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EP 0 403 178 A2

(54) Toner including suspension polymerised binder.

(57) A toner comprising as a binder a polymer obtained by polymerizing a polymerizable vinyl monomer by suspension polymerization with a nonionic dispersing agent and an azo initiator. According to the present invention, there is provided a toner which produces copied images having excellent stability of image quality (life) even after a large number of times of copying.

Toner Including Suspension Polymerised Binder

The present invention relates to a toner which includes a vinyl polymer binder that has been prepared by a particular polymerisation method. The vinyl polymer binder used in the toner of the present invention is prepared by suspension polymerisation using a particular dispersing agent and initiator.

There have been a large number of inventions relating to binder resins for dry toners. Vinyl polymers for use as binder resins in toners are produced by many different types of polymerisation such as suspension polymerisation, bulk polymerisation, solution polymerisation, emulsion polymerisation, etc. Suspension polymerisation is preferred because the manufacturing costs are minimised.

However, suspension polymerisation is disadvantageous in that the binder resin produced will contain residues of the suspension polymerisation process, including residues of the dispersing agent and initiator used in the polymerisation. These binder resins are undesirable because toners prepared using them are problematic in terms of chargeability and stability (life) of the image quality. The present inventors have studied these problems and found that if the toner is prepared using a vinyl polymer binder obtained by suspension polymerisation of a polymerised vinyl monomer with a non-ionic dispersing agent and an azo initiator, the resultant toner will have superior stability of image quality.

According to the present invention, there is provided a toner comprising a polymeric binder obtained by suspension polymerisation of a polymerisable vinyl monomer, characterised in that the suspension polymerisation is carried out using a non-ionic dispersing agent and an azo initiator.

According to a preferred feature of the invention the toner comprises a binder prepared by suspension polymerisation of polymerisable vinyl monomer including an acid monomer.

The vinyl monomer used in the present invention may be any of those that may be polymerised by suspension polymerisation, for example, styrene and styrene derivatives such as α-methylstyrene and substituted styrenes having methyl at an o- or m-position of the benzene ring, or methyl, ethyl, butyl, hexyl, octyl, nonyl, decyl, methoxy, phenyl or vinyl at a p-position of the benzene ring, or methyl at 2- and 4-positions thereof; acrylic acid esters and methacrylic acid esters represented by the formula: $CH_2 = CR\text{-}COOR'$, where R represents hydrogen or methyl, and R′ represents methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-bytyl, n-pentyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, isononyl, decyl, dodecyl, tridecyl, stearyl, docosyl, cyclohexyl, benzyl, phenyl, methoxyethyl, ethoxyethyl, butoxyethyl, phenoxyethyl, etc.; vinyl esters such as vinyl acetate, vinyl propionate, etc.; and acrylic acid derivatives or methacrylic acid derivatives such as acrylonitrile, methacrylonitrile, etc. These polymerisable vinyl monomers are used alone or in admixture of two or more of them.

When a combination of two or more polymerisable vinyl monomers is used, preferred monomer mixtures include those having styrene and/or its derivatives and alkyl (meth) acrylates as the main constituents of the mixture.

When the acid monomer is used as one component of the polymerisable vinyl monomers, the life of the toner obtained is further improved. The amount of the acid monomer is 0.5 to 10 wt.% based on she total weight of the polymerisable vinyl monomers. When the vinyl polymer is obtained by copolymerising 0.5 wt% or less of the acid monomer, toners containing this vinyl polymer as a binder exhibit no effect of copolymerisation of the acid monomer. On the other hand, when the vinyl polymer is obtained by copolymerising 10 wt.% or more of the acid monomer, toners containing this vinyl monomer as a binder exert adverse effects on their other characteristics.

Suitable acid monomers for use in the present invention are monomers having one or more acid substituents in addition to the polymerisable vinyl group. For example, suitable monomers are acrylic acid, methacrylic acid, itaconic acid, citraconic acid, maleic acid, fumaric acid, crotonic acid, monobutyl itaconate, monomethyl maleate, monobutyl maleate, monooctyl maleate, monooctyl itaconate, 2-sulfoethyl methacrylate, 2-sulfoethyl acrylate, 2-acrylamide-2-methylpropanesulfonic acid, vinylbenzenesulfonic acid, etc. These acid monomers are used alone or in admixture of two or more of them.

The vinyl polymer used in the present invention is produced by suspension polymerisation.

The azo initiator used in this method is not critical, it being possible to use the well-known ones. Suitable examples are azobisisobutyronitrile, 2,2′-azobis- (2,4-dimethylvaleronitrile), dimethyl-2,2′-azobisisobutyronitrile, 2,2′-azobis-(2-methylbutyronitrile), 1,1′-azobis-(cyclohexane-1-carbonitrile), 2,2′-azobis-(2-cyclopropylpropionitrile), 2,2′-azobis-(4-methoxy-2,4-dimethylvaleronitrile), etc. Among these initiators, it is preferred to use azobisisobutyronitrile, 2,2′-azobis- (2,4-dimethylvaleronitrile), dimethyl-2,2′-azobisisobutyronitrile or 2,2′-azobis- (2-methylbutyronitrile) because these

initiators have properties to keep a polymerisation activity upon the monomer and complete the polymerisation in a relatively short time, and because they do not have a high tendency to leave their decomposition by-products in the resulting polymer.

These azo initiators are used alone or in admixture of two or more of them.

The toner of the present invention has a remarkably improved life as compared with toners containing binder polymers obtained by the conventional methods, because it uses a vinyl polymer binder obtained by suspension polymerisation with a non-ionic dispersing agent.

The non-ionic dispersing agents for use in the present invention are preferably polymeric. Suitable examples include polyvinyl alcohol, methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, gelatin, polyethylene oxide, etc. of these nonionic dispersing agents, polyvinyl alcohol having a saponification degree of 70 to 90% and a polymerisation degree of 500 to 3000 is preferred because resins obtained with it have good binder characteristics for toners.

The nonionic dispersing agent is used in such an amount that the polymerisation operation can be completed without causing aggregation of the produced resin particles in the course of the polymerisation. The amount of the agent is usually 0.01 to 5 parts by weight, preferably 0.05 to 2 parts by weight based on 100 parts by weight of water.

If necessary, a dispersion auxiliary may be used. It includes for example electrolytes such as sodium chloride, potassium chloride, sodium sulfate, potassium sulfate, etc.

The necessary conditions for the suspension polymerisation vary with the particular polymerisable vinyl monomer/s, and azo initiator/s used and the amounts thereof. However, the optimum polymerisation temperature is generally 30° to 130° C, preferably 60° to 100° C, and the polymerisation time is preferably about 1 to about 10 hours.

After the completion of the suspension polymerisation, the reaction solution is filtered, and the resulting polymer is thoroughly washed, dehydrated and dried. A coloring agent and other additives are added to this polymer to obtain the toner of the present invention.

The present invention is illustrated below with reference to the following examples. In the examples, parts are by weight. However, these examples are not to be construed to limit the present invention.

Example 1

3 Parts of azobisisobutyronitrile, an azo initiator, was dissolved in a polymerizable vinyl monomer comprising 93 parts of styrene, 17 parts of 2-ethylhexyl acrylate and 0.3 part of divinylbenzene. The resulting mixture was mixed with a polymerization medium obtained by dissolving 0.2 part of partially saponified polyvinyl alcohol (PVA-224E produced by KURARAY CO., LTD.) in 220 parts of deionized water. The mixture was heated to 80° C, and suspension polymerization was carried out for 90 minutes at this temperature. The resulting polymer dispersion was cooled to room temperature and filtered. The solid matter obtained was thoroughly washed, dehydrated and dried to obtain a bead-form binder resin.

92 Parts of the above binder resin, 7 parts of carbon black (#40 produced by Mitsubishi Kasei Corp.) and 1 part of a charge control agent (BONTRON S-34 produced by ORIENT CHEMICAL INDUSTRIES, LTD.) were kneaded at 150° C for about 5 minutes on a twin-screw extruder. After cooling, the kneaded product was finely pulverized on a jet mill. The fine powders obtained were classified to collect fine powders having a particle size of 5 to 15 μm. The volume mean diameter of the fine powders was 9.6 μm.

A copying test was carried out on a commercially available copying machine (Ricopy FT 4510 produced by RICOH CO., LTD.) using the above fine powders as a toner. As a result, fog-free high-resolution clear images were obtained at the initial stage of copying and after 10,000 copying operations. After 20,000 copying operations, however, the images showed a faint touch of fog and a somewhat lowered resolution degree, which were however of such a degree as to be out of the question in practical use.

Example 2

A toner was obtained in the same manner as in Example 1 except that 82 parts of styrene, 17 parts of 2-ethylhexyl acrylate, 1 part of methacrylic acid and 0.3 part of divinylbenzene were used as the polymerizable vinyl monomer. The performances of this toner were evaluated, and it was found that fog-free high-resolution clear images were obtained even after 20,000 copying operations.

Example 3

A toner was obtained in the same manner as in Example 1 except that 82.5 parts of styrene, 17 parts of 2-ethylhexyl acrylate, 0.5 part of methacrylic acid and 0.3 part of divinylbenzene were used as the polymerizable vinyl monomer. The performances of this toner were evaluated, and

it was found that fog-free high-resolution clear images were obtained at the initial stage of copying and after 10,000 copying operations, but after 20,000 copying operations, the images showed a faint touch of fog, which was however of such a degree as to be out of the question in practical use.

Example 4

A toner was obtained in the same manner as in Example 1 except that 73 parts of styrene, 17 parts of 2-ethylhexyl acrylate, 10 parts of methacrylic acid and 0.3 part of divinylbenzene were used as the polymerizable vinyl monomer. The performances of this toner were evaluated, and it was found that fog-free high-resolution clear images were obtained even after 20,000 copying operations, but the fixability and grindability were somewhat lowered.

Comparative Example 1

A toner was obtained in the same manner as in Example 1 except that 3 parts of benzoyl peroxide, which is not an azo initiator, was used as the polymerization initiator, and that the polymerization temperature was 85 °C. The performances of this toner were evaluated, and it was found that the images at the initial stage of copying were fog-free high-resolution clear ones, but that after 5,000 copying operations, only images having a touch of fog and a lowered resolution degree were obtained.

Comparative Example 2

A toner was obtained in the same manner as in Example 2 except that 3 parts of benzoyl peroxide was used as the initiator and the polymerization temperature was 85 °C. The performances of this toner were evaluated, and it was found that the images at the initial stage of copying were fog-free high-resolution clear ones, but that after 10,000 copying operations, only images having a touch of fog and a lowered resolution degree were obtained.

Comparative Example 3

A toner was obtained in the same manner as in Example 1 except that 0.2 part of an anion-modified polyvinyl alcohol (KL-318 produced by KURARAY CO., LTD.), which is not a nonionic dispersing agent, was used as the dispersing agent. The performances of this toner were evaluated, and it was found that the images at the initial stage of copying were fog-free high-resolution clear ones, but that after 5,000 copying operations, only images having a touch of fog and a lowered resolution degree were obtained.

Comparative Example 4

A toner was obtained in the same manner as in Example 2 except that 0.2 part of an anion-modified polyvinyl alcohol (KL-318 produced by KURARAY CO., LTD.) was used as the dispersing agent. The performances of this toner were evaluated, and it was found that the images at the initial stage of copying were fog-free high-resolution clear ones, but that after 10,000 copying operations, only images having a touch of fog and a lowered resolution degree were obtained.

Comparative Example 5

A toner was obtained in the same manner as in Example 1 except that 0.2 part of a cation-modified polyvinyl alcohol (C-318 produced by KURARAY CO., LTD.) was used as the dispersing agent. The performances of this toner were evaluated, and it was found that the images at the initial stage of copying were fog-free high-resolution clear ones, but that after 5,000 copying operations, only images having a touch of fog and a lowered resolution degree were obtained.

Comparative Example 6

A toner was obtained in the same manner as in Example 2 except that 0.2 part of a cation-modified polyvinyl alcohol (C-318 produced by KURARAY CO., LTD.) was used as the dispersing agent. The performances of this toner were evaluated, and it was found that the images at the initial stage of copying were fog-free high-resolution clear ones, but that after 10,000 copying operations, only images having a touch of fog and a lowered resolution degree were obtained.

Claims

1. A toner comprising a polymeric binder obtained by suspension polymerisation of a polymerisable vinyl monomer characterised in that the polymerisation is carried out using a nonionic dispersing agent and an azo initiator.

2. A toner according to claim 1, wherein the polymerisable vinyl monomer includes an acid

monomer.

3. A toner according to claim 2 wherein the amount of acid monomer is 0.5 to 10 wt.% based on the total weight of the polymerisable vinyl monomers.

4. A toner according to any preceding claim wherein the nonionic dispersing agent is polyvinyl alcohol.

5. A toner according to claim 4 wherein the polyvinyl alcohol has a saponification degree of 70 to 90%.

6. A toner according to claim 4 or claim 5 wherein the polyvinyl alcohol has a polymerisation degree of 500 to 3000.

7. A toner according to any preceding claim wherein the amount of nonionic dispersing agent is 0.05 to 2 parts by weight based on 100 parts by weight of water.

8. A toner according to any preceding claim wherein the azo initiator is at least one member selected from the group consisting of azobisisobutyronitrile, 2,2′-azobis-(2,4-diemethyl-valeronitrile), dimethyl-2,2′-azobisisobutyronitrile and 2,2′-azobis-(2-methylbutyronitrile).

9. A toner according to any preceding claim wherein the polymerisable vinyl monomer is at least one member selected from the group consisting of styrene, styrene derivatives, acrylic acid esters and methacrylic acid esters.