

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 569 074 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **93201135.6**

(51) Int. Cl.⁵: **G03C 5/17, G03C 1/005,
G03C 7/388**

(22) Date of filing: **20.04.93**

(30) Priority: **04.05.92 EP 92201228**

(43) Date of publication of application:
10.11.93 Bulletin 93/45

(84) Designated Contracting States:
BE DE FR GB NL

(71) Applicant: **AGFA-GEVAERT naamloze
vennootschap
Septestraat 27
B-2640 Mortsel(BE)**

(72) Inventor: **Vandenabeele, Hubert, c/o
Agfa-Gevaert N.V.
DIE 3800,
Septestraat 27
B-2640 Mortsel(BE)**
Inventor: **Lambrecht, Hendrik, c/o
Agfa-Gevaert N.V.
DIE 3800,
Septestraat 27
B-2640 Mortsel(BE)**

(54) **Method of preparing an aqueous solid particle dispersion of a photographically useful compound.**

(57) A method of preparing of fine, stable, homogeneous and reproducible silica particle dispersions of a photographically useful compound, to be incorporated before or during the coating procedure into at least one hydrophilic layer of a photographic material on at least one side of a support comprising the steps of dissolving a non-watersoluble but alkali-soluble compound in an aqueous alkaline solution, if necessary with the help of an organic water soluble solvent; precipitating the said compound from said solution in the presence of colloidal silica sol, preferably in the further presence of a dispersing agent by lowering the pH of the solution; removing water-soluble salts formed by the precipitation and any organic solvent used and concentrating the dispersion either during or after the precipitation by dialysis or ultrafiltration or after precipitation by flocculation and decantation, followed by washing and further decantation.

EP 0 569 074 A1

FIELD OF THE INVENTION.

This invention relates to dispersion methods for chemical compounds which are intended for incorporation in photographic silver halide materials and to photographic materials with coated layers incorporating dispersions prepared by such dispersion methods.

BACKGROUND OF THE INVENTION

It is well-known that before coating of layers in the manufacturing of a photographic silver halide material many ingredients, including e.g. spectral sensitizers or desensitizers, emulsion stabilizers or antifoggants, development activators or restrainers, filter, antihalation or screening dyes, colour couplers, hardeners, surfactants, thickening agents, anti static agents etc. are mixed in the reaction vessels wherein said coating compositions are prepared.

When such ingredients cannot be incorporated from aqueous solutions, or water-compatible solvents, they should be dispersed in the form of finely divided particles.

One general suitable dispersion method consists of ball-milling the compound in gelatinous medium. It is also possible to disperse an organic solution of the compound in an aqueous gelatinous medium followed by removal of the solvent e.g. by evaporation under vacuum.

Alkaline-soluble compounds can be incorporated by a dispersion method based on decreasing the pH (pH shift) of an aqueous alkaline gelatin solution.

All of these dispersion techniques have one or more disadvantages. The stability of the aqueous gelatin dispersion before or after incorporating into the gelatinous coating compositions is often unsatisfactory and leads to unreproducible results. When organic solvents are used compatibility problems with the aqueous gelatin composition may occur and the solvents themselves may be ecologically disadvantageous. The ball-milling process wherein metal or glass beads are used to pulverize the ingredients is a slow dispersion technique, requiring relatively complicated apparatus difficult to clean and presenting mechanical and thermal problem. The dispersions obtained are of relatively coarse particle size, difficult to reproduce both in particle size and particle size distribution.

The coarse particle size dispersions also have disadvantageous effects on the photographic characteristics as the physical and chemical properties are the better the finer the particle sizes are. For example colour couplers have improved coupling activity and dyes have improved light absorption.

Another disadvantage is that the aqueous gelatin compositions comprising dispersed ingredients, which are stored as such before being incorporated in the actual coating composition for forming the photographic layers, represent an extra amount of gelatin that is combined with the gelatin coating composition thus increasing the binder content of the photographic material and reducing the capability of rapid access processing after exposure due to the increased drying times necessary.

OBJECTS OF THE INVENTION

It is a first object of this invention to provide an easy, ecologically justified method requiring a simple apparatus to get a fine, stable and reproducible solid particle dispersion of a photographically useful compound within an acceptably short preparation time, providing improved characteristics for a coating composition for a photographic material.

It is a second object of this invention to provide a photographic material wherein said fine solid particle dispersions are incorporated in at least one of the layers of said material and show good physical and chemical stability in rapid processing conditions without effecting sensitometric characteristics.

Other objects will become apparent from the description hereinafter.

SUMMARY OF THE INVENTION

In accordance with the present invention a method is provided for the preparation of an aqueous solid particle dispersion of a photographically useful compound, for being incorporated in one of the layers of a photographic silver halide material, comprising the steps of

- dissolving a non-watersoluble but alkali-soluble compound in an aqueous alkaline solution, if necessary with the help of an organic water soluble solvent
- precipitating the said compound from said solution in the presence of colloidal silica sol, preferably in the further presence of a dispersing agent by lowering the pH of the solution,
- removing water-soluble salts formed by the precipitation and any organic solvent used, and

- concentrating the dispersion either during or after the precipitation by dialysis or ultrafiltration or after precipitation by flocculation and decantation, followed by washing and further decantation.

More particularly, lowering of the pH of the alkaline solution occurs by neutralizing with an aqueous acidic solution. The silica may be present in the aqueous alkaline solution and/or in the aqueous acidic solution or it may be present in a separate aqueous alkaline solution into which both the aqueous alkaline solution and the aqueous acidic solution are added.

Particularly in accordance with the present invention it has been found that fine, homogeneous and reproducible dispersions can be made with a relatively simple apparatus and within a reasonable preparation time of about one hour by the adsorption of finely divided silica particles onto flocculated or coagulated particles prepared by neutralization of an alkaline solution of a photographically useful compound in the presence of said silica particles and preferably, in the presence of a surfactant.

It has further been found in accordance with this invention that fine silica dispersions of dyes can be prepared for incorporation in at least one of the layers of a photographic material e.g. as filter, screening or antihalation dye, thereby showing an increased efficiency of light absorption, requiring a reduced coating amount of a dye and showing a high decolouration speed in the processing of said photographic material, making it particularly suitable for rapid processing applications.

It was further found that fine silica dispersions of colour couplers can be made which have high coupling activity.

DETAILED DESCRIPTION OF THE INVENTION

Silica is well-known as suitable hydrophilic binder for replacing gelatin in hydrophilic layers and more particularly in silver-halide emulsion layers. As has been disclosed in EP Application No 91.202082/3 an increased amount of silica sol used as a protective colloid in the preparation of silver halide emulsions results in an acceptable physical stability of the emulsion after coating.

According to the present invention aqueous alkaline-soluble compounds as e.g. dyes, dissolved in an aqueous alkaline solution having a pH value of at least 8.0, are precipitated by mixing the alkaline solution with an aqueous acidic solution in an aqueous silica medium under partially or fully controlled conditions of temperature, concentration, sequence of addition, and rates of addition. Preferably this precipitation may be performed in the presence of a dispersing agent which is an ionizable polymer and/or an amphoteric and/or a surface active agent present in the alkaline solution and/or in the reaction vessel to get a finely dispersed compound in a stable colloidal medium. Although it may be possible to put the alkaline solution into the reaction vessel and to acidify said solution by means of the single jet technique to the preferred pH value, it has to be recommended to precipitate the compound e.g. dye from the solution by means of the double jet technique under carefully controlled conditions at a constant pH value, adjusted in the reaction vessel containing the silica and/or dispersing agent(s). Of course the presence of silica and/or dispersing agent(s) is not limited to the reaction vessel: silica may be divided partially between the reaction vessel and the solution(s) to be added to said vessel. Making use of a so-called "pH-stat" it is possible to measure the pH value in the vessel continuously with a glass electrode and to derive the rate of addition of the acidic aqueous solution therefrom electronically so that it is possible to conduct this acidifying step in perfectly controlled conditions. This preferably constant value should be low enough to get a quantitative flocculate of the compound e.g. dye, a pH value lower than 6.0 being recommended and a value of about 3.0 being particularly preferred. The rate of addition of the alkaline solution strongly depends on the concentration of the alkaline solution, of the stirring rate and of the constant pH value to be maintained in the reaction vessel. The rate of addition of the alkaline solution to the reaction vessel and/or the stirring rate in the vessel may be increased during the precipitation procedure. Even continuous on-line preparation procedures are possible provided that the requirements mentioned in this paper concerning factors to be held constant are taken into account. In that case a continuous third stream with the solution normally present in the vessel is brought into contact in a small reaction vessel where the three streams are mixed with a stirrer followed by on-line diafiltration or ultrafiltration.

Depending on the chemical structure of the compound to be dispersed, determining its pKa values in aqueous solutions, the pH precipitation value can be chosen beforehand. It is clear that the preferred rate of addition of the aqueous alkaline solution also depends on the pH value of the aqueous alkaline solution of the compound or compounds and on the stirring rate in the vessel. Amounts of silica present in the reaction vessel with relation to the amount of compound may vary from weight ratios of 5/1 to 1/5.

The precipitated compound(s) prepared in accordance with the present invention is(are) very finely divided by using this technique and is(are) covered with a protective layer of silica particles, adsorbed onto the compound or coprecipitated with the compound. It is possible to store the very stable and concentrated

particle dispersions at room temperature for at least some weeks and even months before the ingredient is used in a coated layer of a photographic material.

Obviously the dispersability of an ingredient in silica strongly depends on the differences in pH values where the ingredient is fully ionizable or fully insoluble. If the pH values can be sharply defined it is possible to get very finely dispersed ingredients with a high quantitative yield and neglectable losses.

Since during the neutralization of the alkaline solution soluble alkali salts are formed, said salts should be removed to improve the stability and coating properties of the hydrophilic layer(s) in which the compound(s) should be incorporated. Desalting and concentration of the newly formed silica dispersion is possible using the well-known techniques as dialysis, ultrafiltration and flocculation, said last technique being described in the EP Application No. 517 961, filed June 11, 1991, for silver halide crystals with silica as a protective colloid. In the present invention, the ultrafiltration technique is preferred: in about half an hour it is possible to get a stable silica dispersion concentrated to about 6% and even to about 10% by weight for the compound although these higher values are not recommended as the viscosity may rise and as afterwards a dilution may become necessary before addition to coating compositions.

If compared with the well-known mechanical milling techniques in the presence of gelatin and surfactant taking at least 12 hours and sometimes several days, this technique really saves quite a lot of time. Furthermore qualitatively better and more reproducible fine solid particles are obtained with sizes of about 150 nm, whereas more irreproducible amorphous particles are formed by said mechanical milling techniques with a quite complicated energy consuming apparatus that has to be cleaned thoroughly before starting a new batch. Besides, there is no need to make use of an excessive amount of organic solvents, so that this technique is particularly favourable from an ecological viewpoint.

Any compound that is normally used in photographic materials can be dispersed in accordance with the present invention, provided that their chemical structure allows the essential condition of having a water-solubility depending on pH.

For example, according to the present invention aqueous-insoluble compounds as e.g. colour couplers without an ionizable soluble group are dissolved in a minimum amount of an organic solvent and added to an aqueous alkaline solution. The solution is slowly added, simultaneously with a neutralizing acidic solution to a reaction vessel containing a stirred aqueous dispersion of silica particles wherein preferably a suitable dispersing agent is present. These additions are preferably performed under partially or fully controlled stirring conditions of temperature, concentration, sequence of addition, and rates of addition. It should be recommended to perform this precipitation in the presence of at least one polymer and/or surfactant present in the reaction vessel to get a finely dispersed compound in a stable colloidal medium. It is of course possible to make any combination to make the required ingredients to come into contact with each other provided that the conditions are rigorously held constant to get a stable and reproducible solid particle dispersion, the name "solid" referring to the "silica particles" surrounding and stabilizing the aqueous-insoluble photographically useful compound.

It is clear that this handsome preparation technique to form stable and homogeneous "silica particle dispersions" may be applied to every photographically useful compound.

As an essential ingredient the usual silica sols are suitable for the process according to the invention. Suitable silica sols are commercially available such as the "Syton" silica sols (a trademarked product of Monsanto Inorganic Chemicals Div.), the "Ludox" silica sols (a trademarked product of du Pont de Nemours & Co., Inc.), the "Nalco" and "Nalcoag" silica sols (trademarked products of Nalco Chemical Co), the "Snowtex" silica sols of Nissan Kagaku K.K. and the "Kieselsoel", Types 100, 200, 300, 500 and 600 (trademarked products of Bayer AG). Especially colloidal silicas having a specific surface area between 100 and 600 m²/g are preferred.

It has to be recommended to add an auxiliary dispersing agent to the reaction vessel in the preparation step, although this is not always required. Said dispersing agent may be chosen from the classes of chemical compounds known as partially ionizable polymers and surfactants and may act as a synergetically working co-stabilizer. Any combination may be used to optimize the stabilization of the silica particle dispersion of the organic compound obtained.

Suitable co-stabilizing agents are surface-active agents which as is known have a hydrophobic moiety e.g. a long-chain aliphatic group or an aliphatic-aromatic group and a hydrophilic moiety e.g. an anionic or cationic group, an amphoteric group or a non-ionic group as ethylene oxide groups. They include surface anionic agents comprising an acid group such as a carboxy, sulphy, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonyl acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as alkylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. According to this invention said agents especially have the function of facilitating the

dispersive emulsification of ingredients in silicic acid during the preparation procedure. These surface-active compounds may e.g. be added to the reaction vessel, to the aqueous alkaline solution whether or not containing an organic solvent, of the ingredient to be dispersed or may be divided between those two solutions. Especially preferred are ampholytic compounds as 2-N,N,N-trialkylaminoacetic acid compounds.

5 The dispersing agents are preferably present in amounts from 1 to 20 % by weight versus the photographically useful compound.

The preparation procedure described hereinbefore may be applied to prepare fine, stable and homogeneous silica dispersions for all organic compounds that are normally used in dissolved or finely divided state in the coated layers of photographic materials as e.g. spectrally sensitizing or desensitizing dyes, 10 stabilizers, developers or developer accelerators, coupler compounds as DIR-couplers, coloured mask couplers and couplers, being coloured or uncoloured after coupling reactions with oxidised developer compounds as those used in colour photographic materials, coupler precursors etc..

If the organic compounds are not soluble in aqueous alkaline solutions due to the absence of an ionizable group auxiliary organic solvents may be used to dissolve said organic compound before addition 15 to an aqueous alkaline solution containing colloidal silica particles and preferably containing an auxiliary co-stabilizing dispersing agent. Preferred organic solvents are methyl alcohol, ethyl alcohol, isopropyl alcohol, tetrahydrofuran, dimethylformamide, dioxane, N-methyl-pyrrolidone, acetonitrile, ethylene glycol, ethyl acetate etc..

The aqueous solution is made alkaline with a base as sodium hydroxide. In the neutralization step 20 organic acids as acetic acid, propionic acid and the like are used or diluted anorganic acids as hydrochloric acid, sulphuric acid or phosphorous acid.

Obviously the dispersability of an aqueous-insoluble ingredient in silica strongly depends on the degree of partition obtained as a function of the relative amounts of the said ingredient, of silica and of ionizable polymer(s) and/or surfactant(s) present in the reaction vessel and of the stirring rate applied during the 25 neutralization step. Accordingly it is possible to get very finely dispersed ingredients with a high quantitative yield and neglectable losses when the procedure is fully optimized. The silica dispersion obtained may be concentrated making use of the techniques as have been described hereinbefore. It is clear that these very finely divided photographically useful compounds are characterized by a very high photographic activity, if compared with the compounds in a gelatinous dispersion prepared from ball-mill techniques and the like.

30 The following is a non-limitative list of photographically useful compounds of which dispersions can be made in accordance with the method of the present invention for incorporation in a photographic silver halide material.

Spectral sensitizers with methine groups may be used in accordance with this invention. Examples are e.g. described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. 35 Dyes that can be used for the purpose of spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, homopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes that can be dispersed in silica are those belonging to the cyanine dyes, merocyanine dyes and complex merocyanine dyes.

Other dyes, which per se do not have any spectral sensitization activity or certain other compounds, 40 which do not substantially absorb visible radiation, can have a supersensitization effect when they are incorporated together with said spectral sensitizing agents into a silver halide emulsion. Suitable supersensitizers that can be added as silica dispersions are i.a. heterocyclic mercapto compounds containing at least one electronegative substituent as described e.g. in US-A 3,457,078, nitrogen-containing heterocyclic ring-substituted aminostilbene compounds as described e.g. in US-A 2,933,390 and US-A 3,635,721, aromatic 45 organic acid/formaldehyde condensation products as described e.g. in US-A 3,743,510, cadmium salts, and azaindene compounds.

Compounds preventing the formation of fog or stabilizing the photographic characteristics during the production or storage of photographic elements or during the photographic treatment thereof may be added as dispersions of fog-inhibiting agent or stabilizer to the silver halide emulsion. Making use of silica 50 dispersions of such ingredients avoids the otherwise required addition of pH buffers. Suitable examples of stabilizers of which silica dispersions can be made are i.a. the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, 55 in particular 1-phenyl-5-mercapto-tetrazole, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione, oxazoline-thione, triazaindenes, tetrazaindenes and pentazaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in, GB-A 1,203,757, GB-A 1,209,146, JA-Appl. 75-39537, and GB-A 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-

pyrimidines as described in US-A 4,727,017.

These fog-inhibiting agents or stabilizers can be added to the silver halide emulsion prior to, during, or after the chemical ripening thereof and mixtures of two or more of these compounds can be used.

Other examples are additives such as e.g. compounds improving the dimensional stability of the photographic element, UV-absorbers, hardeners, plasticizers, coating aids, compounds preventing electric charges, compounds improving slidability, compounds preventing or reducing adhesion, compounds improving the photographic characteristics e.g. higher contrast, sensitization, and development acceleration. Preferred development accelerators are e.g. polyalkylene derivatives having a molecular weight of at least 400.

Further ingredients that may be incorporated from silica dispersions in hydrophilic layers are e.g. developing agents as dihydroxy benzene or derivatives, phenidones and the like, whether or not in combination with other organic compounds used in developers as e.g. stabilizers as benzotriazole and/or indazole or benzimidazole derivatives.

If necessary analogously prepared silica dispersions of UV-absorbers may be added such as i.a. aryl-substituted benzotriazole compounds as described in US-A 3,533,794, 4-thiazolidone compounds as described in US-A 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US-A 3,705,805 and 3,707,375, butadiene compounds as described in US-A 4,045,229, and benzoxazole compounds as described in US-A 3,700,455.

The silica dispersions of photographically useful compounds made in accordance with the present invention can be added to the coating composition of light-sensitive silver halide emulsion layers or of light-insensitive auxiliary layers known in the art of silver halide photography.

Suitable further additives for improving the dimensional stability of the photographic element comprising silica dispersions of ingredients according to the description given hereinbefore may be added, i.a. dispersions of a water-soluble or hardly soluble synthetic polymer e.g. polymers of alkyl (meth)acrylates, alkoxy(meth)acrylates, glycidyl (meth)acrylates, (meth)acrylamides, vinyl esters, acrylonitriles, olefins, and styrenes, or copolymers of the above with acrylic acids, methacrylic acids, Alpha-Beta-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphonylalkyl (meth)acrylates, and styrene sulphonic acids.

The same can be applied to plasticizers suitable for incorporation in the emulsion layers according to the present invention e.g. glycol glycerine, or the latexes of neutral film forming polymers including polyvinylacetate, acrylates and methacrylates of lower alkanols, e.g. polyethylacrylate and polybutylmethacrylate.

The light-sensitive silver halide emulsion can be a conventional emulsion or an emulsion made with silica as protective colloid according to the published EP Application 392,092.

If in the photographic compositions use is made of a gelatinous binder, said binder can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type e.g. 1,3-vinylsulphonyl-2-propanol, chromium salts e.g. chromium acetate and chromium alum, aldehydes e.g. formaldehyde, glyoxal and glutaraldehyde, N-methylol compounds e.g. dimethylolurea and methylol - dimethylhydantoin, dioxan derivatives e.g. 2,3-dihydroxy-dioxan, active vinyl compounds e.g. 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids e.g. mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The binders can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts. Even hardeners may be incorporated as a silica dispersion in a hydrophilic layer containing gelatin provided that hardening proceeds in the layers during processing at high pH values. In this case the hardener is present in the material as a "latent hardener", being inactive at lower coating pH values.

In the coating solutions of the photographic layers pH values of about 6.5 to 7.0 are measured, whereas in the developing step the application of a developing solution having a much higher pH value makes the pH value in the photographic layers to increase.

The dispersion technique according to the present invention is particularly suitable for ingredients that should be non-migratory during coating and drying as migration from one layer to another in the usually multi-layered photographic coatings would mutually disturb the photographic properties. These ingredients include non-spectrally sensitizing dyes which are used in a photosensitive silver halide emulsion layer as screening dyes, in an undercoat adjacent to the photosensitive layer and/or in a backing layer on the side of the support opposite to the photosensitive layer(s) to absorb reflected and scattered light thereby serving as antihalation dye or in an overcoat or interlayer to shield a particular photosensitive layer against undesired exposure being therefore referred to as filter or absorber dye, thereby adjusting the sensitivity of a photographic element as required in the manufacturing.

Such an absorber dye can e.g. be present in one or more filter layers between silver halide emulsion layers that are coated at opposite sides of a transparent film support of a duplitized X-ray recording material in order to improve image sharpness. The imagewise exposure of said recording material proceeds in a cassette between a pair of X-ray intensifying screens that each are held in contact with an adjacent silver halide emulsion layer. By said arrangement the imaging light that would cross the support and to some extent becomes scattered thereby, is considerably attenuated and cannot give rise to an unsharp image in an opposite silver halide emulsion layer.

The dye absorption spectrum should spectrally be approximately equal to the sensitivity spectrum of the corresponding silver halide emulsion in the layer of which a sharp image has to be reproduced. According to the method of this invention the amount of very fine, homogeneously divided silica dispersed dye can be reduced due to its enhanced photographic activity. The non-migratory dye dispersion is completely removed in rapid processing conditions as no colour stain is observed on the film afterwards.

Hydrophilic layers containing silica dispersions in accordance with the present invention may be coated on any suitable substrate such as, preferably, a thermoplastic resin e.g. polyethyleneterephthalate or a polyethylene coated paper support.

The ingredients prepared in accordance with the present invention may be added in silica dispersed form in various types of photographic elements such as i.a. in photographic elements for graphic arts and for so-called amateur and professional photography, diffusion transfer reversal photographic elements, low-speed and high-speed photographic elements, X-ray materials, colour materials etc..

The following examples illustrate the invention, without limiting it thereto.

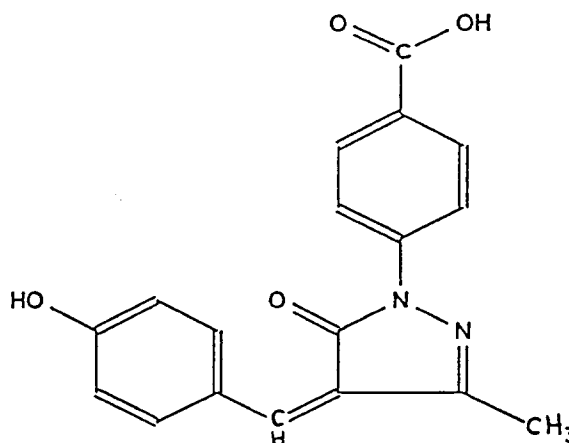
EXAMPLES

COMPARATIVE EXAMPLE 1

Comparative gelatinous dispersion of dye 1.

From dye 1, the formula of which is given hereinafter, a gelatinous dispersion was made by the ball mill technique using glass beads of zirconium oxide to pulverize the dye. After a total milling time of 6 hours a dispersion was obtained with 10 g of dye for a total weight of the aqueous dispersion of 40 g containing 15 g of gelatin, from which 12.5 g was added after the mechanical procedure was ended. As a result a very heterogeneous dispersion was obtained for particles with an average size of about 650 nm. Said dispersion was called the comparative dispersion GEL COMP.

formula of dye 1



EXAMPLE 1

Silica dispersion of dye 1.

A silica dispersion was made from dye 1, in a vessel containing an aqueous silica sol 'Kieselsol 500' (product of Bayer AG). Therefore an alkaline solution of dye 1 in demineralized water the pH value of which had been adjusted at 8.0 was added at a constant rate to said silica sol together with a solution of sulphuric acid which was added at a controlled rate of addition determined by the starting pH of 3.0 which was

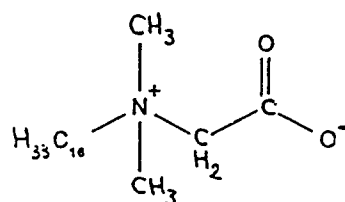
initially set up in the reaction vessel.

The procedure was carried out at room temperature for the reaction vessel, the acidic and alkaline solutions. During the double-jet addition the reaction mixture was stirred. After the end of the precipitation the ultrafiltration procedure was started. The resulting silica dispersion of dye 1 was called "SILICA A". With a nanosizer measuring instrument "Coulter Nano-Sizer TM" an average particle size diameter of 330 nm was measured.

EXAMPLE 2

Dispersion of dye 1 in a mixture of silica sol and surfactant 1 in the reaction vessel.

The dispersion called SILICA B was made in the presence of an amphoteric surfactant corresponding to the formula given hereinafter (surfactant 1). During the preparation of said dispersion the procedure was followed as for SILICA A except for the further presence of surfactant 1 in the reaction vessel. Nanosizer measurements gave an average particle diameter of 320 nm.



formula of surfactant 1

COMPARATIVE EXAMPLE 2

Dispersion of dye 1 in surfactant 1.

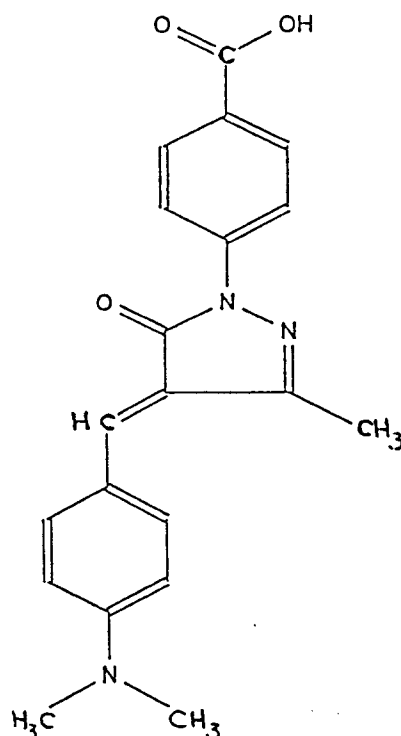
This dispersion called SURF COMP was made in the same way as SILICA A except for the presence of surfactant 1 in the reaction vessel instead of silica sol, surfactant 1 being present in an amount of 1g, added from an aqueous 1% solution of said surfactant.

EXAMPLE 3

Silica dispersions of dye 2.

A silica dispersion was made from dye 2, the formula of which is given hereinafter, in a vessel containing aqueous silica sol 'Kieselsol 500' (product of Bayer AG) by the addition of an alkaline solution of dye 2 the pH value of which was adjusted at 11.5 at a constant rate of addition and the simultaneous addition of a citric acid solution at a constant pH value of 3.0. The dispersion called SILICA C had an average particle diameter of 175 nm.

formula of dye 2



EXAMPLE 4

Dispersion of dye 2 in a mixture of silica and surfactant 1 in the reaction vessel.

The dispersion called SILICA D was made in the presence of the amphoteric surfactant 1. During the preparation of said dispersion the procedure was followed as for SILICA C except for the further presence of surfactant 1 in the reaction vessel added from an aqueous solution of 1% by weight of said surfactant to the reaction vessel. An average particle diameter of 250 nm was obtained.

EXAMPLE 5

Dispersion of dye 2 from an alkaline solution containing silica sol in a mixture of silica and surfactant 1 in the reaction vessel.

This dispersion, called SILICA E, was prepared in the same way as dispersion SILICA D, the only difference being the use of a ten times diluted silica sol. The pH value of this alkaline solution was adjusted at 11.5.

In Table I data of the evaluation of the different dispersions are summarized, comprising a qualitative analysis of its stability, its degree of homogeneity and the measurement of its dispersion particle sizes. The stability of the dispersion was evaluated qualitatively, the judgement being given to it expressed as "very good", "good" or "bad", depending on the degree of sedimentation of the solid particles standing in a beaker for at least 48 hours at room temperature in its dispersed form.

The size of the dispersion particles was measured with a "nanosizer" measuring apparatus "Coulter Nano-Sizer TM" as already mentioned hereinbefore.

The homogeneity was qualitatively determined by observation of photographs of the dispersion particles with a "scanning electron microscope" and qualitatively expressed as being "very homogeneous", "homogeneous", "heterogeneous" or "very heterogeneous".

Table I

Evaluation of the different dispersions.			
Name of the dispersion	Stability	Particle size (nm)	Homogeneity
GEL COMP (comparative ex.)	"bad"	650 nm	"very heterogeneous"
SILICA A (invention)	"good"	330 nm	"homogeneous"
SILICA B (invention)	"very good"	320 nm	"very homogeneous"
SURF COMP (comparative ex.)	"very bad"	not measurable	"not interpretable"
SILICA C (invention)	"good"	175 nm	"homogeneous"
SILICA D (invention)	"very good"	250 nm	"very homogeneous"
SILICA E (invention)	"very good"	220 nm	"very homogeneous"

Table I clearly illustrates that it is possible to get very fine, very stable and very homogeneous dispersion particles in the absence of any organic solvent by the formation of a "solid silica dispersion" in accordance with the present invention whether or not in the presence of a surfactant added to the silica sol.

EXAMPLE 6

Dispersion of COLOUR COUPLER COMPOUND 1.

A solution was made of COUPLER COMPOUND 1, the formula of which is given hereinafter, in ethanol/water 1/1 and the pH was adjusted to 11.0 with sodium hydroxide.

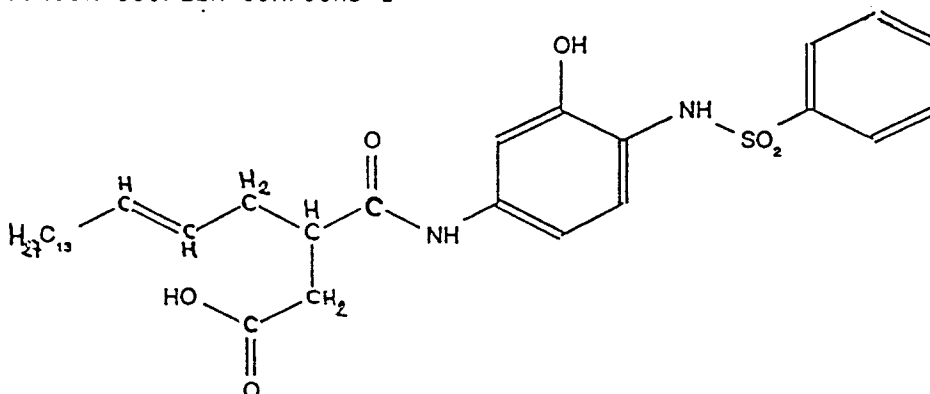
The preparation procedure described hereinbefore in example 1 was applied in the presence of silica sol and surfactant 1 as a co-stabilizer (see 1 in Table II); in the presence of silica sol without co-stabilizer (see 2) and in the presence of surfactant 1 as the only stabilizing agent (see 3). In Table II the evaluation is given of the corresponding "stability", "homogeneity" and "particle size", terms of which the definition is given hereinbefore. The organic solvent can be removed by dialysis.

Table II

Evaluation of the dispersions of COUPLER COMPOUND 1			
Number	Stability	Particle size (nm)	Homogeneity
1 (silica + co-stabilizer)	"very good"	75 nm	"homogeneous"
2 (silica)	"good"	80 nm	"homogeneous"
3 (co-stabilizer)	"bad"	not measurable	"not interpretable"

Table II clearly illustrates that it is possible to get very fine, very stable and very homogeneous dispersion particles in the presence of silica sol and a surfactant being present as a co-stabilizer.

formula of COLOUR COUPLER COMPOUND 1



EXAMPLE 7

Incorporation of silica dye dispersion in a photographic material.

From dye 2 a gelatinous dispersion was made as has been described for dye 1 in comparative example 1 and was called GEL COMP2.

The dispersion called SILICA D, the preparation of which has been described in example 4 and the evaluation of which has been given in Table I, being in accordance with this invention was incorporated in a filter layer of an X-ray material and compared with the incorporated GEL COMP2 dispersion. The preparation and coating procedure is given hereinafter.

Chromium (III) acetate as hardening agent and additional gelatin in amounts to obtain the same total amounts of gelatin in the filter dye layers were added to the above prepared dye dispersions kept at a temperature of 36 °C and pH 6.1.

Said dispersions were double-side coated and dried on a polyethylene terephthalate film support of 175 μm . thickness in order to obtain at each side a dye coverage of 0.025 g/m² for the SILICA D dispersion and of 0.075 g/m² for the GEL COMP2 dispersion respectively, a gelatin coverage of 1 g/m² and coverage of hardening agent of 0.016 g/m².

Said dyes being coated on both sides of a polyethylene terephthalate film support in an anti cross-over layer were overcoated with an emulsion and a protective layer, the silver halide emulsion being spectrally unsensitized.

Samples of these coatings were illuminated using a continuous wedge with blue light during 0.1 seconds and were processed under a 38 seconds processing cycle applied in rapid processing applications of X-ray materials and the cross-over was determined as described hereinafter.

Therefor the double side coated samples were placed between a single blue light emitting screen (CURIX BLUE: Agfa trade name) and a white paper replacing the second screen. This film-screen element, directed with its light emitting screen to the X-ray tube, was then exposed with varying doses (log E) of X-rays. After processing these samples in a 38 seconds rapid processing cycle, the minimal dose (log E) needed to obtain a density of 0.5 above fog was determined for the frontlayer (log E front) and the backlayer (log E back) separately. The % cross-over was then calculated according to the following equation

$$\% \text{ cross-over} = 100 / \text{antilog}(\log E \text{ back} - \log E \text{ front})$$

The density as a function of the light dose was measured and therefrom were determined the following sensitometric characteristics: fog level (with an accuracy of 0.001 density), the relative speed S at a density of 1 above fog (the sample with the gelatinous dispersion GEL COMP2 was set to a speed of 100), maximum density DMAX and the contrast calculated between the densities 0.25 and 2.0 above fog.

In table III the results of this photographic test are tabulated. This table shows that even with a threefold reduction in the amount of dye dispersion coated the cross-over percentage obtained with the SILICA D dispersion filter layer is lower than the value obtained with the GEL COMP2 dispersion. Moreover no residual colour could be observed.

Table III

Evaluation of the cross-over % in coated filter layers.					
FILTER DYE DISPERSION	FOG	SPEED	CONTRAST	DMAX %	CROSS-OVER
GEL COMP2	9	100	250	3.325	31.5
SILICA D	10	103	251	3.314	26.1

In the above anti cross-over layer the gelatin binder can be successfully replaced by other non gelatinous layers allowing lower swelling degree and faster drying e.g. a polyvinyl alcohol binder.

Claims

1. A method of preparing an aqueous solid particle dispersion of a photographically useful compound, for incorporation in one of the layers of a photographic silver halide material comprising the steps of

- dissolving a non-watersoluble but alkali-soluble compound in an aqueous alkaline solution, if necessary with the help of an organic water soluble solvent
- precipitating the said compound from said solution in the presence of colloidal silica sol, preferably in the further presence of a dispersing agent by lowering the pH of the solution,
- removing water-soluble salts formed by the precipitation and any organic solvent used, and
- concentrating the dispersion either during or after the precipitation by dialysis or ultrafiltration or after precipitation by flocculation and decantation, followed by washing and further decantation.

2. Method according to claim 1 wherein said precipitation in the presence of colloidal silica sol occurs in the further presence of a dispersing agent.

3. Method according to claims 1 or 2 wherein the pH is lowered by neutralizing with an aqueous acidic solution.

4. Method according to any of claims 1 to 3, wherein said precipitation is performed by simultaneous addition of an aqueous alkaline solution comprising the alkaline-soluble compound and an aqueous acidic solution, to a stirred solution comprising the total or partial amount of colloidal silica sol and of dispersing agent while keeping the pH constant, the rest of said amount if any being present in at least one of said solutions.

5. Method according to claim 4, wherein the constant pH value is adjusted to a value of less than 6.0.

6. Method according to any of claims 1 to 5, wherein said dispersing agent is a partially ionizable polymer or a surfactant or a combination thereof.

7. Method according to any of claims 1 to 6, wherein said photographically useful compound is present in a weight ratio versus said colloidal silica sol from 1:5 to 5:1.

8. Method according to any of claims 1 to 7 wherein the dispersing agent when present is present in an amount of 1 to 20 % by weight versus said compound.

9. Method according to any of claims 1 to 8, wherein the colloidal silica has a specific surface area between 200 and 600 m²/g.

10. Method according to any of claims 1 to 9, wherein said photographically useful compound is a dye, a stabilizer, a coloured or uncoloured coupler, a colour coupler precursor, a developing agent, a development activator, a hardener or a desensitizer.

11. Method according to any of claims 1 to 10, wherein said dispersing agent when present is a 2-N,N,N-trialkylamino-acetic acid.

12. Photographic material wherein a solid particle dispersion, prepared by a method according to any of claims 1 to 11, is incorporated into a hydrophilic layer before or during coating thereof on at least one side of a support.

13. Photographic material according to claim 12, wherein said photographic material is a duplitized X-ray material and said photographically useful compound is a filter dye present in a filter layer between the silver halide emulsion layer and a film support.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 20 1135

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.5)
X	US-A-5 079 134 (I.TOYA) * compounds I-1, I-16; claims * * column 4, line 59 - column 5, line 15 * -----	1-13	G03C5/17 G03C1/005 G03C7/388
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02 AUGUST 1993	Examiner BUSCHA A.J.
CATEGORY OF CITED DOCUMENTS			
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		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	