	6,200	6,200
	Molecular Weight Distribution, Mw	1.7	1.7	1.7	1.7	1.7
	Acid Value	225	225	226	225	224
10	Volatile content(%)	1.2	1.1	1.5	1.7	1.8

COMPARATIVE EXAMPLES IV AND V

Water-soluble styrene/acrylic resins were prepared in the same manner as that of Example IV, but under the devolatilizer conditions indicated in Table 4, below, for comparison. The results are also given in Table 4.

TABLE 4

20	No. of Examples	IV	C. IV	C. V
	Devolatilizer Temp. (°C)	195	170	235
	Devolatilizer Press. (mmHg)	-750	-350	-750
	Number. Avg. Mw, Mn	3,600	3,600	2,800

Weight Avg. Mw, Mw	6,200	6,200	5,850
Molecular Weight Distribution, Mw	1.7	1.7	2.1
Acid Value	225	225	214
Volatile content (%)	1.2	3.8	0.6

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The data of Table 4 show that the volatile content is high upon maintaining the devolatilizer at low temperatures and at high pressures while the devolatilizer condition of high temperature and low pressure decreases the volatile content, but makes the molecular weight distribution broad and
10 decreases the acid value to some extent.

EXAMPLES X TO XIII

Water-soluble styrene/acrylic resins were prepared in a similar manner
15 to that of Example IV, except that the solvent mixture of dipropylene glycol methyl ether and water was changed in amount and water content according to the indications of Table 5, below.

COMPARATIVE EXAMPLE VI

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The same procedure as that of Example X was repeated, except that dipropylene glycol methyl ether alone was used as a solvent.

The results are given as shown in Table 5, below.

TABLE 5

No. of Examples	IV	X	XI	XII	XIII	C. VI
Solvent Amount (wt part)	15	10	15	5	10	15*
Water content in Solvent (wt%)	35	35	45	20	25	0
Number. Avg. Mw, Mn	3,600	3,500	3,600	3,200	3,600	3100
Weight Avg. Mw, Mw	6,200	6,300	6,200	6,500	6,200	6500
Molecular Weight Distribution, Mw	1.7	1.8	1.7	1.8	1.8	2.1
Acid value	225	220	230	205	203	180
Volatile content(%)	1.2	1.1	1.3	1.1	1.2	1.5

* dipropylene glycol methyl ether alone

EXAMPLES XIV TO XVII

In order to investigate the influence that the styrenic monomer content has on the physical properties of the resin, polymerization was carried out in the same manner as that of Example IV, but under the condition of changing the amount of the styrenic monomers according to the indication of Table 6, below. The results are also given in Table 6.

TABLE 6

No. of Examples	IV	XIV	XV	XIV	XVII
Styrene (wt part)	35	43	52	60	67

	α -Methyl Styrene (wt part)	32	24	15	7	0
	Acrylic acid (wt part)	33	33	33	33	33
	Number. Avg. Mw, Mn	3,600	3,200	3,750	3,800	4,100
	Weight Avg. Mw, Mw	6,200	5,750	6,800	7,500	8,150
5	Molecular Weight Distribution, Mw	1.7	1.8	1.8	2.0	2.0
	Acid value	225	223	225	227	227
	Volatile content (%)	1.2	1.4	1.3	1.3	1.3

EXAMPLES XVIII TO XX

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In order to investigate the influence that the acrylic monomer content has on the physical properties of the resin, polymerization was carried out in the same manner as that of Example IV, but under the condition of changing the amount of the acrylic monomer according to the indication of

15 Table 7, below. The results are also given in Table 7.

TABLE 7

20

No. of Examples	IV	XVIII	XIX	XX
Styrene (wt part)	35	35	35	35
α -Methyl Styrene (wt part)	32	32	32	32

	Acrylic acid (wt part)	33	29.5	28.5	27
	Methyl Acrylate (wt part)	0	3.5	4.5	6
	Number. Avg. Mw, Mn	3,600	3,650	3,700	3,700
	Weight Avg. Mw, Mw	6,200	6,600	6,700	7,350
5	Molecular Weight Distribution, Mw	1.7	1.8	1.8	2.0
	Acid value	225	220	213	204
	Volatile content (%)	1.2	1.3	1.4	1.4

COMPARATIVE EXAMPLE VII

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According to the process suggested in U.S. Pat. No. 4,414,370, water-soluble styrene/acrylic resins were prepared from styrenic monomers (styrene and alpha-methyl styrene) and acrylic monomers (acrylic acid) at the amount and reaction temperature indicated in Table 8, below, using a

15 temperature-controllable continuous stirred reactor which has an external jacket through which heat transfer oil flows, and has a cooling coil set inside. For this polymerization, diethylene glycol monoethyl ether is used as a reaction solvent. The results are given in Table 8.

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TABLE 8

No. of Example	C. VII
Styrene (wt part)	31
α -Methyl Styrene (wt part)	37
Acrylic acid (wt part)	32
Rxn. Temp. ($^{\circ}$ C)	263
Solvent amount (wt part)	20
Devolatilizer Temp. ($^{\circ}$ C)	263
Number. Avg. Mw, Mn	1,700
Weight Avg. Mw, Mw	2,650
Molecular Weight Distribution, Mw	1.56
Acid value	160

15 EXAMPLES XXI AND XXII

In order to investigate the influence that the alpha-methyl styrene oligomer has on the physical properties of the resin, polymerization was carried out in the same manner as that of Example IV, but under the condition of changing the amount of the alpha-methyl styrene oligomer according to the indication of Table 9, below. The results are also given in Table 9.

TABLE 9

No. of Examples	XXI	XXII
Styrene (wt part)	35	35
α -Methyl Styrene (wt part)	32	32
Acrylic acid (wt part)	33	33
α -Methyl styrene oligomer (wt part)	3	5
Number. Avg. Mw, Mn	3800	3950
Weight Avg. Mw, Mw	6100	5900
Molecular Weight Distribution, Mw	1.6	1.5
Acid value	226	225
Volatile content (%)	1.2	1.2

Industrially Applicability

As described hereinbefore, the continuous bulk polymerization process of the present invention is quite different from conventional processes in solvent used (a mixture of dipropylene glycol methyl ether and water), reaction-temperature control manner, devolatilizer type and devolatilizer operation condition. The water-soluble styrene/acrylic resins prepared according to the process of the present invention take industrial advantages over the conventional resins because the resins of the present

invention, if polymerized at lower temperatures, show lower molecular weights, narrower molecular weight distributions, higher acid values and lower volatile contents than the resins prepared by conventional processes.

The present invention has been described in an illustrative manner,
5 and it is to be understood the terminology used is intended to be in the nature of description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings. Therefore, it is to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as
10 specifically described.



Claims

1. A process for preparing water-soluble styrene/acrylic resins by continuous bulk polymerization, in which styrenic monomer components and an acrylic monomer components are polymerized at a reaction temperature of 150-220 °C in a solvent mixture of dipropylene glycol methyl ether and water to give a polymer and the polymer is deprived of volatile contents by a falling-strand type devolatilizer.

2. The process as set forth in claim 1, wherein the solvent mixture is used at an amount of approximately 5 to 15 parts by weight based on the 100 parts by weight of the monomer components.

3. The process as set forth in claim 1, wherein the solvent mixture contains water at an amount of approximately 20 to 45 % by weight.

4. The process as set forth in claim 1, wherein the styrenic monomer component and the acrylic monomer component range, in weight ratio, from 60:40 to 80:20.

5. The process as set forth in claim 1 or 4, wherein the styrenic monomer component comprises styrene alone or in combination with alpha-methyl styrene with the weight ratio of styrene to alpha-methyl styrene



ranging from 50:50 to 90:10.

6. The process as set forth in claim 1 or 4, wherein the acrylic monomer component comprises acrylic acid, alone or in combination with
5 alkylacrylate of not more than 20 % by weight.

7. The process as set forth in claim 1, wherein the devolatilizer is operated at temperature of 180-210 °C under pressure of -500 to -750 mmHg.

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8. The process as set forth in claim 1, wherein the monomer components are polymerized in a temperature-controllable continuous stirred reactor equipped externally with an oil jacket containing a cooling coil therein.

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9. The process as set forth in claim 1, wherein the monomer components further comprise an alpha-methyl styrene oligomer at an amount of approximately 2-6 parts by weight based on 100 parts by weight of the monomer components.