

DESCRIPTION

METHOD OF PREVENTING COLORATION OF WATER-ABSORBING RESIN

5

TECHNICAL FIELD

The present invention relates to a method for preventing discoloration of a water-absorbent resin. More specifically, the present invention relates to a method for preventing discoloration of a water-absorbent resin which can be suitably used as an absorbent for an absorbent article for hygienic materials such as paper diapers and sanitary napkins.

BACKGROUND ART

Water-absorbent resins have been widely used as absorbents for absorbent articles for hygienic materials such as paper diapers and sanitary napkins, utilizing the feature that a water-based liquid, for instance, a body fluid such as human urine, blood or sweat is quickly absorbed in a large amount, so that the liquid once absorbed is not released even under a load.

Conventional water-absorbent resins have some problems that the water-absorbent resins are likely to discolor into yellow, brown or the like by an external factor such as heat or humidity when the resins are allowed to stand. Particularly, in the field of the above-mentioned hygienic materials, when the water-absorbent resin discolors in the absorbent article such as paper diapers and sanitary napkins, the commercial value as an absorbent article is drastically lowered. Therefore, even when the water-absorbent resins usable for absorbent

articles are allowed to stand under severe high-temperature, high-humidity environment such as storehouse in the summer time, there has been desired not to discolor the water-absorbent resin.

As water-absorbent resins having an effect of preventing discoloration, there have been known, for instance, a high water-absorbent polymer composition in which an organophosphoric acid compound or a salt thereof is added to a high water-absorbent polymer (Japanese Patent Laid-Open No. Hei 5-86251); an absorbent composition comprising an acidic water-swellaable crosslinked polymer, a basic water-swellaable crosslinked polymer, a discoloration preventive and/or an antioxidant and/or a boron-containing compound (Japanese Patent Laid-Open No. 2000-230129); an absorbent composition comprising a water-absorbent resin, and an organic carboxylic acid and/or a salt thereof (Japanese Patent Laid-Open No. 2000-327926) and the like. However, these compositions do not exhibit a sufficiently satisfactory effect when allowed to stand under severe high-temperature, high-humidity environment for a long period of time.

An object of the present invention is to provide a method for preventing discoloration of a water-absorbent resin capable of preventing discoloration even when allowed to stand under high-temperature, high-humidity conditions for a long period of time.

These and other objects of the present invention will be apparent from the following description.

DISCLOSURE OF INVENTION

Specifically, the present invention relates to:

[1] a method for preventing discoloration of a water-absorbent resin made from an unsaturated carboxylic acid as an essential monomer, characterized in that the method comprises adding an aminocarboxylic acid-based metal chelating agent to a system in at least any one of the stages during a preparation process of the water-absorbent resin or to the water-absorbent resin obtained after the preparation; and

[2] a method of use of an aminocarboxylic acid-based metal chelating agent for preventing discoloration of an obtainable water-absorbent resin made from an unsaturated carboxylic acid as an essential monomer, characterized in that the method comprises adding an aminocarboxylic acid-based metal chelating agent to a system in at least any one of the stages during a preparation process of the water-absorbent resin or to the water-absorbent resin obtained after the preparation.

15 BEST MODE FOR CARRYING OUT THE INVENTION

The method for preventing discoloration of a water-absorbent resin made from an unsaturated carboxylic acid as an essential monomer of the present invention has a feature that the discoloration of the water-absorbent resin is suppressed even under high-temperature, high-humidity conditions by adding an aminocarboxylic acid-based metal chelating agent to a system in at least any one of the stages during a preparation process of the water-absorbent resin or to the water-absorbent resin obtained after the preparation.

The aminocarboxylic acid-based metal chelating agent usable in the present invention includes, for instance, iminodiacetic acid, hydroxyethyliminodiacetic acid, nitrilotriacetic acid, nitrilotripropionic acid,

ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, trans-1,2-diaminocyclohexanetetraacetic acid, N,N-bis(2-hydroxyethyl)glycine, diaminopropanoltetraacetic acid, ethylenediaminedipropionic acid, hydroxyethylenediaminetriacetic acid, glycol ether diaminetetraacetic acid, diaminopropanetetraacetic acid, N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N-diacetic acid, 1,6-hexamethylenediamine-N,N,N',N'-tetraacetic acid, and salts thereof, and the like. Among them, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, trans-1,2-diaminocyclohexanetetraacetic acid, and salts thereof are preferably used, from the viewpoint of having a greater effect of preventing discoloration.

In order to add an aminocarboxylic acid-based metal chelating agent to a system in any one of stages during the preparation of a water-absorbent resin, or to a water-absorbent resin obtained after the preparation, there are included (i) a method of adding the above-mentioned aminocarboxylic acid-based chelating agent to an aqueous solution of the monomer comprising an unsaturated carboxylic acid before the polymerization; (ii) a method of adding the above-mentioned aminocarboxylic acid-based metal chelating agent to a water-containing gelated product after the polymerization; (iii) a method of adding the above-mentioned aminocarboxylic acid-based metal chelating agent to a water-absorbent resin during drying; (iv) a method of powder-blending the above-mentioned aminocarboxylic acid-based metal chelating agent with a water-absorbent resin after drying; (v) a method of adding the above-mentioned aminocarboxylic acid-based metal chelating agent to a water-absorbent resin dispersed in an organic solvent, and heating and removing the solvent from the

mixture; and the like.

In the present invention, it is preferable that the aminocarboxylic acid-based metal chelating agent is dispersed in the water-absorbent resin by a convenient method, or dispersed homogeneously on the surface of the water-absorbent resin as much as possible, from the viewpoints of maintaining productivity and highly giving an effect of preventing discoloration. In order to obtain a water-absorbent resin in which the aminocarboxylic acid-based metal chelating agent is homogeneously dispersed, especially (ii) a method of adding the above-mentioned aminocarboxylic acid-based metal chelating agent to a water-containing gelated product after the polymerization; (iii) a method of adding the above-mentioned aminocarboxylic acid-based metal chelating agent to a water-absorbent resin during drying, and (iv) a method of powder-blending the above-mentioned aminocarboxylic acid-based metal chelating agent with a water-absorbent resin after drying are preferable.

It is preferable that the embodiment of adding an aminocarboxylic acid-based metal chelating agent is, but not particularly limited to, an embodiment of adding a solution prepared by dissolving a liquid or powder aminocarboxylic acid-based metal chelating agent in a hydrophilic solvent such as water, or an embodiment of adding a fine powder of an aminocarboxylic acid-based metal chelating agent in a powdery state, in order that the aminocarboxylic acid-based metal chelating agent is homogeneously dispersed in the water-absorbent resin. Here, the particle size of the fine powder of the aminocarboxylic acid-based metal chelating agent is not particularly limited. It is preferable that 80% by weight of the entire particles have particle sizes of 100 μm or less, from the viewpoint that a satisfactory effect of preventing discoloration is obtained when

the amount of coarse grain portions is smaller.

The amount of the above-mentioned aminocarboxylic acid-based metal chelating agent used is preferably from 0.001 to 6 parts by weight, more preferably from 0.006 to 3 parts by weight, most preferably from 0.01 to 2 parts by weight, based on 100 parts by weight of the unsaturated carboxylic acid, which is an essential monomer for preparing the water-absorbent resin, from the viewpoints of obtaining a satisfactory effect for preventing discoloration, and obtaining the effect corresponding to the amount used, thereby being economically advantageous.

Therefore, according to the present invention, there is provided a method of use of an aminocarboxylic acid-based metal chelating agent for preventing discoloration of an obtainable water-absorbent resin made from an unsaturated carboxylic acid as an essential monomer, characterized in that said method comprises adding an aminocarboxylic acid-based metal chelating agent to a system in at least any one of the stages during a preparation process of the water-absorbent resin or to the water-absorbent resin obtained after the preparation.

The water-absorbent resin made from an unsaturated carboxylic acid as an essential monomer prepared in the present invention includes crosslinked products of acrylate polymers, crosslinked products of hydrolysates of starch-acrylate graft copolymers, crosslinked products of vinyl alcohol-acrylate copolymers, crosslinked products of maleic anhydride-grafted polyvinyl alcohol, crosslinked isobutylene-maleic anhydride copolymers, partially neutralized crosslinked products of polyacrylic acid, saponified products of vinyl acetate-acrylic ester copolymers, and the like. Among them, preferable are the

crosslinked products of acrylate polymers which are capable of absorbing a large amount of water and retaining absorbed water in the molecule even when a certain load is applied.

5 The unsaturated carboxylic acid includes, for instance, acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid and the like. These can be used alone or in admixture of two or more kinds. The unsaturated carboxylic acid may be partially neutralized with an alkali metal or the like, and especially acrylic acid, methacrylic acid, and an alkali metal salt thereof, such as sodium or potassium are preferably used.

10 The above-mentioned unsaturated carboxylic acid may be copolymerized with other monomers as occasion demands. Other monomers include, for instance, nonionic, hydrophilic group-containing monomers such as (meth)acrylamide [“(meth)acryl-” means “acryl-” and “methacryl-;” hereinafter referred to the same], N-substituted (meth)acrylamide, 2-hydroxyethyl
15 (meth)acrylate, 2-hydroxypropyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, and polyethylene glycol (meth)acrylate; unsaturated amino group-containing monomers such as N,N-dimethylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylamide; sulfonic acid-based monomers such as vinylsulfonic acid,
20 styrenesulfonic acid, 2-(meth)acrylamide-2-methylpropanesulfonic acid, 2-(meth)acryloylethanesulfonic acid and salts thereof; and the like.

As the polymerization method for the above-mentioned water-absorbent resin, representative preparation processes such as reversed phase suspension polymerization method and aqueous solution polymerization method are usable
25 without being limited thereto. The reversed phase suspension polymerization

method will be exemplified hereinbelow.

In the reversed phase suspension polymerization method, the polymerization is carried out by using, for instance, a polymerization initiator in a state that an aqueous solution of the monomers is dispersed in an organic solvent in the presence of at least one of the surfactants and the polymeric protective colloids.

It is preferable that the concentration of the monomers in the above-mentioned aqueous solution of the monomers is from 25% by weight to a saturated concentration. In addition, the above-mentioned aqueous solution of the monomers may be added at once or may be added in divided portions in the polymerization reaction.

The above-mentioned organic solvent includes aliphatic hydrocarbon solvents such as n-pentane, n-hexane, n-heptane, and ligroin; alicyclic hydrocarbon solvents such as cyclopentane, methylcyclopentane, cyclohexane, and methylcyclohexane; aromatic hydrocarbon solvents such as benzene, toluene and xylene; and the like. Among them, n-heptane and cyclohexane are preferably used.

The amount of the organic solvent used is preferably from 50 to 600 parts by weight, more preferably from 100 to 550 parts by weight, based on 100 parts by weight of the total amount of the monomers, from the viewpoints of removing heat of polymerization, thereby making it easy to control the polymerization temperature.

The above-mentioned surfactant includes nonionic surfactants such as sorbitan fatty acid esters, monoglycerol fatty acid esters, polyglycerol fatty acid esters, sucrose fatty acid esters, polyoxyethylene hydrogenated castor oil,

polyoxyethylene laurate hydrogenated castor oil, polyoxyethylene triisostearate hydrogenated castor oil, polyoxyethylene alkylphenyl ethers, polyoxyethylene lauryl ethers, and polyoxyethylene hexyldecyl ethers.

5 The above-mentioned polymeric protective colloid includes ethyl cellulose, hydroxyethyl cellulose, polyethylene oxide, polyethylene modified with maleic anhydride, polybutadiene modified with maleic anhydride, ethylene-propylene-diene terpolymers modified with maleic anhydride, and the like.

These nonionic surfactants and polymeric protective colloids may be used in admixture of two or more kinds.

10 The nonionic surfactant and/or the polymeric protective colloids mentioned above can be used together with an anionic surfactant. The anionic surfactant includes salts of fatty acids, alkylbenzenesulfonates, alkyl methyl taurates, polyoxyethylene alkylphenyl ether sulfate esters, polyoxyethylene alkyl ether sulfonates and the like.

15 The amount of the surfactant and/or the polymeric protective colloid used is preferably from 0.1 to 5 parts by weight, more preferably from 0.2 to 3 parts by weight, based on 100 parts by weight of the total amount of the monomers, from the viewpoints of having satisfactory dispersion of the aqueous solution of monomers, obtaining an effect corresponding to the amount used, and being
20 economically advantageous.

The above-mentioned water-absorbent resin can be prepared in a self-crosslinking reaction without using a crosslinking agent. Also, the resin can be crosslinked using an internal crosslinking agent having two or more polymerizable unsaturated groups or two or more reactive groups. The internal
25 crosslinking agent includes a compound having two or more unsaturated

ethylenic groups in one molecule, such as N,N'-methylenebis(meth)acrylamide, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolpropane di(meth)allyl ether, and triallylamine; 5 polyglycidyl ethers, such as (poly)ethylene glycol diglycidyl ether and glycerol triglycidyl ether; halogenated epoxy compounds, such as epichlorohydrin and epibromohydrin; and the like. One or more of these can be used upon considering the reactivity and water solubility in the polymerization system. It is preferable that the compound having two or more glycidyl groups in one 10 molecule is used as the internal crosslinking agent.

The amount of the internal crosslinking agent used is preferably from 0.001 to 3 parts by weight, more preferably from 0.003 to 1 part by weight, even more preferably from 0.005 to 0.5 parts by weight, based on 100 parts by weight of the total amount of the above-mentioned monomers, from the viewpoints of 15 suppressing the water-soluble nature of the resulting water-absorbent resin by an appropriate crosslinking, and showing a satisfactory water absorbency.

The polymerization initiator includes radical polymerization initiators such as potassium persulfate, sodium persulfate, ammonium persulfate, benzoyl peroxide, hydrogen peroxide, 1,1'-azobis(cyclohexane-1-carbonitrile), 20 2,2'-azobis(2-methyl-butyronitrile), 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-amidinopropane)dihydrochloride, 2-cyano-2-propylazofornamide, dimethyl 2,2'-azobis(2-methylpropionate). The radical polymerization initiator as mentioned above may be used together with a sulfite or the like as a redox-system polymerization initiator.

25 It is desired that the amount of the polymerization initiator used is from

0.005 to 1.0 mol per 100 mol of the total amount of the above-mentioned monomers, from the viewpoints of shortening the time for the polymerization reaction, preventing an unreasonable polymerization reaction, and facilitating the control of the polymerization reaction.

5 The surfactant and/or the polymeric protective colloid mentioned above is dissolved in an organic solvent, and the mixture of the above-mentioned aqueous solution of the monomers, the polymerization initiator and the like are added to the above-mentioned organic solution. The mixture is heated while stirring, and subjected to reversed phase suspension polymerization in a water-in-oil system.

10 The reaction temperature of the above-mentioned polymerization reaction differs depending upon the kinds of the polymerization initiator and the monomers used, or the concentration of the aqueous solution of the monomers. The reaction temperature is preferably from 20° to 110°C, more preferably from 40° to 80°C, from the viewpoints of rapidly progressing the polymerization, shortening the
15 polymerization time, being economically favorable, making the removal of the heat of polymerization easier, and smoothly carrying out the reaction. The reaction time is usually from 0.5 to 4 hours.

 The resulting water-absorbent resin may be subjected to surface-crosslinking by treating the water-absorbent resin with a crosslinking agent
20 having two or more functional groups having reactivity with carboxyl groups. The surface-crosslinking agent includes, for instance, those capable of reacting with carboxyl groups in the water-absorbent resin, for instance, epoxy compounds such as (poly)ethylene glycol diglycidyl ether, (poly)propylene glycol diglycidyl ether, (poly)glycerol polyglycidyl ethers, and glycidol;
25 halogenated epoxy compounds such as epichlorohydrin, epibromohydrin,

α-methylepichlorohydrin; polyhydric alcohol compounds such as (poly)ethylene glycol, (poly)propylene glycol, (poly)glycerol, diols, pentanediols, hexanediols, trimethylolpropane, diethanolamine, and triethanolamine; and the like. Among them, the epoxy compound is more preferably used. These surface-crosslinking agents can be used alone or in combination of two or more kinds.

The amount of the surface-crosslinking agent used is preferably from 0.01 to 5 parts by weight, more preferably from 0.02 to 4 parts by weight, even more preferably from 0.03 to 3 parts by weight, based on 100 parts by weight of the total amount of the above-mentioned monomer, from the viewpoints of obtaining satisfactory gel strength and water absorbency during water absorption of the water-absorbent resin.

The method of adding the above-mentioned surface-crosslinking agent is not particularly limited. The method includes, for instance, a method comprising adding the surface-crosslinking agent to a water-absorbent resin dispersed in an organic solvent; a method comprising spraying the surface-crosslinking agent to a water-absorbent resin with a spray or the like while stirring; and the like. The timing of the addition for the surface-crosslinking agent includes the stage of the water-containing gelated product obtained after the polymerization; the stage of the water-containing particles during drying; the stage after drying; and the like. Among them, a method comprising adding the surface-crosslinking agent to a water-absorbent resin dispersed in an organic solvent at the stage of the water-containing gelated product obtained after the polymerization, and a method comprising spraying the surface-crosslinking agent with a spray or the like at the stage of the water-containing particles during drying are preferable.

The embodiment of adding the surface-crosslinking agent is not

particularly limited. In order that the surface-crosslinking agent is homogeneously added to the water-absorbent resin, it is preferable that the surface-crosslinking agent is dissolved in a hydrophilic solvent such as water before addition.

5

The present invention will be specifically explained hereinbelow by means of Examples, without intending to limit the present invention only to these Examples.

10

Example 1

15

Five-hundred milliliters of n-heptane was added to a 1000-ml five-necked cylindrical round bottomed flask equipped with a stirrer, a reflux condenser, a dropping funnel, a thermometer and a nitrogen gas inlet tube. Thereto was added 1.38 g of decaglycerol pentastearate (surfactant: SUNSOFT Q-185S, manufactured by Taiyo Kagaku Co., Ltd.) having an HLB of 5.0 and dispersed. The temperature of the dispersion was raised to dissolve the surfactant, and thereafter cooled to 55°C.

20

Separately from the above, 92 g of a 80% by weight aqueous solution of acrylic acid was added to a 500-ml Erlenmeyer flask. Thereto was added dropwise 102.2 g of a 30% by weight aqueous sodium hydroxide solution while externally cooling, to neutralize 75% by mol of acrylic acid, to give an aqueous solution of a partially neutralized salt of acrylic acid. Further, 50.2 g of water, 0.11 g of a polymerization initiator potassium persulfate, and 18.4 mg of a crosslinking agent ethylene glycol diglycidyl ether were added thereto, to give an aqueous solution of a monomer for a polymerization.

25

The entire amount of this aqueous solution of the monomer for a polymerization was added to the above-mentioned five-necked cylindrical round bottomed flask under stirring and dispersed. After the internal of the system was sufficiently replaced with nitrogen, the temperature of the mixture was raised, and the polymerization reaction was carried out for 1 hour while keeping its bath temperature at 70°C. To a water-containing gelated product after the termination of the polymerization was added 0.66 g of a 14% by weight aqueous solution of tetrasodium trans-1,2-diaminocyclohexanetetraacetate as an aminocarboxylic acid-based metal chelating agent under stirring. Subsequently, water of the water-containing gelated product was removed to the external of the system by azeotropic dehydration. To the resulting gelated product was added 4.14 g of a 2% by weight aqueous solution of ethylene glycol diglycidyl ether, and water and n-heptane were further removed from the mixture by distillation, and the residue was dried, to give 93.0 g of a water-absorbent resin.

Example 2

Five-hundred milliliters of n-heptane was added to a 1000-ml five-necked cylindrical round bottomed flask equipped with a stirrer, a reflux condenser, a dropping funnel, a thermometer and a nitrogen gas inlet tube. Thereto was added 0.92 g of sucrose fatty acid ester (surfactant: S-370, manufactured by MITSUBISHI CHEMICAL CORPORATION) having an HLB of 3.0 and dispersed. The temperature of the dispersion was raised to dissolve the surfactant, and thereafter cooled to 55°C.

Separately from the above, 92 g of a 80% by weight aqueous solution of acrylic acid was added to a 500-ml Erlenmeyer flask. Thereto was added

dropwise 102.2 g of a 30% by weight aqueous sodium hydroxide solution while externally cooling, to neutralize 75% by mol of acrylic acid, to give an aqueous solution of a partially neutralized salt of acrylic acid. Further, 50.2 g of water, 0.11 g of a polymerization initiator potassium persulfate, and 9.2 mg of a crosslinking agent ethylene glycol diglycidyl ether were added thereto, to give an aqueous solution of a monomer for a first step polymerization.

The entire amount of this aqueous solution of the monomer for a first step polymerization was added to the above-mentioned five-necked cylindrical round bottomed flask under stirring and dispersed. After the internal of the system was sufficiently replaced with nitrogen, the temperature of the mixture was raised, and the polymerization reaction was carried out for 1 hour while keeping its bath temperature at 70°C. Thereafter, the polymerization slurry was cooled to room temperature.

Further, 119.1 g of a 80% by weight aqueous solution of acrylic acid was added to a separate 500-ml Erlenmeyer flask. Thereto was added dropwise 132.2 g of a 30% by weight aqueous sodium hydroxide solution while cooling, to neutralize 75% by mol of acrylic acid. Further, 27.4 g of water, 0.14 g of potassium persulfate, and 35.7 mg of ethylene glycol diglycidyl ether were added thereto, to give an aqueous solution of a monomer for a second step polymerization. The aqueous solution was cooled in an ice water bath.

The entire amount of this aqueous solution of the monomer for a second step polymerization was added to the above-mentioned polymerization slurry. After the internal of the system was again sufficiently replaced with nitrogen, the temperature of the mixture was raised, and the second-step polymerization reaction was carried out for 2 hours while keeping its bath temperature at 70°C.

After the termination of the polymerization, 0.53 g of a 40% by weight aqueous solution of pentasodium diethylenetriaminepentaacetate was added as an aminocarboxylic acid-based metal chelating agent to a water-containing gelated product dispersed in n-heptane under stirring. Subsequently, water of the water-
5 containing gelated product was removed to the external of the system by azeotropic dehydration. To the resulting gelated product was added 8.44 g of a 2% by weight aqueous solution of ethylene glycol diglycidyl ether, and water and n-heptane were further removed from the mixture by distillation, and the residue was dried, to give 214.8 g of a water-absorbent resin.

10

Example 3

Five-hundred milliliters of n-heptane was added to a 1000-ml five-necked cylindrical round bottomed flask equipped with a stirrer, a reflux condenser, a dropping funnel, a thermometer and a nitrogen gas inlet tube. Thereto was added
15 0.92 g of sucrose fatty acid ester (surfactant: S-370, manufactured by MITSUBISHI CHEMICAL CORPORATION) having an HLB of 3.0 and dispersed. The temperature of the dispersion was raised to dissolve the surfactant, and thereafter cooled to 55°C.

20

Separately from the above, 92 g of a 80% by weight aqueous solution of acrylic acid was added to a 500-ml Erlenmeyer flask. Thereto was added dropwise 102.2 g of a 30% by weight aqueous sodium hydroxide solution while externally cooling, to neutralize 75% by mol of acrylic acid, to give an aqueous solution of a partially neutralized salt of acrylic acid. Further, 50.2 g of water, 0.11 g of a polymerization initiator potassium persulfate, and 9.2 mg of a
25 crosslinking agent ethylene glycol diglycidyl ether were added thereto, to give an

aqueous solution of a monomer for a polymerization.

The entire amount of this aqueous solution of the monomer for a polymerization was added to the above-mentioned five-necked cylindrical round bottomed flask under stirring and dispersed. After the internal of the system was sufficiently replaced with nitrogen, the temperature of the mixture was raised, and the polymerization reaction was carried out for 1 hour while keeping its bath temperature at 70°C. After the termination of the polymerization, water of the water-containing gelated product was removed to the external of the system by azeotropic dehydration. To the resulting gelated product was added 4.14 g of a 2% by weight aqueous solution of ethylene glycol diglycidyl ether, and water was removed again together with n-heptane by distillation. Thereafter, 0.46 g of a powder triethylenetetraminehexaacetic acid (87% by weight of the entire particles thereof having particle sizes of 100 μm or less) was added to the residue as an aminocarboxylic acid-based metal chelating agent under stirring. The mixture was further dried, and water was removed together with n-heptane, to give 92.8 g of a water-absorbent resin.

Example 4

The same procedures as in Example 3 were carried out except that triethylenetetraminehexaacetic acid in Example 3 was not added, to give 92.0 g of a water-absorbent resin. Inside the polyethylene bag were added the entire amount of the above-mentioned water-absorbent resin and 0.46 g of a powder disodium diethylenetriaminepentaacetate (85% by weight of the entire particles thereof having particle sizes of 100 μm or less), and the mixture was thoroughly blended, to give 92.5 g of a water-absorbent resin.

Example 5

Five-hundred milliliters of n-heptane was added to a 1000-ml five-necked cylindrical round bottomed flask equipped with a stirrer, a reflux condenser, a dropping funnel, a thermometer and a nitrogen gas inlet tube. Thereto was added 0.92 g of sorbitan monostearate (surfactant: Nonion SP-60R, manufactured by NOF Corporation) having an HLB of 4.7 and dispersed. The temperature of the dispersion was raised to dissolve the surfactant, and thereafter cooled to 50°C.

Separately from the above, 92 g of a 80% by weight aqueous solution of acrylic acid was added to a 500-ml Erlenmeyer flask. Thereto was added dropwise 102.2 g of a 30% by weight aqueous sodium hydroxide solution while externally cooling, to neutralize 75% by mol of acrylic acid, to give an aqueous solution of a partially neutralized salt of acrylic acid. Further, 20.8 g of water, 0.11 g of a polymerization initiator potassium persulfate, and 23.0 mg of a crosslinking agent N,N'-methylenebisacrylamide were added thereto. To the mixture was added 0.23 g of a 40% by weight aqueous solution of pentasodium diethylenetriaminepentaacetate as an aminocarboxylic acid-based metal chelating agent, to give an aqueous solution of a monomer for a polymerization.

The entire amount of this aqueous solution of the monomer for a polymerization was added to the above-mentioned five-necked cylindrical round bottomed flask under stirring and dispersed. After the internal of the system was sufficiently replaced with nitrogen, the temperature of the mixture was raised, and the polymerization reaction was carried out for 2 hours while keeping its bath temperature at 70°C. After the termination of the polymerization, water of the water-containing gelated product was removed to the external of the system

by azeotropic dehydration. To the resulting gelated product was added 4.60 g of a 2% by weight aqueous solution of ethylene glycol diglycidyl ether, and water and n-heptane were further removed by distillation, and the residue was dried, to give 93.8 g of a water-absorbent resin.

5

Example 6

Five-hundred-and-fifty milliliters of n-heptane was added to a 1500-ml five-necked cylindrical round bottomed flask equipped with a stirrer, a reflux condenser, a dropping funnel, a thermometer and a nitrogen gas inlet tube.

10 Thereto was added 0.84 g of sorbitan monolaurate (surfactant: Nonion LP-20R, manufactured by NOF Corporation) having an HLB of 8.6 and dispersed. The temperature of the dispersion was raised to dissolve the surfactant, and thereafter cooled to 40°C.

15 Separately from the above, 70 g of a 80% by weight aqueous solution of acrylic acid was added to a 500-ml Erlenmeyer flask. Thereto was added dropwise 77.8 g of a 30% by weight aqueous sodium hydroxide solution while externally cooling, to neutralize 75% by mol of acrylic acid, to give an aqueous solution of a partially neutralized salt of acrylic acid. Further, 33.3 g of water and 0.084 g of a polymerization initiator potassium persulfate were added thereto,

20 to give an aqueous solution of a monomer for a polymerization.

The entire amount of this aqueous solution of the monomer for a polymerization was added to the above-mentioned five-necked cylindrical round bottomed flask under stirring and dispersed. After the internal of the system was sufficiently replaced with nitrogen, the temperature of the mixture was raised,

25 and the polymerization reaction was carried out for 3 hours while keeping its

bath temperature at 70°C. To the water-containing gelated product after the termination of the polymerization was added 0.175 g of a 40% by weight aqueous solution of pentasodium diethylenetriaminepentaacetate as an aminocarboxylic acid-based metal chelating agent under stirring. Subsequently, water of the water-containing gelated product was removed to the external of the system by azeotropic dehydration. To the resulting gelated product was added 3.15 g of a 2% by weight aqueous solution of ethylene glycol diglycidyl ether, and water and n-heptane were further removed by distillation, and the residue was dried, to give 74.0 g of a water-absorbent resin.

Example 7

The same procedures as in Example 5 were carried out except that 1.21 g of a 38% by weight aqueous solution of tetrasodium ethylenediaminetetraacetate was added in place of pentasodium diethylenetriaminepentaacetate in Example 5, to give 93.6 g of a water-absorbent resin.

Comparative Example 1

The same procedures as in Example 1 were carried out except that the aminocarboxylic acid-based metal chelating agent in Example 1 was not added, to give 92.1 g of a water-absorbent resin.

Comparative Example 2

The same procedures as in Example 2 were carried out except that the aminocarboxylic acid-based metal chelating agent in Example 2 was not added, to give 212.5 g of a water-absorbent resin.

Comparative Example 3

The same procedures as in Example 3 were carried out except that the aminocarboxylic acid-based metal chelating agent in Example 3 was not added,
5 to give 92.1 g of a water-absorbent resin.

Comparative Example 4

The same procedures as in Example 1 were carried out except that an aqueous solution prepared by dissolving 0.92 g of citric acid in 9.2 g of water
10 was added in place of tetrasodium trans-1,2-diaminocyclohexanetetraacetate in Example 1, to give 92.8 g of a water-absorbent resin.

Comparative Example 5

The same procedures as in Example 3 were carried out except that 0.46 g
15 of sodium tripolyphosphate (90% by weight of the entire particles thereof having particle sizes of 100 μm or less) was added in place of triethylenetetraminehexaacetic acid in Example 3, to give 92.6 g of a water-absorbent resin.

20 The discoloration test of the water-absorbent resins obtained in Examples and Comparative Examples mentioned above was carried out in accordance with the following methods.

[Discoloration Test of Water-Absorbent Resins]

25 Into a polypropylene vessel having an inner diameter of 3 cm and a depth

of 1 cm was evenly placed 2.0 g of a water-absorbent resin. This vessel was allowed to stand for 20 days in a bench-type thermohygrostat set at a temperature of $50^{\circ} \pm 2^{\circ}\text{C}$ and relative humidity of $90 \pm 2\%$ RH. After allowing to stand, the vessel was taken out from the thermohygrostat, and allowed to stand for some
5 time to cool to room temperature. The entire amount of the water-absorbent resin in the vessel was added to a glass measuring vessel having an inner diameter of 3 cm, and Yellow Index of the water-absorbent resin was determined with a double beam-type spectrophotometer Z-1001DP (manufactured by Nippon Denshoku Kogyo Industries, Co., Ltd.), in which X, Y and Z, tristimulus
10 values of the spectrophotometer are corrected with a standard white board. Yellow Index was calculated by the following equations from X, Y and Z (tristimulus values) of the resulting water-absorbent resin. Similarly, Yellow Index of the water-absorbent resin before the test of allowing to stand in the bench-type thermohygrostat for 20 days was obtained. The above-mentioned
15 determinations were taken thrice, and an averaged value was applied.

$$\text{Yellow Index} = 100 (1.28X - 1.06Z)/Y$$

The aminocarboxylic acid-based metal chelating agents used in Examples mentioned above, and the results of the discoloration test for the water-absorbent
20 resins obtained in Examples and Comparative Examples mentioned above are shown in Table 1. The amount inside the parenthesis in Table 1 is an amount based on 100 parts by weight of acrylic acid.

Table 1

Aminocarboxylic Acid-Based Metal Chelating Agent		Results for Discoloration Test		
	Kind (parts by weight)	Yellow Index Before Test	Yellow Index Degree After Test	Difference in Yellow Index
Ex. 1	Tetrasodium trans-1,2-Diaminocyclohexanetetraacetate (0.126)	9.5	12.6	3.1
Ex. 2	Pentasodium Diethylenetriaminepentaacetate (0.125)	9.7	12.9	3.2
Ex. 3	Triethylenetetraminehexaacetic acid (0.625)	9.9	12.9	3.0
Ex. 4	Disodium Diethylenetriaminepentaacetate (0.625)	10.1	13.1	3.0
Ex. 5	Pentasodium Diethylenetriaminepentaacetate (0.125)	9.8	12.8	3.0
Ex. 6	Pentasodium Diethylenetriaminepentaacetate (0.125)	5.5	7.0	1.5
Ex. 7	Tetrasodium Ethylenediaminetetraacetate (0.625)	10.0	15.9	5.9
Comp. Ex. 1	(Not Added)	10.8	21.9	11.1
Comp. Ex. 2	(Not Added)	10.4	21.1	10.7
Comp. Ex. 3	(Not Added)	10.2	21.5	11.3
Comp. Ex. 4	Citric Acid (1.25)	10.0	20.7	10.7
Comp. Ex. 5	Sodium Tripolyphosphate (0.625)	9.9	20.0	10.1

It can be seen from Table 1 that the water-absorbent resins obtained in Examples in which the aminocarboxylic acid-based metal chelating agent is added have little change in Yellow Index before and after the tests, so that the discoloration is suppressed. On the other hand, it can be seen that the water-absorbent resins obtained in Comparative Examples in which the aminocarboxylic acid-based metal chelating agent was not added have a large change in Yellow Index, so that considerable discoloration is found.

INDUSTRIAL APPLICABILITY

According to the present invention, there can be suppressed the discoloration of a water-absorbent resin by preparing a water-absorbent resin in the presence of an aminocarboxylic acid-based metal chelating agent even under severe environmental conditions such as high temperature and high humidity.

The present invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

CLAIMS

1. A method for preventing discoloration of a water-absorbent resin made from an unsaturated carboxylic acid as an essential monomer, characterized in that said method comprises adding an aminocarboxylic acid-based metal
5 chelating agent to a system in at least any one of the stages during a preparation process of the water-absorbent resin or to the water-absorbent resin obtained after the preparation.
- 10 2. The method for preventing discoloration according to claim 1, wherein the amount of the aminocarboxylic acid-based metal chelating agent used is from 0.001 to 6 parts by weight, based on 100 parts by weight of the unsaturated carboxylic acid.
- 15 3. The method for preventing discoloration according to claim 1 or 2, wherein the aminocarboxylic acid-based metal chelating agent is at least one member selected from the group consisting of diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, trans-1,2-diaminocyclohexanetetraacetic acid, and salts thereof.
- 20 4. A method of use of an aminocarboxylic acid-based metal chelating agent for preventing discoloration of an obtainable water-absorbent resin made from an unsaturated carboxylic acid as an essential monomer, characterized in that said method comprises adding an aminocarboxylic acid-based metal chelating agent
25 to a system in at least any one of the stages during a preparation process of the

water-absorbent resin or to the water-absorbent resin obtained after the preparation.

5. The method of use according to claim 4, wherein the amount of the
5 aminocarboxylic acid-based metal chelating agent used is from 0.001 to 6 parts
by weight, based on 100 parts by weight of the unsaturated carboxylic acid.

6. The method of use according to claim 4 or 5, wherein the
aminocarboxylic acid-based metal chelating agent is at least one member
10 selected from the group consisting of diethylenetriaminepentaacetic acid,
triethylenetetraminehexaacetic acid, trans-1,2-diaminocyclohexanetetraacetic
acid, and salts thereof.