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(54) **Photographic assembly.**

(57) The preparation of monodisperse polystyrene beads is described. These polystyrene beads are of use in anti-block layers of photographic assemblies.

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Description

PHOTOGRAPHIC ASSEMBLY

This invention relates to a new photographic assembly which has an anti-static layer.

Static electricity is generated when an insulating material, such as film base, comes into close contact with another surface, e.g. a roller or another piece of film base and the two surfaces are then separated. When the accumulation of static charge reaches a critical point discharge sparks occur. When the film base carries a photosensitive layer a latent image is formed by this discharge and on photographic development a static mark is found to be present on the processed film material which can be of a feather form or a radical spot. Such marks are often of sufficient density to render the processed material useless. To reduce the incidence of static discharge various methods have been introduced such as earthing all the transport rollers in a film manufacturing plant. The other main method is to coat a so-called antistatic agent on one and/or other side of the film base. Such substances include antiblocking agents which form a rough surface on the film and prevent close contact with another surface. Mineral particles and in particular silica particles are often used in anti-block (anti-stick) layers but a number of disadvantages are encountered when using mineral particles. In most cases, materials are used which have a broad particle size distribution, which means that a high concentration of the matting agent is required, as it is the only larger particles that provide the antiblocking effect.

The presence of the smaller particles can lead to a "milky" appearance, which is undesirable when transparent images are required. The relatively high density of mineral particles may result in settling during coating, thus causing the particles not to be at the surface of the gelatin layer thus reducing their efficiency.

Hydrophobic polymer particles have also been employed as antiblocking agents. Fine dispersions of polymeric materials are obtained when the polymers are formed using emulsion polymerisation techniques. The particle sizes are, however, always less than 1 μm , which makes them unsuitable as antiblocking agents. Other methods are available to produce larger polymer particles between 1 and 10 μm , however the size distribution is usually very wide leading to a large proportion of undersized particles. It has proved difficult to prepare polymer particles with a predetermined particle size.

Polymethyl methacrylate (PMMA) is the most commonly used polymeric antiblocking agent in the photographic industry. Generally PMMA has a particle size distribution between 1 and 7 μm , with a mean value of 3.5 μm . The particle size distribution does not appear to be designed for this application, and is a result of the difficulty in preparing monodisperse particles.

In U.S. patent specification 4,614,708, a method for the preparation of polymer particles between 0.5 and 5 μm is reported. However even with this method a size distribution is observed.

Polystyrene particles have also been proposed to be used as antiblocking agents in the photographic industry, but the size distribution of the particles is also great.

It is the object of the present invention to provide a photographic assembly which comprises a layer having dispersed therein monosized particles of polystyrene. For example if the mean average size is 8 μm a size distribution of at least 90% of the particles is between 7.5 and 8.5 μm is considered to be monosized.

Therefore according to the present invention there is provided a photographic assembly which comprises on a base at least one silver halide emulsion layer and at least one gelatinous layer which comprises a dispersion of monosize solid spherical beads of polystyrene having a size between 2 and 15 μm , said beads having been prepared by a process of dissolving in a substantially non-aqueous solvent from 12 - 40 % by weight based on the solvent of styrene, from 0.5 - 3 % by weight based on the styrene of a free radical forming polymerisation initiator and as stabiliser a mixture of polyvinyl pyrrolidone and an anionic or a non-ionic surfactant, the amount of polyvinyl pyrrolidone being from 1.0 to 3.0 % by weight based on the total weight of the reaction mixture and the amount of the surfactant being from 0.2 to 1.5 % by weight also based on the total weight of the reaction mixture, the reaction mixture being heated to 68 - 72°C for at least 18 hours with continuous stirring and separating the polystyrene beads so formed. Preferably the size of the polystyrene is between 2 and 8 μm . Preferably the reaction time is from 18 to 36 hours.

Usefully a paddle stirrer is used in the preparation of the polystyrene beads and this is rotated between 20 - 150 r.p.m. during the reaction.

Preferably the substantially non-aqueous solvent used is ethanol as absolute alcohol or so called 99% industrial methylated spirits (IMS 99).

Other suitable non-aqueous solvents for use in the preparation of the polystyrene beads include for example ethylene glycol methyl ether, pentane, hexane, n-heptane, n-octane and cyclohexane, methanol and isopropanol. These solvents can be used alone or in admixture or mixed with ethanol.

For example suitable solvents are a 40:60 mixture of methanol and isopropanol and ethanol containing 10% of cyclohexane.

In order to obtain harder polystyrene beads up to 0.5 % weight/weight based on the styrene present of divinyl benzene may be used.

A particularly useful surfactant is the anionic sulphosuccinate range of surfactants. These are manufactured by American Cyanamid under the name of "Aerosol". (R.T.M.).

A particularly useful free radical polymerisation initiator is azobisisobutyronitrile.

In general it has been found that the more styrene there is present in the initial reaction mixture the greater

the particle size of the polystyrene beads which are formed. This is shown in the Example 1 which follows.

In order to exert its anti-blocking effect the layer which comprises the dispersion of polystyrene beads must be either a non-stress layer coated as a top layer on the silver halide emulsion layer or it must be coated on the side of the assembly distal to the silver halide emulsion layer as a top coating.

The photographic assembly of the present invention may comprise any type of silver halide emulsion layer or layers as used for black and white or colour photography. The photographic base may be any base used for photographic materials such as biaxially oriented polystyrene, polycarbonate or polyethylene terephthalate or a cellulose based material such as cellulose acetate-butylate or cellulose triacetate. Alternatively the base may be a polyethylene coated paper base. Static electricity is often generated by such paper bases but as the silver halide coated on paper base is usually not very light sensitive static discharge is usually not strong enough to form a latent image.

The preferred amount of polystyrene beads to be present in the gelatinous layer is from 0.01 to 20.0 g per 100 g of gelatin and most preferably from 0.1 to 5.0 g.

The gelatinous layer may be pure gelatin or it may comprise modified gelatin for example phthalated gelatin or it may comprise so-called gelatin extenders such as polyvinylpyrrolidone or polyvinyl alcohol.

The gelatinous layer may comprise additives in addition to the polystyrene beads. Examples of such additives are humectants, U-V absorbing compounds, electro-conductive compounds such as anionic fluorinated surfactants, coating aids and gelatin hardening agents such as formaldehyde.

When the layer which comprises the dispersion of polystyrene beads is coated on the side of the assembly distal to the silver halide emulsion layer or layers it may also act as an antihalation layer and comprise process dischargeable antihalation dyes.

Any of the known techniques used for the application of aqueous coating compositions may be used to coat the layer which comprises the dispersion of polystyrene beads. For example, the layer can be coated by spray coating, dip coating, swirl coating, extrusion hopper coating, curtain coating, air knife coating, or other coating techniques. The thickness of the coated layer will depend upon the particular requirements of the element involved. Typically, the dry weight coverage is in the range of 0.2 to 4 grams per square meter and most usually in the range from 1 to 3 grams per square meter.

Drying of the coated layer can be carried out over a wide range of temperatures. For example; temperatures of from 20°C to 130°C and preferably from 75°C to 115°C generally give satisfactory results.

When the photographic antiblock coating composition is applied indirectly to a polyester film support, a subbing layer is advantageously employed to improve the bonding of the antistatic layer to the support. Subbing compositions for this purpose are known in the art and include, for example, interpolymers of vinylidene chloride such as vinylidene chloride/acrylonitrile/acrylic acid terpolymers.

The following Examples will serve to illustrate the invention.

Example 1

Preparation of monodisperse polystyrene beads 2µm

At room temperature, polyvinylpyrrolidone 146.85g and anionic sulphosuccinate surfactant, 40.71 g, are dissolved in absolute alcohol 7270 g. Styrene 909 g (12.5 % wt/wt based on solvent), and initiator, azoisobutyronitrile 27.26 g are then added and the solution heated to 70°C for 24 hours.

A 10 l stainless steel vessel was employed with a two blade paddle stirrer (50 - 150 rpm) after 24 hours a stable alcohol dispersion of monodisperse 2 µm polystyrene microsphere beads are obtained. All of the ethanol was replaced by water to provide a stable aqueous dispersion of the polystyrene microspheres.

Preparation of monodisperse polystyrene beads 4µm

The preparation was carried out as above except that 1818g (25% wt/wt based on the solvent) of styrene was used. The size of the monodisperse polystyrene beads was 4 µm.

Preparation of monodisperse polystyrene beads 6 µm

The preparation was carried out as above except that 2726 g (37.5 % wt/wt based on the solvent) of styrene was used. The size of the monodisperse polystyrene beads was 6 µm.

Another similar preparation was carried out using 1818g of styrene. But the conditions were not controlled as rigorously as in the above preparation. For example the temperature was not maintained at 70°C for 24 hours but 55°C for 16 hours. The resultant polystyrene beads had a size range varying from 1 to 10 µm.

Preparation of photographic assembly

A photographic silver halide iodobromide emulsion comprising 40% iodide and having an average particle size of 0.5 µm was coated on a subbed polyethylene terephthalate film base. On this was coated by dip coating an aqueous coating solution which comprised a portion of the stable aqueous dispersion of the monodisperse polystyrene beads having a particle size of 2 µm sufficient to provide 5 g per 100 g of gelatin. This coating was dried to provide an anti-block layer.

Similar assemblies were made using the 4 µm and 6 µm polystyrene bead dispersions as just prepared and

also the 1 - 10 μm control polystyrene bead dispersion as just prepared.

Also as a further control an assembly was prepared which comprised only gelatin and no polystyrene beads in the top coating.

All the dried assemblies were then tested for their anti-block properties.

- 5 An adhesive tape was placed on the surface of all the photographic assemblies in contact with the bead-containing layer. No pressure was applied. The adhesive tape was of high quality with a very even coating of adhesive. The force required to separate the adhesive tape from the film bead-containing layer was then measured using a Instron table model 1026. The results are showing in the Table below (cross-head speed 50 cm/min; chart recorder speed 20 cm/min).

10 TABLE 1

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20 SAMPLE	FORCE (g)
25 GELATIN (NO ANTIBLOC)	135 g
30 POLYSTYRENE ANTIBLOC 1 - 10 μm	90 g
POLYSTYRENE ANTIBLOC 2 μm	60 g
POLYSTYRENE ANTIBLOC 4 μm	67 g
35 POLYSTYRENE ANTIBLOC 6 μm	73 g

40 The greatest force required to separate the adhesive tape was when no antibloc is present at all, due to a large surface area of contact. The force is reduced for the 1 - 10 μm size range. However there is a significant reduction in force required to separate the adhesive tape from the photographic assemblies containing the 2, 4 and 6 μm monodisperse polystyrene antibloc, when compared with the polydisperse polystyrene bead sample (1 - 10 μm).

45 This demonstrates the greater effectiveness of the monodisperse polystyrene antiblocking agents prepared according to the method hereinbefore set forth.

No adverse sensitometric effects were observed in the photographic film due to the inclusion of the polystyrene beads.

50 Example 2

55 Similar preparations of monodisperse polystyrene beads were carried out as in Example 1 except that the amount of styrene used and the solvent used was changed. These amounts of styrene and the solvent used are shown in the table below together with the mean size of the resultant polystyrene beads.

TABLE 2

			5
Weight of styrene	Solvent	Size of beads	10
1818 g	IMS 99	2 μm	15
2776 g	IMS 99	4 μm	20
2726 g	methanol 40% isopropanol 60%	4 μm	25
2626 g	absolute alcohol 90% cyclohexane 10%	6 μm	30

Claims

1. A photographic assembly which comprises on a base at least one silver halide emulsion layer and at least one gelatinous layer which comprises a dispersion of monosize solid spherical beads of polystyrene having a size between 2 and 15 μm , said beads having been prepared by a process of dissolving in a substantially non-aqueous solvent from 12 - 40 % by weight based on the solvent of styrene, from 0.5 - 3 % by weight based on the styrene of a free radical forming polymerization initiator and as stabiliser a mixture of polyvinyl pyrrolidone and an anionic or a non-ionic surfactant, the amount of polyvinyl pyrrolidone being from 1.0 to 3.0 % by weight based on the total weight of the reaction mixture and the amount of the surfactant being from 0.2 to 1.5 % by weight also based on the total weight of the reaction mixture, the reaction mixture being heated to 68 - 72°C for at least 18 hours with continuous stirring and separating the polystyrene beads so formed. 35
2. A photographic assembly according to claim 1 wherein the size of the polystyrene beads used was from 2 to 8 μm . 40
3. A photographic assembly according to claim 1 wherein the non-aqueous solvent used in preparation the gelatinous layer is ethanol. 45
4. A photographic assembly according to claim 1 wherein up to 0.5 % weight/weight based on the styrene of divinyl benzene is used to prepare the gelatinous layer. 50
5. A photographic assembly according to claim 1 wherein the surfactant used as the stabiliser in the preparation of the polystyrene beads is an anionic sulphosuccinate. 55
6. A photographic assembly according to claim 1 wherein the polymerisation initiator used in the preparation of the polystyrene beads is azobisisobutyronitrile. 60
7. A photographic assembly according to claim 1 wherein the amount of polystyrene beads present in the gelatinous layer is from 0.01 to 20.0 g per 100 g of gelatin. 65
8. A photographic assembly according to claim 7 wherein the amount of polystyrene beads in the gelatinous layer is from 0.1 to 5.0 g per 100 g of gelatin.
9. A photographic assembly according to claim 1 wherein the gelatinous layer containing the polystyrene beads is a supercoat layer over a silver halide emulsion layer.
10. A photographic assembly according to claim 1 wherein the gelatinous layer containing the polystyrene beads also comprises an anti-halation dye and is coated in the photographic assembly on the side distal to the photographic silver halide emulsion layer or layers.
11. A process for the reduction of the incidence of static discharge in a photographic silver halide assembly which comprises incorporating into a supercoat layer over a silver halide emulsion layer or a

layer coated onto the side of the assembly distal to the silver halide emulsion layer a dispersion of monosize solid spherical beads of polystyrene having a size between 2 and 15 μm , said beads having been prepared by a process of dissolving in a substantially non-aqueous solvent from 12 - 40 % by weight based on the solvent of styrene, from 0.5 to 3 % by weight based on the styrene of a free radical forming polymerisation initiator and as stabiliser a mixture of polyvinyl pyrrolidone and an anionic or a non-ionic surfactant, the amount of polyvinyl pyrrolidone being from 1.0 to 3.0 % by weight based on the total weight of the reaction mixture and the amount of the surfactant being from 0.2 to 1.5 % by weight also based on the total weight of the reaction mixture, the reaction mixture being heated to 68 - 72°C for at least 18 hours with continuous stirring and separating the polystyrene beads so formed.

12. A process for the preparation of a dispersion of monosize solid spherical beads of polystyrene, which comprises of dissolving in a substantially non-aqueous solvent from 12 - 40 % by weight based on the solvent of styrene, from 0.5 to - 3 % by weight based on the styrene of a free radical forming polymerisation initiator and as stabiliser a mixture of polyvinyl pyrrolidone and an anionic or a non-ionic surfactant, the amount of polyvinyl pyrrolidone being from 1.0 to 3.0 % by weight based on the total weight of the reaction mixture and the amount of the surfactant being from 0.2 to 1.5 % by weight also based on the total weight of the reaction mixture, the reaction mixture being heated to 68 - 72°C for at least 18 hours with continuous stirring and separating the polystyrene beads so formed.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	RESEARCH DISCLOSURE, no. 216, April 1982, page 109, abstract no. 21617, Havant, Hampshire, GB: "Use of monodisperse matte to improve resistance of photographic film to handling and coating defects" * Abstract *	1-12	G 03 C 1/76 G 03 C 1/82
Y	JOURNAL OF POLYMER SCIENCE: PART A: POLYMER CHEMISTRY EDITION, vol. 24, no. 11, 1986, pages 2995-3007, John Wiley & Sons, Inc.; C.M. TSENG et al.: "Uniform polymer particles by dispersion polymerization in alcohol" * Whole document *	1-12	
Y,D	EP-A-0 080 225 (AGFA-GEVAERT) * Page 2, line 23 - page 3, line 11 * & US-A-4 614 708	1-12	
A	US-A-4 022 622 (D.M. TIMMERMAN) * Whole document *		TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	CHEMICAL ABSTRACTS, vol. 104, no. 23, 9th June 1986, page 7, abstract no. 207786x, Columbus, Ohio, US; C.M. TSENG et al.: "Uniform polymer particles by dispersion polymerization in alcohol", & POLYM. MATER. SCI. ENG. 1986, 54, 362-6 * Abstract *		G 03 C 1/00
A	US-A-4 221 862 (K. NAITO et al.) * Whole document *		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23-08-1989	Examiner BOLGER W.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			