(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 610 522 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
21.04.1999 Bulletin 1999/16

(51) Int Cl.[6]: **G03C 1/95**, C08F 2/08

(21) Application number: **93101906.1**

(22) Date of filing: **08.02.1993**

(54) **Silver halide photographic material comprising monodispersed polymer particles and process for the production thereof**

Photographisches Silberhalogenidmaterial, das monodisperse Polymerteilchen enthält

Matériau photographique à l'halogénure d'argent comprenant de particules de polymères monodispersées

(84) Designated Contracting States:
DE FR GB IT

(43) Date of publication of application:
17.08.1994 Bulletin 1994/33

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EP 0 610 522 B1

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] The present invention relates to a silver halide photographic material having a support, at least one light-sensitive silver halide emulsion layer and at least one outer light-insensitive layer comprising a dispersion of polymer particles as matting agents. In another aspect the invention relates to a method of producing polymer particles and more particularly to the production of polymer particles having a narrow particle size distribution.

BACKGROUND OF THE ART

[0002] In the field of photography, water-insoluble matting agents have been used in top or back hydrophilic layers of silver halide light-sensitive materials to prevent adhesion when materials are stored in rolls, cartridges or cassettes in conditions of relatively high humidity and temperature, to prevent electrostatic charges by reducing the area of contact of the photographic material, to prevent the formation of Newton's rings during printing and enlargement, or to decrease the occurrence of scratches during storage or packing of the photographic material.

[0003] It is well known in the art that, in order to solve these problems, fine particles of inorganic substances such as silicon dioxide, magnesium oxide, calcium carbonate and the like, or organic substances such as polymethylmethacrylate, cellulose acetate propionate and the like are incorporated as matting agents into the outermost layers of a photographic material. These and other matting agents are described, for example, in US 3,411,907 and GB 837,529. Said matting agents are insoluble in alkaline processing solutions and remain in the processed photographic material.

[0004] In same cases it is desired to remove the matting agent for the purposes of improving transparency and graininess of the final image. Therefore, matting agents insoluble in neutral or acidic solutions and soluble in alkaline medium have been described in the art. In particular, alkali-soluble matting agents consisting of methacrylic acid - methylmethacrylate copolymers have been described in US 2,391,181, US 2,992,101, US 3,767,448, US 4,142,894, and in GB 878,520, and copolymers of styrene and α,β-ethylenically unsaturated carboxy containing monomers have been described in GB 1,055,713. Such matting agents are incorporated in the photographic layers in the form of discrete particles by dispersing a solution of the matting agent in a water-insoluble organic solvent in an aqueous gelatin solution, eliminating the organic solvent, and then introducing the obtained dispersion into the coating composition of the photographic layer. Alkali-soluble matting agents consisting of methacrylic acid - ethylmethacrylate copolymers containing from 20 to 50 % by weight of methacrylic acid have been described in US 4,447,525 and in EP 370,405. These copolymers dissolve in high concentrations in high volatile organic solvent such as ethylacetate, a solvent which can be easily removed by evaporation from the dispersion of the polymer in aqueous gelatin.

[0005] The matting agents are characterized by the average particle sizes (APS) of their discrete particles and in the patents there are teachings on how to control the APS in the process of synthesis thereof.

[0006] Another characteristic of matting agents is their particle size distribution (PSD), i.e., the measure of the relative percentage of particles having a particle size lower than or higher than the average particle size. This distribution can be well represented, on Cartesian axis having the relative percentage on ordinate and the particle size on abscissa, by a Gaussian distribution curve. Processes described in the art for the synthesis of matting agent dispersions may result in the formation of huge particles exceeding 10 μm of diameter. The presence of such huge particles of matting agents may cause undesirable side effects such as disturbance of uniform coating of the photographic material and disturbance of the distinct layer relationship of a plurality of superposed layers of the photographic material.

[0007] Various method for obtaining monodispersed polymer particles are known in the art and various scientific publications and patent applications relate to the production of such polymer particles.

[0008] For example, a method comprising carrying out a bulk polymerization followed by a suspension polymerization; a method comprising partly dissolving a polymer in a monomer to provide a dispersion liquid which is then subjected to suspension polymerization; suspension polymerization methods using various suspension stabilizers having strong surface activity, using finely-divided inorganic particles which are slightly dissolved in water or using such suspension stabilizers and inorganic particles in combination; micro suspension polymerization methods in which the liquid particles of monomer are stabilized by high concentration of suspension stabilizer in water; emulsion polymerization methods in which polymerization takes place through micelles; seed emulsion polymerization in which small polymer particles are used as seeds or core particles; and the like.

[0009] All these proposed methods suffer of some drawbacks which cause a broad particle size distribution, or a too small average particle size, or a too long and expensive polymerization process.

[0010] In recent years another method for the production of monodispersed polymer particles has been proposed, i.e., the so-called dispersion polymerization in organic liquid method. In this method, polymerization is performed in an organic solvent in which a polymerizable monomer is soluble, but the obtained polymer is not and separates out. A dispersion stabilizer and optionally a dispersion co-stabilizer have been proposed to obtain a narrower particle size

distribution and to recover the polymer particles.

[0011] This method has been extensively studied and some references can be found in scientific papers such as, for example, in C.M.Tseng, et al. "Uniform Polymer Particles by Dispersion Polymerization in Alcohol", Journal of Polymer Science, Part A:Polymer Chemistry, Vol. 24, pp. 2995, Y.Y. Lu et al. "A Comment on the Paper "Uniform Particles by Dispersion Polymerization in Alcohol", Journal of Polymer Science, Part A:Polymer Chemistry, Vol. 28, pp. 2569, A.J.Paine et al. "Dispersion Polymerization of Styrene in Polar Solvents", Macromolecules, 1990, Vol. 23, No. 12, pp. 3104-9, and pp. 3109-17.

[0012] Other references can be found in GB 2,161,170 disclosing a method for the production of polymer particles having an average particle size of from 1 to 100 μm wherein 95% by weight or more of the particles have a particle size within ±25% of the average particle size, in US 5,093,445, describing a method for the production of monodispersed polymer beads containing fluorine and having an average particle size of from 0.5 to 10μm, and in US 4,614,708 disclosing a method to prepare monodispersed polymer beads from a α,β-ethylenically unsaturated monomer and a graft polymerizable monomer, having an average particle size of from 0.5 to 5μm.

[0013] Additionally, DE 4,001,784 discloses a color photographic material having coated thereon two additional light-insensitive layers A and B, B being further from the base than A. Layer B comprises, inter alia, an alkali soluble matting agent having an average particle size of from 0.5 to 8μm, and an alkali insoluble matting agent having an average particle size of from 0.5 to 10 μm. Research Disclosure vol. 216, no. 17, April 1982, Havant GB, page 109 discloses the use of monodispersed matting agents in photographic films to provide physical isolation of one sheet or lap of film from the other, wherein the polymethylmethacrylate matting agent is added to an emulsion or overcoat layer.

[0014] In spite of this extensive literature and patent references the above mentioned problem of tackiness still needs to be completely solved.

SUMMARY OF THE INVENTION

[0015] The present invention relates to a silver halide photographic material having at least one light-sensitive layer coated on a support base and at least one outer light-insensitive layer comprising polydispersed alkali soluble polymer particles and monodispersed alkali insoluble polymer particles having an average particle size of from 1 to 10 μm wherein at least 95% by number of said polymer particles have a diameter within ± 15% of the average particle size.

[0016] In another aspect the present invention relates to a process for the production of monodispersed acrylic polymer particles having an average diameter of from 1 to 10 μm wherein at least 95% by number of said polymer particles have a particle size within ± 15% of the average particle size, comprising the steps of:

A) dissolving in a hydrophilic organic solvent:

- an acrylic acid derivative monomer soluble in said organic solvent and capable of forming a polymer which is substantially insoluble in said organic solvent,
- a polymeric dispersion stabilizer,
- a surface active dispersion co-stabilizer,

B) heating the obtained solution to the boiling point of said organic solvent, under a stirring speed lower than 80 revolutions per minute,

C) adding a polymerization initiator to start the polymerization.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The present invention relates to a process for the production of monodispersed acrylic polymer particles having an average diameter of from 1 to 10 μm wherein at least 95% by number of said polymer particles have a particle size within ± 15% of the average particle size, comprising the steps of:

A) dissolving in a hydrophilic organic solvent:

- an acrylic acid derivative monomer soluble in said organic solvent and capable of forming a polymer which is substantially insoluble in said organic solvent,
- a polymeric dispersion stabilizer,
- a surface active dispersion co-stabilizer,

B) heating the obtained solution to the boiling point of said organic solvent, under a stirring speed lower than 80 revolutions per minute,

C) adding a polymerization initiator to start the polymerization.

[0018] Examples of hydrophilic organic solvents in which the process of the present invention can be performed are aliphatic alcohols having from 1 to 10 carbon atoms, such as, for example, methanol, ethanol, propanol, isopropanol, butanol, t-butanol, pentanol, neopentanol, cyclohexanol, octanol. These organic solvents can be used alone or in combination each other. The choice of the most suitable hydrophilic organic alcohol can depend on the solubility properties of the monomer employed for the production of the polymer particle and on the polymer so obtained. In a preferred embodiment of the present invention the hydrophilic organic solvent is methanol or ethanol.

[0019] Examples of acrylic derivatives useful in the process of the present invention are methylacrylate, ethylacrylate, n-propylacrylate, isopropylacrylate, n-butylacrylate, isobutylacrylate, sec-butylacrylate, amylacrylate, hexylacrylate, octylacrylate, 2-phenoxyethylacrylate, 2-chloroethylacrylate, 2-acetoxyethylacrylate, dimethylaminoethylacrylate, benzylacrylate, cyclohexylacrylate, phenylacrylate, 2-methoxyethylacrylate, methylmethacrylate, ethylmethacrylate, n-propylmethacrylate, isopropylmethacrylate, n-butylmethacrylate, sec-butylmethacrylate, tert-butylmethacrylate, amylmethacrylate, hexylmethacrylate, cyclohexylmethacrylate, benzylmethacrylate, octylmethacrylate, N-ethyl-N-phenylaminoethylmethacrylate, dimethylaminophenoxyethylmethacrylate, phenylmethacrylate, naphthylmethacrylate, cresylmethacrylate, 2-hydroxyethylmethacrylate, 4-hydroxybutylmethacrylate, 2-methoxyethylmethacrylate, 2-butoxyethylmethacrylate, and the like. The acrylic derivative should be soluble in the hydrophilic organic solvent, but the polymer obtained therefrom should be substantially insoluble. By the term "soluble" it is intended a full solubility of the monomer in the hydrophilic solvent in all proportions. By the term "substantially insoluble" it is intended a solubility lower than 0.1 g/l. In a preferred embodiment of the invention methylmethacrylate is used.

[0020] Copolymers of the above mentioned acrylic derivatives and other vinyl monomers could also be useful in the process of the present invention. Examples of co-monomers are, for example, styrene derivatives such as styrene, methylstyrene, β-methylstyrene and chloromethylstyrene, vinyl esters such as vinyl benzoate, vinylphenyl acetate and vinyl naphthoate, vinyl ethers such as allyl butyl ether, methoxyethyl vinyl ether and phenyl vinyl ether, olefins such as ethylene, propylene, 1-butene and 1-pentene, unsaturated nitriles such as acrylonitrile and methacrylonitrile, vinyl ketones such as vinyl methyl ketone and methoxyethyl vinyl ketone, and vinyl chloride. According to a preferred embodiment of the present invention poly(methylmethacrylate-co-styrene) is used. Although the weight ratio of the co-monomers is not considered to be relevant to obtain the results of the present invention, good results have been obtained with a MMA/ST weight ratio of from 30/70 to 60/40.

[0021] Examples of polymer dispersion stabilizers are homopolymers or copolymers of monomers containing nitrogen atoms or heterocyclic rings having an average number molecular weight in the range of from 20,000 to 60,000. Specific examples of monomers are, for example, vinylpyridine, vinylpyrrolidone, N-vinylimidazole, ethyleneimine. In a preferred embodiment of the present invention the polymer dispersion stabilizer is a polyvinylpyrrolidone having an average number molecular weight of from 30,000 to 50,000.

[0022] Examples of surface active dispersion co-stabilizers are surface active agents. Specific examples of surface active agents are cationic surfactants, such as, for example, alkylamine salts, aminoalcohol fatty acid derivatives, polyamine fatty acid derivatives, imidazolines, quaternary nitrogen salts, anionic surfactants, such as, for example, alkylsulfates, alkyl and aralkyl sulfonates, alkyl phosphates, fatty acid salts, phosphorus derivatives, and non-ionic surfactants, such as, for example, fatty acid amide derivatives, polyhydroxy alcohol derivatives, polyoxyalkyl derivatives.

[0023] The polymerization initiator useful in the process of the present invention is an azo type initiator, such as, for example, 2,2'-azobisisobutyronitrile, or 2,2'-azobis(2,4-dimethylvaleronitrile).

[0024] Generally the reactant concentrations are chosen in accordance with the desired average particle size. As a general rule a higher concentration of monomer causes the production of broader particles, and a higher concentration of stabilizer promotes the formation of smaller particles. The concentration of co-stabilizer slightly affects the particle size only at low concentrations of stabilizer.

[0025] The concentration of monomer and of stabilizer, as well as the average molecular weight of the stabilizer, also influences the particle size distribution. A man skilled in the art can properly choose the right balance of these reaction components to obtain the range of particle size and particle size distribution desired. As an indication, the monomer concentration should range from 0.05 to 0.30, preferably from 0.1 to 0.2, the stabilizer concentration should range from 0.001 to 0.1, preferably from 0.01 to 0.1, and the concentration of the co-stabilizer should range from 10^{-4} to 0.01, preferably from 0.001 to 0.01. All concentrations are expressed in terms of grams per grams of hydrophilic solvent.

[0026] The temperature of polymerization is an important parameter in the production of monodispersed polymer particles because, if a variation thereof takes place in the reaction solution, a broad particle size distribution will be obtained, in spite of a proper choice of other parameters (such as reactant concentrations or average molecular weight of stabilizer). The problem of temperature control becomes more and more important when large quantities of polymer particles have to be obtained using a large reaction vessel. In this case, a temperature gradient is formed in the reaction

vessel, causing a broadening of the particle size distribution. On the other hand, we have found that a faster stirring speed, to ensure an appropriate thermal and mass transfer, promotes the formation of large and polydispersed particles and therefore does not solve the problem.

[0027] The choice of conducting the polymerization at the boiling point has shown the advantages of a self-control of temperature, and of better thermal and mass transfer, due to convective motion of the boiling solution, causing a reduction of the stirring speed. These effect has led to the production of smaller polymer particle having a narrow particle size distribution.

[0028] In the process of the present invention the acrylic acid derivative monomer, the polymeric dispersion stabilizer, and the surface active dispersion co-stabilizer are dissolved in the hydrophilic organic solvent contained in a vessel equipped with a condenser, a thermometer and a stirrer. After dissolution, the temperature is raised until reaching the boiling point, and the stirring speed is adjusted to a value lower than 80 revolutions per minute, preferably at 60 revolutions per minute. After that the polymerization is started by the introduction of the polymerization initiator. The polymerization is conducted for 12 to 36 hours, preferably 24 hours, and a second addition of initiator can be performed after from 9 to 27 hours, to promote the growth of the preformed particles. After the completion of all the polymerization steps, the dispersion is cooled and the agitation is stopped. The polymer particles can be separated by sedimentation, centrifugation or decantation. Thereafter the settled polymer particles are washed, filtered and re-suspended in water or dried.

[0029] The polymer particles obtained with the process of the present invention show an average diameter of from 1 to 10 μm, preferably of from 3 to 7 μm, and at least 95% by number, preferably at least 99% by number, show a diameter within ± 15%, preferably within ± 10%, of the average diameter.

[0030] The polymer particles obtained with the process of the present invention can be used for a number of application. A preferred application thereof relates to the use as matting agents in photographic elements.

[0031] According to another aspect, the present invention relates to a silver halide photographic material having at least one light-sensitive layer coated on a support base and at least one light-insensitive layer comprising polydispersed alkali soluble polymer particles and monodispersed alkali insoluble polymer particles having an average particle size of from 1 to 10 μm wherein at least 95% by number of said polymer particles have a diameter within ± 15% of the average particle size.

[0032] With the process of the present invention, a matting agent dispersion having an average particle size of from 1 to 10 μm wherein at least 95% by number of said polymer particles have a diameter within ± 15% of the average diameter can be obtained. We have unexpectedly found that the combination of polydispersed alkali soluble polymeric matting agents and monodispersed alkali insoluble polymeric matting agents can solve the problem of stickiness of photographic materials.

[0033] Polydispersed alkali soluble polymeric matting agents have been widely disclosed in the art, such as, for example, in US 2,391,181, US 2,992,101, US 3,767,448, US 4,142,894, US 4,447,525, GB 878,520 and GB 1,055,713. According to a preferred embodiment of the present invention useful alkali soluble polymeric matting agents comprise particles of methacrylic acid - ethylmethacrylate copolymers containing from 20 to 50% by weight of methacrylic acid as described in US 4,447,525 or in EP 370,405. Dispersions of these matting agents show an average particle size in the range of from 1 to 10 μm and a particle size distribution within about ± 50% of the average particle size.

[0034] The matting agents used in the present invention are incorporated into the outer layer of the photographic material. They can be for instance incorporated into the surface protective layer coated on the silver halide emulsion layers, or into the backing layer coated on the support base on the side opposite to that containing the light-sensitive layers, or on both sides. It is more preferred, in any case, to incorporate the matting agents used in the present invention into outer protective layer. Matting agents are incorporated into the layer under the form of small particles uniformly dispersed therein having an average diameter preferably in the range of from 3 to 6 μm.

[0035] Matting agents may be either directly dispersed in the photographic layer or may be dispersed in water solutions or in the water dispersions of the photographic layer binding material and then added to the coating composition prior to coating itself. They may also be incorporated in the photographic layer by dispersing a solution of the matting agent in a water-insoluble organic solvent, in an aqueous gelatin solution, eliminating the organic solvent, and then introducing the obtained dispersion into the coating composition of the photographic layer.

[0036] Matting agents are incorporated in a quantity of 50 to 600 mg/m^2, more preferably from 150 to 400 mg/m^2 relative to the surface layer. In particular, the amount of the polydispersed alkali soluble polymeric matting agent ranges from 40 to 250 mg/m^2, more preferably from 80 to 150 mg/m^2; and the amount of the monodispersed alkali insoluble polymeric matting agent ranges from 10 to 110 mg/m^2, preferably from 10 to 50 mg/m^2. The binding agent of such layer preferably is gelatin, but treated gelatins like the so-called acid or basic gelatins, the gelatins treated with enzymes, gelatin derivatives and modified gelatins can also be used.

[0037] Photographic materials in which the particles used in the invention can be used generally comprise at least one light sensitive layer, such as a silver halide emulsion layer, coated on at least one side of a support. This layer can be sensitized to a particular range of wavelengths with a sensitizing dye. Additional light sensitive layers can be sen-

sitized to a different wavelength range. The light sensitive layers can contain or have associated therewith dye-forming compounds or couplers. For example, a red-sensitive emulsion would generally have a cyan coupler associated therewith, a green-sensitive emulsion would generally have a magenta coupler associated therewith, and a blue-sensitive emulsion would generally have a yellow coupler associated therewith. Other layers and additives, such as antistatic compositions, subbing layers, surfactants, filter dyes, intermediate layers, protective layers, anti-halation layers, barrier layers, development inhibiting compounds can be present in the photographic element.

[0038] Specific photographic materials, in which the polymer particles used in this invention specifically are applicable, are light-sensitive photographic color materials such as color negative films, color reversal films, color papers, as well as black-and-white light-sensitive photographic materials such as X-ray light-sensitve materials, lithographic light-sensitive materials, black-and-white photographic printing papers, black-and-white negative films. A detailed description of photographic elements and of various layers and additives can be found in Research Disclosure 17643 December 1978, 18431 August 1979, 18716 November 1979, 22534 January 1983, and 308119 December 1989.

[0039] The present invention will now be further illustrated by reference to the following examples.

EXAMPLE 1

Preparation of monodispersed PMMA

[0040] In a 1-liter four necks flask equipped with a condenser, a thermometer and a stirrer were added 420 g of methanol, 10 g of PVP™ K30 (a polyvinylpyrrolidone manufactured by GAF, having an average number molecular weight of 30,000), and 2.65g of Surfynol™ 104 (a non-ionic surfactant manufactured by Air Products) under stirring at 45°-50°C until dissolution. Stirring was adjusted at 60 rpm, 67 g of methyl methacrylate (MMA) were added, and the temperature was increased to reach the boiling point. After that, 0.05 g of 2,2'-azobis(isobutyrronitrile) (AIBN, manufactured by Rhone-Poulenc) were added to start the polymerization. After 18 hours, a second addition of 0.05 g of AIBN was made, and the dispersion was allowed to react further 6 hour. Then the dispersion was cooled at room temperature and stirring was stopped.

[0041] The dispersion was left to sediment for 24 hours. After that the clear supernatant was removed and the settled polymethylmethacrylate (PMMA) particles were washed in water.

[0042] After observation of the polymer particle by a scanning electron microscopy, we found an average diameter of 4.18 μm and a standard deviation of 0.17. About 99% by number of polymer particles showed a diameter of from 3.7 to 4.7 μm.

EXAMPLE 2

Preparation of monodispersed PMMA

[0043] The same procedure of example 1 was used in a 25-liter kettle with the following amounts of reactants:

Methanol	11,200 g
PVP™ K30	280 g
Surfynol™ 104	74.2 g
MMA	1,862 g
AIBN	1.4 g (twice)

[0044] PMMA particles having an average diameter of 4.6 μm and a standard deviation of 0.32 were obtained. 95% of polymer particles showed a diameter of from 4 to 5.2μm.

EXAMPLE 3

Preparation of monodispersed PMMA

[0045] The same procedure of example 1 was used in a 50-liter vessel with the following amounts of reactants:

Methanol	24,900 g
PVP™ K30	600 g
Surfynol™ 104	160 g

(continued)

MMA	4,000 g
AIBN	3 g (twice)

[0046] PMMA particles having an average diameter of 3.6 μm and a standard deviation of 0.3 were obtained. 95% of polymer particles showed a diameter of from 2.8 to 3.8μm.

EXAMPLE 4

Preparation of monodispersed PMMA

[0047] The same procedure of example 1 was used in a 100-liter vessel with the following amounts of reactants:

Methanol	101 Kg
PVP™ K30	1.5 Kg
Surfynol™ 104	400 g
MMA	10 Kg
AIBN	7.5 g (twice)

[0048] PMMA particles having an average diameter of 4.66 μm and a standard deviation of 0.39 were obtained. 95% of polymer particles showed a diameter of from 4.1 to 5.2μm.

EXAMPLE 5

Preparation of monodispersed PMMA

[0049] The same procedure of example 1 was used in a 1-liter flask with the following amounts of reactants:

Methanol	420 g
PVP™ K30	10 g
Surfynol™ 104	2.65 g
MMA	67 g
AIBN	0.075 g (twice)

[0050] PMMA particles having an average diameter of 6.1 μm and a standard deviation of 0.98 were obtained. 95% of polymer particles showed a diameter of from 5.2 to 7.2μm. The same reaction was performed in a 6-liter vessel giving the same results.

EXAMPLE 6

Preparation of monodispersed poly(MMA-co-ST)

[0051] The same procedure of example 1 was used in a 1-liter flask by employing 67 grams of a methylmethacrylate (MMA) and styrene (ST) mixture in a MMA/ST weight ratio of 45/55. Poly(MMA-co-ST) particles having an average diameter of 3 μm and a standard deviation of 0.28 were obtained. 99% by number of polymer particles showed a diameter of from 2.8 to 3.2 μm.

EXAMPLE 7

Preparation of polydispersed PMMA

[0052] In a 1-liter flask a solution of 0.7 g of polyvinylalcohol (Mowiol™ 10/98) and 0.21 g of sodium laurylsulfate (Maprofix™) in 450ml of water was prepared. In another flask, 0.63 g of benzoylperoxide were dissolved in 70 ml of methylmethacrylate. The solution of MMA-benzoylperoxide was added to the water solution and mixed by a Silverson mixer. After the emulsification, the reaction mixture was heated at 74°C for 7 hours. The obtained dispersion of PMMA

particles was evaporated at 70°C to separate the polymer particles. PMMA particles having an average diameter of 2.4 μm and a standard deviation of 1.12 were obtained. 99% by number of polymer particles showed a diameter of from 0.2 to 5.2 pm.

EXAMPLE 8

[0053] A set of silver halide photographic films has been coated consisting of a cellulose triacetate support, a red-sensitive silver halide emulsion layer comprising a cyan-dye forming coupler, a green-sensitive silver halide emulsion layer comprising a magenta-dye forming coupler, a blue-sensitive silver halide emulsion layer comprising a yellow-dye forming coupler and an outer gelatin layer.

[0054] Different matting agents were introduced into the outer gelatin layer according the following Table 1.

TABLE 1

Sample	Matting agent	mg/m^2
1(C)	A	138
2 (C)	A	173
3 (C)	A	208
4 (C)	B	109
5 (C)	C	109
6 (C)	D	273
7(I)	A+B	139+11
8(I)	A+C	139+11
9 (C)	A+D	138+82

(C) = comparison (I) = invention

A = Alkali soluble polydispersed Poly(ethylmethacrylate-co-methacrylic acid) 57:43, prepared according to EP 370,405, having an average diameter of 2.6 μm and 99% by number of polymer particles showing a diameter of from 0.5 to 6.0 μm

B = Alkali insoluble monodispersed PMMA prepared according to Example 1, having an average diameter of 4.18 μm and 99% by number of polymer particles showing a diameter of from 3.7 to 4.7 μm

C = Alkali insoluble monodispersed Poly(MMA-co-ST), prepared according to Example 6, having an average diameter of 3 μm and 99% by number of polymer particles showing a diameter of from 2.8 to 3.2 μm.

D = Alkali insoluble polydispersed PMMA, prepared according to Example 7, having an average diameter of 2.4 μm and 99% by number of polymer particles showing a diameter of from 0.2 to 5.2 μm.

[0055] The resulting photographic films were evaluated according the following tests.

Stickiness test n° 1

[0056] The samples were cut into pieces measuring 2m x 35mm and fixed on a plastic core having a diameter of 5cm at a temperature of 21°C and 50% relative humidity. At the opposite side a weight of 334 grams was bound to obtain a uniform draught and a uniform rolling up of the film on the core. The samples were completely rolled on the core and the end was fixed with adhesive tape. The resulting samples were conditioned for 5 days at 50°C and 75% relative humidity, after that they were allowed to stand at room temperature for two hours. These samples were evaluated by unrolling them and by listening carefully to the noise produced in the points inside the coils where stickiness took place. At the end of the unrolling procedure the film surface was investigated to evaluate the percentage of glazing surface. All the samples were rank-ordered as far as noise and glazing surface are concemed, and the mark 1 was given to the best sample and 12 to the worst. The test was repeated for three times and the final result was the average of the three evaluations.

Stickiness test n° 2

[0057] Each sample was cut into 24 pieces measuring 6cm x 3.5cm. The resulting samples were conditioned at 24°C and 90% relative humidity for at least 15 hours. With the samples six couples of film having the emulsion layer against the emulsion layer and six having the emulsion layer against the backing layer were prepared. Each couple of samples was loaded with a weight of 1.5Kg for 15 hours at 24°C and 90% relative humidity. At the end the force necessary to

detach every couple of samples was measured and the final result was the average of the six measurements.

[0058] The results are summarized in the following Table 2.

TABLE 2

Sample	Stickiness test no. 1 (score)	Stickiness test no. 2 (grams)	
		Em//Em	Em//Bk
1 (C)	8	28.4	17.9
2 (C)	7	32.0	15.3
3 (C)	5	30.5	12.4
4 (C)	11	30.7	13.6
5 (C)	10	41.5	28.6
6 (C)	9	26.2	23.0
7 (I)	3	28.5	14.5
8 (I)	2	29.7	12.9
9 (C)	4	32.0	16.5

[0059] The data of Table 2 clearly show that the monodispersed matting agent, whether PMMA (sample 4) or poly (MMA-co-ST) (sample 5), are detrimental to stickiness, when compared to the standard polydispersed PMMA matting agent (sample 6). The soluble matting agent is slightly better for both characteristics (samples 1,2,3). The combination used in the present invention gives rise to a synergic effect with a dramatical reduction of the stickiness of the samples.

[0060] Granularity evaluation of the samples showed that samples 7 and 8 used in the present invention had the best performance relative to the comparison examples. Granularity measurements were conducted by scanning the surface of the sample with a microdensitometer having a circular aperture of 48μm.

[0061] Accordingly, the monodispersed alkali insoluble polymer particles obtained with the process of the present invention, in combination with polydispersed alkali soluble polymer particles can improve both stickiness and granularity of a silver halide photographic material.

Claims

1. A silver halide photographic material having at least one light-sensitive layer coated on a support base and at least one outer light-insensitive layer comprising polydispersed alkali soluble polymer particles and monodispersed alkali insoluble polymer particles having an average particle size of from 1 to 10 μm wherein at least 95% by number of said polymer particles have a diameter within ± 15% of the average particle size.

2. The silver halide photographic material of claim 1 characterized in that said polydispersed alkali soluble polymer particles comprise methacrylic acid - ethylmethacrylate copolymers containing from 20 to 50% by weight of methacrylic acid.

3. The silver halide photographic material of claim 1 characterized in that said monodispersed alkali insoluble polymer particles comprise an acrylic polymer.

4. The silver halide photographic material of claim 1 characterized in that said monodispersed alkali insoluble polymer particles comprise polymethylmethacrylate.

5. The silver halide photographic material of claim 1 characterized in that said monodispersed alkali insoluble polymer particles comprise poly(methylmethacrylate-co-styrene).

6. The silver halide photographic material of claim 1 characterized in that said monodispersed alkali insoluble polymer particles have an average diameter of from 3 to 7 μm, wherein more than 99% by weight of said polymer particles have a diameter within ± 15% of the average diameter.

7. A process for the production of monodispersed particles having an average diameter of from 1 to 10 μm wherein at least 95% by number of said polymer particles have a particle size within ± 15% of the average particle size, comprising the steps of:

A) dissolving in a hydrophilic organic solvent:

- an acrylic acid derivative monomer soluble in said organic solvent and capable of forming a polymer which is substantially insoluble in said organic solvent,
- a polymeric dispersion stabilizer,
- a surface active dispersion co-stabilizer,

B) heating the obtained solution to the boiling point of said organic solvent, under a stirring speed lower than 80 revolutions per minute,

C) adding a polymerization initiator to start the polymerization.

8. The process of claim 7 characterized in that said acrylic acid derivative is methylmetacrylate.

9. The process of claim 7 characterized in that a co-monomer selected in the class of vinyl derivatives is added together with the acrylic acid derivative monomer.

10. The process of claim 9 characterized in that said co-monomer is a styrene derivative.

11. The process of claim 7 characterized in that said polymeric dispersion stabilizer is a polyvinylpyrrolidone having an average number molecular weight in the range of from 20,000 to 60,000.

12. The process of claim 7 characterized in that said surface active dispersion co-stabilizer is a non ionic surfactant.

13. The process of claim 7 characterized in that said hydrophilic organic solvent is an aliphatic alcohol having from 1 to 10 carbon atoms.

14. The process of claim 7 characterized in that said polymerization initiator is selected in the class of azo type initiators.

15. The process of claim 7 characterized in that said polymer particles have an average diameter of from 3 to 7 μm, wherein more than 99% by weight of said polymer particles have a diameter within ± 15% of the average diameter.

Patentansprüche

1. Photographisches Silberhalogenidmaterial mit wenigstens einer lichtempfindlichen Schicht, die auf einer Trägerbasis aufgetragen ist, und wenigstens einer äußeren lichtunempfindlichen Schicht, umfassend polydisperse alkalilösliche Polymerteilchen und monodisperse alkaliunlösliche Polymerteilchen mit einer mittleren Teilchengröße von 1 bis 10 μm, wobei wenigstens 95 % der Anzahl der Polymerteilchen einen Durchmesser innerhalb von ±15% der mittleren Teilchengröße besitzen.

2. Photographisches Silberhalogenidmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die polydispersen alkalilöslichen Polymerteilchen Methacrylsäure-Ethylmethacrylatcopolymere umfassen, die 20 bis 50 Gewichts-% Methacrylsäure enthalten.

3. Photographisches Silberhalogenidmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die monodispersen alkaliunlöslichen Polymerteilchen ein Acrylpolymer umfassen.

4. Photographisches Silberhalogenidmaterial nach Anspruch 1, dadurch gckennzeichnet, daß die monodispersen alkaliunlöslichen Polymerteilchen Polymethylmethacrylat umfassen.

5. Photographisches Silberhalogenidmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die monodispersen alkaliunlöslichen Polymerteilchen Poly(methylmethacrylatcostyrol) umfassen.

6. Photographisches Silberhalogenidmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die monodispersen alkaliunlöslichen Polymerteilchen einen mittleren Durchmesser von 3 bis 7 μm aufweisen, wobei mehr als 99 Gewichts-% der Polymerteilchen einen Durchmesser innerhalb von ±15% des mittleren Teilchendurchmessers besitzen.

7. Verfahren zur Herstellung von monodispersen Teilchen mit einem mittleren Durchmesser von 1 bis 10 µm, wobei wenigstens 95 % der Anzahl der Polymerteilchen einen Durchmesser innerhalb von ±15% der mittleren Teilchengröße besitzen, umfassend die Schritte:

A) Auflösen, in einem hydrophilen organischen Lösungsmittel,

- eines Acrylsäurederivat-Monomers, das im organischen Lösungsmittel löslich ist, und ein Polymer erzeugen kann, das im organischen Lösungsmittel im wesentlichen unlöslich ist,
- eines polymeren Dispersionsstabilisators,
- eines oberflächenaktiven Dispersionscostabilisators,

B) Erwärmen der erhaltenen Lösung auf den Siedepunkt des organischen Lösungsmittels bei einer Rührgeschwindigkeit von weniger als 80 Umdrehungen je Minute,
C) Zugeben eines Polymerisationsstarters, um die Polymerisation zu beginnen.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das Acrylsäurederivat Methylmetacrylat ist.

9. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß ein Comonomer, ausgewählt aus der Klasse der Vinylderivate, zusammen mit dem Acrylsäuremonomerderivat zugegeben wird.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet daß das Comonomer ein Styrolderivat ist.

11. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß der polymere Dispersionsstabilisator ein Polyvinylpyrrolidon mit einem Zahlenmittel des Molekulargewichts im Bereich von 20.000 bis 60.000 ist.

12. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß der oberflächenaktive Dispersionscostabilisator eine nichtionische oberflächenaktive Substanz ist.

13. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das hydrophile organische Lösungsmittel ein aliphatischer Alkohol mit 1 bis 10 Kohlenstoffatomen ist.

14. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß der Polymerisationsstarter aus der Klasse der Starter vom Azotyp ausgewählt ist.

15. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die Polymerteilchen einen mittleren Durchmesser von 3 bis 7 µm aufweisen, wobei mehr als 99 Gewichts-% der Polymerteilchen einen Durchmesser innerhalb von ±15% des mittleren Durchmessers besitzen.

Revendications

1. Matériau photographique aux halogénures d'argent portant au moins une couche sensible à la lumière appliquée sur un support de base et au moins une couche externe insensible à la lumière comprenant des particules de polymère solubles dans les bases, polydispersées, et des particules de polymère insolubles dans les bases, monodispersées, ayant une granulométrie moyenne de 1 à 10 µm, dans lequel au moins 95% en nombre desdites particules de polymère ont un diamètre égal à la granulométrie moyenne à ± 15% près.

2. Matériau photographique aux halogénures d'argent de la revendication 1 caractérisé en ce que lesdites particules de polymère solubles dans les bases, polydispersées, comprennent des copolymères acide méthacrylique/méthacrylate d'éthyle contenant de 20 à 50% en poids d'acide méthacrylique.

3. Matériau photographique aux halogénures d'argent de la revendication 1 caractérisé en ce que lesdites particules de polymère insolubles dans les bases, monodispersées, comprennent un polymère acrylique.

4. Matériau photographique aux halogénures d'argent de la revendication 1 caractérisé en ce que lesdites particules de polymère insolubles dans les bases, monodispersées, comprennent du poly(métracrylate de méthyle).

5. Matériau photographique aux halogénures d'argent de la revendication 1 caractérisé en ce que lesdites particules

de polymère insolubles dans les bases, monodispersées, comprennent un copolymère méthacrylate de méthyle/ styrène.

6. Matériau photographique aux halogénures d'argent de la revendication 1 caractérisé en ce que lesdites particules de polymère insolubles dans les bases, monodispersées, possèdent un diamètre moyen de 3 à 7 μm, dans lequel plus de 99% en poids desdites particules de polymère ont un diamètre égal au diamètre moyen à ± 15% près.

7. Procédé pour produire des particules monodispersées ayant un diamètre moyen de 1 à 10 μm, dans lequel au moins 95% en nombre desdites particules de polymère ont une granulométrie égale à la granulométrie moyenne à ± 15% près, comprenant les étapes consistant à:

A) dissoudre dans un solvant organique hydrophile:

- un monomère dérivé d'un acide acrylique soluble dans ledit solvant organique et capable de former un polymère qui est essentiellement insoluble dans ledit solvant organique,
- un stabilisant de dispersion polymère,
- un co-stabilisant de dispersion tensioactif,

B) chauffer la solution obtenue au point d'ébullition dudit solvant organique, à une vitesse d'agitation inférieure à 80 tours par minute,
C) ajouter un amorceur de polymérisation pour démarrer la polymérisation.

8. Procédé de la revendication 7 caractérisé en ce que le dérivé d'acide acrylique est le méthacrylate de méthyle.

9. Procédé de la revendication 7 caractérisé en ce qu'un comonomère choisi dans la catégorie des dérivés vinyliques est ajouté au monomère dérivé d'acide acrylique.

10. Procédé de la revendication 9 caractérisé en ce que ledit comonomère est un dérivé du styrène.

11. Procédé de la revendication 7 caractérisé en ce que ledit stabilisant de dispersion polymère est une polyvinylpyrrolidone ayant une masse moléculaire moyenne en nombre dans la gamme de 20 000 à 60 000.

12. Procédé de la revendication 7 caractérisé en ce que ledit co-stabilisant de dispersion tensioactif est un tensioactif non ionique.

13. Procédé de la revendication 7 caractérisé en ce que ledit solvant organique hydrophile est un alcool aliphatique comportant de 1 à 10 atomes de carbone.

14. Procédé de la revendication 7 caractérisé en ce que ledit amorceur de polymérisation est choisi dans la catégorie des amorceurs de type azoïque.

15. Procédé de la revendication 7 caractérisé en ce que lesdites particules de polymère possèdent un diamètre moyen de 3 à 7 μm, dans lequel plus de 99% en poids desdites particules de polymère possèdent un diamètre égal au diamètre moyen à ± 15% près.