



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C08F 285/00, 2/22, C08J 9/28	A1	(11) International Publication Number: WO 95/11265 (43) International Publication Date: 27 April 1995 (27.04.95)
(21) International Application Number: PCT/KR94/00141 (22) International Filing Date: 20 October 1994 (20.10.94) (30) Priority Data: 1993/22081 20 October 1993 (20.10.93) KR (71) Applicant (for all designated States except US): LUCKY LTD. [KR/KR]; 20, Yoido-dong, Yongdungpo-ku, Seoul 150-010 (KR). (72) Inventors; and (75) Inventors/Applicants (for US only): CHOI, Su, Beom [KR/KR]; Youngjin Haennim Apartment 2-1001, Samchun-dong, Seo-ku, Daejeon 302-222 (KR). JANG, Tae, Hwan [KR/KR]; Lucky Apartment 7-056, Doryong-dong, Youseong-ku, Daejeon 305-340 (KR). YOO, Jin, Nyoungh [KR/KR]; Lucky Apartment 6-302, Doryong-dong, 381-42, Youseong-ku, Daejeon 305-340 (KR). LEE, Chan, Hong [KR/KR]; Lucky Hana Apartment 102-901, Shinseong-dong, Youseong-ku, Daejeon 305-345 (KR). (74) Agents: CHOI, Kyu, Pal et al.; 824-20, Yeoksam-dong, Kangnam-ku, Seoul 135-080 (KR).		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR PREPARING EMULSION POLYMERS HAVING A HOLLOW STRUCTURE		
(57) Abstract <p>The present invention relates to a process for preparing emulsion polymers having a hollow structure. More specifically, the present invention relates to a process for preparing emulsion polymers which comprises forming a core which is an alkali-swellable resin, carrying out a subsequential emulsion polymerization by means of a continuous variation in composition and a kinetic steric barrier to form a hard polymer shell outside the core, swelling the core with an alkali and then drying to remove water contained in the alkali-swellable core, thereby forming a closed internal pore in the center of polymer.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

PROCESS FOR PREPARING EMULSION POLYMERS
HAVING A HOLLOW STRUCTURE

5

TECHNICAL FIELD

The present invention relates to a process for preparing emulsion polymers having a hollow structure. More specifically, the present invention relates to a process for preparing emulsion polymers which comprises forming an internal layer with an alkali-swellable resin, carrying out a subsequential emulsion polymerization by means of a continuous variation in composition and a kinetic steric barrier to form a hard polymer layer outside the internal layer, swelling the internal layer with an alkali and then drying to remove water contained in the alkali-swellable resin, thereby forming a closed internal pore in the center of polymer particle.

20

BACKGROUND ART

Emulsion polymers having a hollow structure have been widely used as a plastic pigment in the field of water-soluble paints, paper coating agents, information recording papers, synthetic resins and the like.

In the prior art, numerous methods for preparing plastic pigments having a hollow structure have been proposed as follows :

- 1) Method for preparing a hollow monocellular particle comprising polymerizing a mixture of monomers containing a blowing agent to prepare a plastic bead which is then blown under heating (see U.S. Patent Specifica-

tion No. 3,615,972);

- 2) Method for preparing a polyester bead with a hollow having a diameter of 1 to 25 micron which comprises mechanically stirring a solution of polyester dissolved in styrene to prepare an emulsion of water/oil/water which is then polymerized (see U.S. Patent Specification No. 3,891,577);
- 3) Method for preparing a hollow particle comprising adding a volatile material to a polymer and then gasifying the volatile material to swell the polymer (see Japanese Patent No. 252635/1985);
- 4) Method for including vesicles into a dissolved polymer by dissolving a polymer and then blowing a gas such as air, etc., therein; and
- 5) Method for preparing a hollow particle which comprises swelling a polymer particle having a glass transition temperature of -10°C or more with hot air in the spray dryer and then immediately cooling the swollen polymer to normal temperature (see Japanese Laid-open Patent Publication No. (Hei) 4-145131).

Although the polymer beads prepared according to the prior methods as mentioned above have a self-hiding property and therefore can serve as a pigment, those prior methods have some disadvantages in that the particle size cannot be uniformly controlled, and those methods cannot properly play a role of a dispersing agent of titanium oxide, poorly contributes to a critical surface porosity and tends to precipitate during the storage, and further the pore size and shell thickness are difficult to control.

In addition, Japanese Patent Publication No. 44282/88

discloses a method for preparing a hollow particle by phase separation and polymerization shrinkage. However, this method has also disadvantages that the hollow portion is not smooth and the method cannot be practically used in industrial scale because of the high material cost resulting from the massive use of cross-linking agent.

In order to improve the disadvantages in such prior methods for preparing plastic pigments having hollow particles, a method for producing hollow particles by preparing a core-shell polymer having an alkali-swella-
ble resin inside the particles via a multi-step continuous polymerization and then subjecting the polymer to alkali swelling and drying has been developed. This multi-step continuous polymerization is influenced by the composition and glass transition temperature of monomers used in each polymerization step, the kind and concentration of an emulsifying agent, the kind and concentration of a polymerization initiator, reaction temperature, etc. Further, the method using alkali-swelling procedure tends to produce a reverse core-shell polymer or a confetti-like abnormal structure due to the hydrophilicity of polymers present inside the particles, which is far greater than that of polymers present on the outer shell of particles. Accordingly, numerous methods have been proposed for inhibiting the formation of such abnormal particle structure.

For example, U.S. Patent Specification No. 4,427,836 discloses a method which comprises polymerizing carboxylic acid-containing hydrophilic polymers of which the volume can be swollen by two times or more with an aqueous solution of volatile base at the first emulsion polymerization step and then forming a sheath of a polymeric material through which the aqueous base solution can be permeated, on the surface of a core by means of thermal or redox initiation emulsion polymerization at the second emulsion

polymerization step. However, this method has the disadvantages in that additional new particles are greatly generated, the stability of latex is poor, and the shell-forming monomers should be used in an amount of 10 times
5 or more the core-forming monomers for providing a uniform core-shell structure and therefore the shell becomes thick.

In addition, Korean Patent Publication No. 87-1808
10 discloses a method wherein a core is formed from the monomer mixture containing monomer having a carboxylic acid group and then at a shell-forming step, in order to effectively inhibit the formation of abnormal particles a copolymer surfactant is used as an emulsifier and the
15 feeding rate of monomers, the kind of polymerization initiator and the reaction temperature are specifically selected. According to this method, the formation of new particles in each polymerization step can be inhibited. However, this method is not greatly useful for improve-
20 ment in the hiding property since the copolymer surfactant, which is a strong electrolyte, present on the surface of core causes an increase in the heterogeneity between the core polymer and the shell polymer which makes the adhesion of hydrophobic shell and hydrophilic core poor.

25

Meanwhile, Korean Patent Publication No. 93-830 discloses a method for preparing emulsion polymer by forming a hydrophilic core with a seed formed from an acid monomer and a vinyl monomer and providing a hard sheath layer with
30 a hydrophobic monomer outside the core, wherein the emulsion polymerization is carried out by adding a group transfer polymerization initiator or an oil-soluble initiator when the seed and the core/sheath layer are produced by emulsion polymerization in the aqueous system. This
35 method can reduce the agglomeration of latex particles but has some disadvantages that the use of oil-soluble initiator results in production of new suspension particles and

the difference in hydrophilicity of core and sheath polymers makes the encapsulation efficiency poor.

5

DISCLOSURE OF INVENTION

Thus, the present inventors have extensively studied to develop a method which can prevent lowering of the encapsulation efficiency due to the great difference in hydrophilicity between a core polymer and a shell polymer and can produce monodisperse hollow particles of emulsion polymer having a uniform hollow size and a uniform shell thickness. As a result, we have identified that the encapsulation efficiency can be maximized by adding a cross-linking agent to the core and shell layers to minimize the mutual interdiffusion of polymer chains, while the hydrophilicity is continuously altered from the inner layer to the outer layer of the shell, and therefore monodisperse hollow particle of emulsion polymer consisting of a solid hydrophobic shell and having uniform hollow size and uniform shell thickness can be produced.

Accordingly, it is an object of the present invention to provide an improved process for preparing emulsion polymers having hollow structure.

It is another object of the present invention to provide a process for preparing emulsion polymers which comprises forming a core polymer with an alkali-swelling resin, carrying out subsequential emulsion polymerization by means of continuous variation in composition and a kinetic steric barrier to form hard polymer shell outside the core, swelling the core with an alkali and then drying to remove water contained in the alkali-swollen core, thereby forming a closed internal pore in the center of polymer particle.

It is still another object of the present invention to provide a process for preparing the hollow particles of emulsion polymer which comprises a seed-forming step for polymerizing the monomer mixture of an acid monomer
5 having a carboxylic acid group and a non-ionic hydrophilic monomer in the presence of a polymerization initiator; a core-forming step for preparing a core, which can be swollen with an alkali, by polymerizing the monomer mixture of an acid monomer having a carboxylic acid group, a
10 non-ionic hydrophilic monomer and a cross-linking agent to the seed latex; a step for forming the hydrophobic shell on the hydrophilic core; and an alkali-swelling step.

Further, it is another object of the present invention
15 to provide a process for preparing hollow particles of the emulsion polymer having a single hollow in the center and a uniform thickness of the shell, wherein the process comprises a seed-forming step polymerizing the mixed monomers of an acid monomer (i) having a carboxylic acid
20 group and a non-ionic hydrophilic monomer (ii) in the presence of a polymerization initiator; a core-forming step for preparing a core, which can be swollen with an alkali, by polymerizing the monomer mixture of an acid monomer (i) having a carboxylic acid group, a non-ionic
25 hydrophilic monomer (ii) and a cross-linking monomer (iii) to the seed latex; a step for forming the hydrophobic shell on the hydrophilic core; and an alkali-swelling step, characterized in that in the core/shell-forming steps an emulsion (I) consisting of up to 10 wt% of a
30 single or mixed acid monomer (i) having a carboxylic acid group, 85 to 100 wt% of a single or mixed non-ionic hydrophilic monomer (ii) and up to 5.0 wt% of a cross-linking monomer (iii) and an emulsion (II) consisting of 95 to 100 wt% of a single or mixed hydrophobic monomers (iv) and up
35 to 5 wt% of a cross-linking agent (iii) are used in the ratio of 1/1-1/10 [emulsion (I)/emulsion (II)], the total amount of the emulsion (I) and the emulsion (II) is two

times or more the weight of the core polymer, and the polymerization is carried out by continuously adding the emulsion (II) dropwise to the emulsion (I) and, at the same time, adding the emulsion (I) together with a water-soluble initiator to the core latex at the same rate as the addition of the emulsion (II) to the emulsion (I).

BEST MODE FOR CARRYING OUT THE INVENTION

10

The process for preparing the hollow particles of emulsion polymers according to the present invention comprises a seed-forming step for polymerizing the monomer mixture of an acid monomer having a carboxylic acid group and a non-ionic hydrophilic monomer in the presence of a polymerization initiator; a core-forming step for preparing a core, which can be swollen with an alkali, by adding the monomer mixture of an acid monomer having a carboxylic acid group, a non-ionic hydrophilic monomer and a cross-linking agent to the seed latex; a step for forming the hydrophobic shell on the hydrophilic core; and an alkali-swelling step.

Although the seed-forming step and the core-forming step can be practiced according to conventional emulsion polymerization methods, the formation of the hydrophobic shell on the hydrophilic core polymer is substantially difficult in a technical view.

30

That is, since the core polymer and the shell polymer have no miscibility due to great difference in their hydrophilicity, in general, the shell polymer cannot completely encapsulate the core polymer, and therefore, the abnormal core-shell structure, in which the core polymer is partially encapsulated by the shell polymer, or discrete particles of the core polymer and the shell

polymer, in which the core polymer is not encapsulated by the shell polymer, may be produced.

Accordingly, in the present invention, the shell is
5 formed by providing an emulsion (I) consisting of an acid monomer, a non-ionic hydrophilic monomer and a cross-linking agent, and an emulsion (II) consisting of a hydrophobic monomer and a cross-linking monomer and then, when
10 the shell-forming monomers are added to the core latex, slowly adding the emulsion (II) dropwise to the emulsion (I) and, at the same time, adding the emulsion (I) partly containing emulsion (II) to the core latex at the same rate as the addition of the emulsion (II) to the emulsion (I). According to this procedure, the production of
15 particles having abnormal structure due to the difference in hydrophilicity can be prevented, the mutual interdiffusion of polymer chains due to cross-linking can be minimized and further the viscosity at the polymerization loci can be optimally controlled to maximize the encapsulation
20 efficiency.

Then, the hollow particles of emulsion polymer according to the present invention can be prepared by swelling the final latex with alkaline solution. Since the re-
25 sulting hollow particles are completely encapsulated by the hard hydrophobic shell, the destruction of hollow during the drying the latex can be prevented and therefore the final latex can be used in the area of paints and paper coating industries.

30

Hereinafter, the present invention will be more specifically illustrated.

The preparation of the seed latex is the pre-step for
35 preparing the core latex. In this step, the monomer mixture of the acid monomer (i) and the non-ionic hydrophilic monomer (ii) is polymerized in the presence of an

emulsifier and a water-soluble polymerization initiator. As the acid monomer (i) for this purpose, any one selected from the group consisting of unsaturated carboxylic acids having a reactive double bond such as acrylic acid, methacrylic acid, crotonic acid, fumaric acid and itaconic acid
5 can be used alone or in combination with one or more other monomers selected therefrom. Such acid monomer (i) is used in an amount of up to 10 wt% based on the weight of the monomer mixture.

10

The non-ionic hydrophilic monomers (ii) which can be used in the present invention can include methyl acrylate, ethyl acrylate, butyl (meth)acrylate, methyl methacrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate,
15 ate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, acrylonitrile, vinyl acetate, vinyl pyridine, acrylamide, methacrylamide, N-methylol (meth)acrylamide, and the like. The non-ionic hydrophilic monomers should have a water-solubility of at least of 0.5%, more preferably at least
20 of 1%. In the present invention, any non-ionic hydrophilic monomer selected from the above mentioned monomers can be used alone or in combination with one or more other monomer selected therefrom.

25

A polymerization initiator to be used for the seed latex and carrying out the subsequent reaction steps can be suitably and optionally selected from conventional initiators for thermal and redox reaction. Specific
30 examples of the polymerization initiator which can be used in the present invention includes ammonium persulfate, potassium persulfate and sodium persulfate. Such polymerization initiator can also be used in the combination with a reducing agent such as sodium bisulfite or sodium
35 formaldehyde sulfoxylate. The reaction temperature is maintained preferably at 70 to 90°C when ammonium persulfate, potassium persulfate or sodium persulfate is used

alone as the initiator. Alternatively, when the initiator is used in the combination with a reducing agent selected from sodium bisulfite and sodium formaldehyde sulfoxylate, the reaction temperature can be controlled preferably in the range of 30 to 70°C.

As the emulsifier an anionic, non-ionic or cationic emulsifier which is conventionally used in the emulsion polymerization can be used either alone or as the mixture thereof. Specific preferred example of the emulsifier which can be used in the present invention include rhodinate salts such as potassium rhodinate, sodium rhodinate, etc.; aliphatic sodium or potassium salts such as potassium oleate, potassium laurate, sodium laurate, sodium stearate, potassium stearate, etc., and sulfuric acid ester salts of aliphatic alcohols such as sodium lauryl sulfate; an anionic emulsifier, for example, alkylaryl sulfonates such as sodium dodecylbenzenesulfonate, sodium dialkylsulfosuccinate, formalin condensate of naphthalene sulfonic acid, and the like; a non-ionic emulsifier, for example, alkyl esters, alkyl ethers, alkylphenyl ethers, etc., of polyethyleneglycol, and the like. Among those emulsifiers, sodium lauryl sulfate, sodium dodecylbenzenesulfonate, sodium dioctylsulfosuccinate, formalin condensate of naphthalene sulfonic acid, alkylphenyl ethers of polyethyleneglycol, etc. can be more preferably used. As a cationic emulsifier, quaternary ammonium salts can be preferably used. However, when the aqueous dispersion is cationic, the cationic emulsifier can be used alone or together with a non-ionic emulsifier. The emulsifier is preferably used in an amount of 0.1 to 10 wt% on the basis of the weight of monomers.

In the core-forming step the monomer mixture consisting of the acid monomer, the hydrophilic monomer and the cross-linking agent is used. For this purpose, the acid monomer which can be used is any one selected from the

acid monomer (i) as mentioned above, either alone or in combination with one or more other monomers selected therefrom, and is used preferably in an amount of 5 to 40 wt% on the basis of the weight of the monomer mixture.

5 As the hydrophilic monomer, one selected from the hydrophilic monomer (ii) mentioned hereinbefore can be used either alone or in combination with one or more other monomer selected therefrom, preferably in an amount of 60 to 95 wt% on the basis of the weight of the monomer mixture.

10 In this step, the cross-linking agent (iii) which can be used is selected from divinyl benzene, ethylenglycol di(meth)acrylate, trimethylol propane trimethacrylate, hexamethyleneglycol diacrylate, allyl methacrylate and the like. The cross-linking agent can be preferably used in

15 an amount of 0.1 to 5.0 wt% on the basis of the weight of the monomer mixture.

The monomer mixture consisting of such acid monomer, hydrophilic monomer and cross-linking agent is slowly

20 added to the seed latex together with the emulsifier and the water-soluble initiator to obtain the monodisperse core latex which can be swollen with an alkaline solution afterwards.

25 Preferably, the monomer composition which can be used in the emulsion (I) for the shell-forming step consists of up to 10 wt% of the acid monomer which is one, or the mixture of two or more, selected from the acid monomer (i) mentioned hereinbefore; 85 to 100 wt% of the hydrophilic

30 monomer which is one, or the mixture of two or more, selected from the hydrophilic monomer (ii) mentioned hereinbefore; and up to 5.0 wt% of the cross-linking agent selected from the cross-linking agent (iii) mentioned hereinbefore.

35

The monomer mixture which is used in the emulsion (II) consists of the hydrophobic monomer and the cross-linking

agent. As hydrophobic monomers (iv) for this purpose, one, or the mixture of two or more, selected from aromatic vinyl monomers such as styrene, methyl styrene, ethyl styrene, vinyl toluene, chlorostyrene, vinyl naphthalene, etc., can be used in an amount of 95 to 100 wt% on the basis of the weight of the monomer mixture. As the cross-linking agent for this purpose, any of the cross-linking agent (iii) is used preferably in an amount of up to 5.0 wt% on the basis of the weight of the monomer mixture.

The ratio of the emulsion (I) and the emulsion (II) is preferably in the range of 1/1 to 1/10 [emulsion (I)/emulsion (II)]. The total mixture of monomers for forming the shell polymer is used preferably in an amount of two times or more an amount of the core polymer on the basis of weight.

The emulsion (I) and the emulsion (II) thus prepared are added to the core latex as described below. Specifically, the emulsion (II) is slowly added to the emulsion (I) and, at the same time, the emulsion (I) partly containing emulsion (II) is added to the core latex together with the water-soluble initiator, at the same rate as the addition of the emulsion (II) to the emulsion (I), to obtain the monodisperse emulsion polymer having a perfect core/shell structure.

The resulting latex having the core/shell structure is adjusted to pH 6 to 12 with aqueous ammonium or a volatile base such as triethylamine, diethanolamine, triethanolamine, etc, or an organic base, swollen for 30 minutes or more at temperature in the range of 60 to 100°C and then dried to obtain the hollow particles having an outer diameter of 0.1 to 5 micron, an inner diameter of 0.05 to 4 micron and the inner diameter/outer diameter ratio of 0.1 to 0.9 and having a uniform shell thickness.

The particle and hollow size of the hollow latex particles obtained according to the present invention are observed by means of a transmission electron microscope (TEM).

5

The present invention is more specifically explained by the following examples. However, it should be understood that the present invention is not limited to those examples in any manner.

10

EXAMPLE 1

(1) Production of the seed latex

15

To a 2L four-necked flask equipped with a stirrer, a thermometer, a refluxing condenser and a nitrogen inlet 300g of deionized water was added and then the flask was purged with nitrogen gas while maintaining the temperature of 75°C. The emulsion consisting of 15g of deionized water, 15g of methyl methacrylate, 0.3g of methacrylic acid and 0.3g of an aqueous solution of sodium dodecylbenzene sulfonate (solid content : 12 wt%), which was prepared in advance, was introduced into the flask and then an aqueous solution of 0.12g of potassium persulfate dissolved in 15g of deionized water was added thereto. After the addition is completed, the reaction mixture was polymerized for 2 hours to obtain the monodisperse emulsion polymer having an average particle diameter of 0.08 micron.

25
30

(2) Production of the core latex

To the flask containing the seed latex was added 600g of deionized water. Thereafter, the emulsion of 168g of methyl methacrylate, 72g of methacrylic acid, 1.2g of ethyleneglycol dimethacrylate and 7.5g of sodium dodecyl-

35

benzene sulfonate (solid content : 12 wt%) in 144g of deionized water and the aqueous solution of 0.96g of potassium persulfate dissolved in 120g of deionized water were slowly added dropwise thereto at the same rate over 4
5 hours at 75°C. The reaction mixture was polymerized for 2 hours to obtain the monodisperse emulsion polymer having an average particle diameter of 0.20 micron.

(3) Production of the core/shell latex

10

171g of the core latex (solid content : 17.5 wt%), as prepared above, and 375g of deionized water were added to a 2L four-necked flask and then heated to 75°C while purging the flask with nitrogen.

15

Separately, two kinds of the emulsion were prepared. One is the emulsion (I) prepared from 90g of methyl methacrylate, 2.7g of sodium dodecylbenzene sulfonate (solid content : 12 wt%) and 54g of deionized water and the other
20 is the emulsion (II) prepared from 180g of styrene, 1.5g of divinyl benzene, 5.4g of sodium dodecylbenzene sulfonate (solid content : 12 wt%) and 108g of deionized water.

The prepared emulsion (II) was added to, and mixed
25 with, the emulsion (I) at the constant rate and, at the same time, the emulsion (I) of which the composition is continuously varied according to the addition of the emulsion (II) was continuously added dropwise to the flask at the same rate as the addition of the emulsion (II) to
30 the emulsion (I), over about 5 hours. Simultaneously, the aqueous solution of 1.08g of potassium persulfate dissolved in 135g of deionized water in another flask was added to the flask over the same period as the addition of the emulsion (I). Thereafter, the reaction mixture was
35 allowed to polymerize and then aged for 2 hours to obtain the core/shell latex. The obtained core/shell latex comprises the monodisperse emulsion polymer of which the

solid content is 25.6 wt% and the average particle diameter is 0.45 micron.

(4) Alkali swelling

5

The core/shell latex was continuously heated to 90°C and then adjusted to pH 10.8 by adding aqueous ammonium (solid content : 28 wt%) and swollen for 2 hours. The obtained latex was identified as being the monodisperse, spherical hollow particle having a hollow size of 0.3 micron and an average latex particle diameter of 0.5 micron.

15 EXAMPLE 2-7

The hollow particles were prepared by a multi-step emulsion polymerization according to the same procedures as Example 1 except that the emulsion (I) and the emulsion (II) having the compositions as described in Table 1 are used in preparation of the core/shell particle. The obtained results are described in Table 1.

25 EXAMPLE 8

The hollow particle was prepared by a multi-step emulsion polymerization according to the same procedures as Example 1 except that the emulsion (I) and the emulsion (II) having the compositions as described in Table 1 are used in preparation of the core/shell particle and the aqueous initiator solution comprises 0.9g of potassium persulfate and 112g of deionized water. The obtained results are described in Table 1.

35

EXAMPLE 9

The hollow particle was prepared by a multi-step emulsion polymerization according to the same procedures as Example 1 except that the emulsion (I) and the emulsion (II) having the compositions as described in Table 1 are used in perparation of the core/shell particle and the aqueous initiator solution comprises 1.8g of potassium persulfate and 225g of deionized water. The obtained results are described in Table 1.

10

EXAMPLE 10

The hollow particle was prepared by a multi-step emulsion polymerization according to the same procedures as Example 1 except that the emulsion (I) and the emulsion (II) having the compositions as described in Table 1 are used in perparation of the core/shell particle and the aqueous initiator solution comprises 0.72g of potassium persulfate and 90g of deionized water. The obtained results are described in Table 1.

25

30

35

Table 1. Composition of the emulsions used in preparing the core/shell latex and the characteristics of the hollow particle prepared therefrom

		EXAMPLES									
		1	2	3	4	5	6	7	8	9	10
Emulsion (I)	MMA	90	90	90	90	90	90	90	45	90	60
	MAA							14			
	EGDMA					0.5	1.5				
	SDBS a.s.	2.7	2.7	2.7	2.7	2.7	2.7	2.7	1.35	2.7	1.8
	WM	54	54	54	54	54	54	54	27	54	36
Emulsion (II)	ST	180	180	180	180	180	180	180	180	360	120
	DVB	1.5	3.0	4.5	6.0	1.0		1.5	1.5	2.5	2.0
	SDBS a.s.	5.4	5.4	5.4	5.4	5.4	5.4	5.4	5.4	10.8	3.6
	WM	108	108	108	108	108	108	108	108	216	72
Outer diameter D (μm)		0.5	0.55	0.5	0.5	0.5	0.524	0.5	0.525	0.65	0.4
Inner diameter d (μm)		0.3	0.375	0.3	0.325	0.275	0.275	0.3	0.15	0.45	0.26
d/D ratio		0.60	0.68	0.60	0.65	0.55	0.45	0.60	0.35	0.69	0.65

Note : 1) outer diameter = particle size

2) inner diameter = hollow size

3) MMA = methyl methacrylate

4) MAA = methacrylic acid

5) EGDMA = ethyleneglycole dimethacrylate

6) SDBS a.s. = 12 wt% aqueous solution of sodium
dodecylbenzene sulfonate

7) ST = styrene

8) DVB = divinyl benzene

10

15

20

25

30

35

WHAT IS CLAIMED IS :

1. A process for preparing hollow particles of the emul-
sion polymer having a single hollow in the center and
a uniform thickness of hollow and shell, wherein the
process comprises a seed-forming step for polymerizing
the mixed monomers of an acid monomer (i) having a
carboxylic acid group and a non-ionic hydrophilic
monomer (ii) in the presence of a polymerization
initiator; a core-forming step for preparing a core,
which can be swollen with an alkali, by polymerizing
the monomer mixture of an acid monomer (i) having a
carboxylic acid group, a non-ionic hydrophilic monomer
(ii) and a cross-linking agent (iii) to the seed
latex; a step for forming the hydrophobic shell on the
hydrophilic core; and an alkali-swelling step,

characterized in that in the core/shell-forming steps
an emulsion (I) consisting of up to 10 wt% of a single
or mixed acid monomer (i) having a carboxylic acid
group, 85 to 100 wt% of a single or mixed non-ionic
hydrophilic monomer (ii) and up to 5.0 wt% of a cross-
linking monomer (iii) and an emulsion (II) consisting
of 95 to 100 wt% of a single or mixed hydrophobic
monomer (iv) and up to 5 wt% of a cross-linking agent
(iii) are used in the ratio of 1/1-1/10 [emulsion
(I)/emulsion (II)], the total amount of the emulsion
(I) and the emulsion (II) is two times or more the
weight of the core polymer, and the polymerization is
carried out by continuously adding the emulsion (II)
dropwise to the emulsion (I) and, at the same time,
adding the emulsion (I) partly containing emulsion
(II) together with a water-soluble initiator to the
core latex at the same rate as the addition of the
emulsion (II) to the emulsion (I).

2. The process for preparing hollow particles of the emulsion polymer according to claim 1, characterized in that the hollow particle as prepared has an outer diameter of particle of 0.1 to 5 micron, a diameter of hollow (inner diameter) of 0.05 to 4 micron, and the inner diameter/outer diameter ratio of 0.1 to 0.9.
3. The process for preparing hollow particles of the emulsion polymer according to claim 1, characterized in that the seed-forming step is carried out by polymerizing the monomer mixture consisting of the acid monomer (i) having a reactive double bond and the non-ionic hydrophilic monomer (ii), wherein the acid monomer (i) is present in an amount of up to 10 wt%, in the presence of an emulsifier and a water-soluble polymerization initiator.
4. The process for preparing hollow particles of the emulsion polymer according to claim 1, characterized in that the step for preparing the core emulsion polymer is carried out by slowly adding dropwise the monomer mixture consisting of the acid monomer (i), the hydrophilic monomer (ii) and the cross-linking agent (iii), wherein the acid monomer (i) is a single component or in the form of a mixture and is present in an amount of 5 to 40 wt% on the basis of the weight of the monomer mixture, the hydrophilic monomer is present in an amount of 60 to 95 wt% on the basis of the weight of the monomer mixture and the cross-linking agent is present in an amount of 0.1 to 5.0 wt% on the basis of the weight of the monomer mixture, together with an emulsifier and a water-soluble polymerization initiator to the seed latex to obtain the monodisperse core latex which can be swollen by an alkali afterwards.
5. The process for preparing hollow particles of the

- emulsion polymer according to claim 1, characterized in that the alkali-swelling step is carried out by adjusting the pH value of the latex having a core/shell structure with a volatile base or an organic base in the range of 6 to 12 and then swelling the latex for 30 minutes or more at temperature of 60 to 100°C.
- 5
6. The process for preparing hollow particles of the emulsion polymer according to claim 1, characterized in that the acid monomer (i) is selected from acrylic acid, methacrylic acid, crotonic acid, fumaric acid and itaconic acid.
- 10
7. The process for preparing hollow particles of the emulsion polymer according to claim 1, characterized in that the non-ionic hydrophilic monomer (ii) has the water solubility of 0.5 wt% or more.
- 15
8. The process for preparing hollow particles of the emulsion polymer according to claim 1 or 7, characterized in that the non-ionic hydrophilic monomer (ii) is one or the mixture of two or more selected from the group consisting of methyl acrylate, ethyl acrylate, butyl (meth)acrylate, methyl methacrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, acrylonitrile, vinyl acetate, vinyl pyridine, acrylamide, methacrylamide and N-methylol (meth)acrylamide.
- 20
- 25
- 30
9. The process for preparing hollow particles of the emulsion polymer according to claim 1, characterized in that the cross-linking agent (iii) is selected from the group consisting of divinyl benzene, ethyleneglycol di(meth)acrylate, trimethylol propane trimethacrylate, hexamethyleneglycol diacrylate and allyl metha-
- 35

crylate.

10. The process for preparing hollow particles of the emulsion polymer according to claim 1, characterized in that the hydrophobic monomer (iv) is selected from the group consisting of styrene, methyl styrene, ethyl styrene, vinyl toluene, chlorostyrene and vinyl naphthanene.
11. The process for preparing hollow particles of the emulsion polymer according to claim 1, characterized in that the emulsifier is used in an amount of 0.1 to 10 wt% on the basis of the weight of the total monomers used in each step.
12. The process for preparing hollow particles of the emulsion polymer according to claim 1, characterized in that the water-soluble polymerization initiator is ammonium persulfate, potassium persulfate or sodium persulfate alone or in a combination with a reducing agent selected from sodium bisulfate and sodium formaldehyde sulfoxylate.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 94/00141

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁶: C 08 F 285/00, 2/22; C 08 J 9/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁶: C 08 F 2/00, 257/00, 265/00, 285/00; C 08 J 9/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A, 0 022 633 (ROHM AND HAAS COMPANY) 21 January 1981 (21.01.81), claims 1-3,5; examples. & US, A, 4 427 836 (cited in the application).	1-12
A	US, A, 5 036 109 (CHIP et al.) 30 July 1991 (30.07.91), claims 1,2,5-7,10-12; examples.	1-12
A	US, A, 4 920 160 (CHIP et al.) 24 April 1990 (24.04.90), claims 1,2,5-8,12-14; examples.	1-12
A	EP, A, 0 342 944 (ROHM AND HAAS COMPANY) 23 November 1989 (23.11.89), claims 1,9,10; examples.	1-12
A	EP, A, 0 188 325 (ROHM AND HAAS COMPANY) 23 July 1986 (23.07.86), claims 1,8; examples.	1,5,6,11,12

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

12 January 1995 (12.01.95)

Date of mailing of the international search report

31 January 1995 (31.01.95)

Name and mailing address of the ISA/AT
AUSTRIAN PATENT OFFICE
Kohlmarkt 8-10
A-1014 Vienna
Facsimile No. 1/53424/535

Authorized officer

Pusterer e.h.

Telephone No.

1/533058/742

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 94/00141

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0203 724 (ROHM AND HAAS COMPANY) 03 December 1986 (03.12.86), claim 1. -----	1

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR 94/00141

Im Recherchenbericht angeführtes Patentedokument Patent document cited in search report Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A2	22633	21-01-81	AU A1 59680/80	08-01-81
			AU B2 539537	04-10-84
			AU B2 561300	07-05-87
			BR A 8004010	21-01-81
			CA A1 1180474	01-01-85
			DE C0 3070204	28-03-85
			DE C0 3072033	29-10-87
			EP A3 22633	15-07-81
			EP A2 73529	09-03-83
			EP A3 73529	11-05-83
			EP B1 22633	20-02-85
			EP B1 73529	23-09-87
			JP A2 56032513	02-04-81
			JP A2 63213509	06-09-88
			JP B4 3007688	04-02-91
			JP B4 3009124	07-02-91
			MX A 155488	18-03-88
			NZ A 194157	30-09-83
			SG A 495/85	13-06-86
			US A 4427836	24-01-84
			US A 4468498	28-08-84
			MY A 163/86	31-12-86
			AU A1 30524/84	29-11-84
US A	5036109	30-07-91	AU A1 25754/88	29-06-89
			AU B2 600182	02-08-90
			CA A1 1299451	28-04-92
			DE C0 3851132	22-09-94
			DE T2 3851132	01-12-94
			DK A0 6996/88	16-12-88
			DK A 6996/88	19-06-89
			EP A2 321096	21-06-89
			EP A3 321096	09-05-90
			EP B1 321096	17-08-94
			ES T3 2058311	01-11-94
			FI A0 885842	16-12-88
			FI A 885842	18-06-89
			FR A1 2624869	23-06-89
			FR B1 2624869	30-10-92
			GB A0 8729399	03-02-88
			GB A0 8826724	21-12-88
			GB A1 2213826	23-08-89
			GB B2 2213826	15-05-91
			JP A2 1201313	14-08-89
US A	4920160	24-04-90	US A 4985469	15-01-91
			ZA A 8808850	30-08-89
			AU A1 18799/88	02-02-89
			AU B2 603464	15-11-90
			BR A 8803725	14-02-89
			DE C0 3884095	21-10-93
			DE T2 3884095	10-03-94
			DK A0 4244/88	29-07-88
			DK A 4244/88	31-01-89
			EP A2 301880	01-02-89
			EP A3 301880	16-05-90
			EP B1 301880	15-09-93
			ES T3 2045129	16-01-94
			FI A0 883583	29-07-88
			FI A 883583	31-01-89
			FR A1 2618790	03-02-89
			FR B1 2618790	27-09-91
			GB A0 8718036	03-09-87
			GB A0 8815871	10-08-88
			GB A1 2207680	08-02-89
			GB B2 2207680	02-01-92
			JP A2 1048805	23-02-89
			US A 4863973	05-09-89
			ZA A 8805493	26-04-89

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR 94/00141

EP A2 342944 23-11-89

AT E	91491	15-07-93
AU A1	34868/89	23-11-89
AU B2	616756	07-11-91
BR A	8902330	09-01-90
CA A1	1303438	16-06-92
CN A	1040039	28-02-90
DE C0	68907521	19-08-93
DE T2	68907521	02-12-93
DK A0	2449/89	19-05-89
DK A	2449/89	21-11-89
EP A3	342944	09-05-90
EP B1	342944	14-07-93
ES T3	2058519	01-11-94
FI A0	892446	19-05-89
FI A	892446	21-11-89
FI B	93017	31-10-94
HK A	1230/93	19-11-93
IL A0	90355	15-12-89
IL A1	90355	01-12-92
JP A2	2064103	05-03-90
MX B	164012	09-07-92
NO A0	891978	18-05-89
NO A	891978	21-11-89
NO B	173391	30-08-93
NO C	173391	08-12-93
NZ A	229145	23-12-91
US A	4880842	14-11-89
US A	4970241	13-11-90

EP A2 188325 23-07-86

AT E	78497	15-08-92
AU A1	52172/86	17-07-86
AU B2	594318	08-03-90
BR A	8600076	23-09-86
CA A1	1271582	10-07-90
DE C0	3686057	27-08-92
DE T2	3686057	18-03-93
EP A3	188325	09-03-88
EP B1	188325	22-07-92
JP A2	61185505	19-08-86
JP B4	1037401	07-08-89
KR B1	9209613	22-10-92
MX B	163420	12-05-92
NZ A	214793	24-02-89
PH A	20889	27-05-87
US A	4594363	10-06-86

EP A2 203724 03-12-86

AT E	68190	15-10-91
AU A1	56516/86	06-11-86
AU B2	585974	29-06-89
BR A	8601895	30-12-86
CA A1	1285092	18-06-91
CN A	86103126	29-10-86
CN A	1041116	11-04-90
CN B	1017339	08-07-92
DE C0	3681825	14-11-91
EP A3	203724	11-01-89
EP B1	203724	09-10-91
IL A0	78606	31-08-86
IL A1	78606	29-04-90
JP A2	61293213	24-12-86
KR B1	9311757	20-12-93
NZ A	215946	24-02-89
PH A	22987	24-02-89
SG A	76/92	20-03-92
US A	4677003	30-06-87
US A	5225279	06-07-93
US A	4985064	15-01-91