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PHOTOGRAPHIC MATERIAL

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The present invention relates to a process for the production of a photographic material containing at least one sensitive layer composed of a hydrophilic layer-forming colloid wherein at least one photographic emulsion of silver halide in a hydrophilic binding agent is emulsified in such a way that the particles of this photographic emulsion are separated from the layer-former by a hydrophobic macro-molecular product.

It is known to emulsify in an aqueous solution of a hydrophilic layer forming binding agent one or more photographic emulsions prepared by dispersing silver halide grains in a solution of a hydrophobic binding agent in organic medium.

According to British specification 524,154, wherein a method for preventing color couplers from diffusing is described, an organic solution of a hydrophobic binding agent containing not only the color coupler but also the sensitive silver salt, is emulsified in an aqueous solution of a hydrophilic layer-forming binding agent. Particularly photographic emulsions containing collodion as hydrophobic binding agent are concerned.

As one embodiment of that process it was disclosed that the siver halide grains to be emulsified in the organic solution of the hydrophobic binding agent, can be obtained by centrifugation of a gelatino-silver halide emulsion.

It is also known that one or more emulsions of silver halide in a hydrophilic binding agent can be emulsified in an organic solution of certain hydrophobic but water-permeable purely synthetical macromolecular compounds (B.P. 536.673) or of cellulose ethers (B.P. 718.404).

It is further known that a photographic emulsion prepared in a solution of a hydrophilic binding agent can be emulsified in a solution of the same or of an other hydrophilic binding agent. In this case the emulsification is based on a modification of the properties of the binding agent by the addition of certain hydrophilic polymers.

It is an object of the present invention to provide a novel and general method for obtaining stable emulsions in a hydrophilic layer-former from photographic emulsions prepared in a hydrophilic binding agent.

It is another object of the present invention to provide a novel photographic material containing at least one emulsion in a hydrophilic layer-former of a photographic emulsion in a hydrophilic binding agent.

Further objects will appear from the following description. These objects are accomplished by

(1) Emulsifying a photographic emulsion, prepared in a solution of a hydrophilic binding agent, in a solution of a hydrophobic macro-molecular product in an organic non water-miscible solvent, and

(2) Emulsifying the emulsion obtained in an aqueous solution of a hydrophilic layer-former.

In this way an emulsion with hydrophilic outer phase containing small drops of silver halide emulsion stabilized towards the surrounding aqueous solution by a thin envelope of hydrophobic macro-molecular substance can be obtained.

For the inner phase, any colloid or mixture of colloids allowing to prepare a photographic emulsion may be used. The photographic emulsion forming the inner phase can be an ordinary photographic emulsion or a photographic emulsion especially prepared for this purpose. This emulsion can possess a high content of gelatin or a high content of silver salt, which frequently is interesting for obtaining a great covering power or also the emulsion can possess a low content of binding agent since the hydrophilic binding agent plays the role of protective colloid.

For the outer phase, any hydrophilic colloid allowing to obtain a layer with appropriate physical properties can be used. The use as layer-former of a thermo-reversible gel (e.g. gelatin) allows to coat this emulsion, to solidify and to dry it just as an ordinary gelatin layer. By the use of a non-gellifying layer-former it is possible to coat and to dry without intermediate solidification.

It is also possible that the emulsion of photographic emulsion in organic solution of hydrophobic colloid be emulsified in water, that the emulsion thus obtained be coated and that the layer be overcoated with an aqueous solution of gelatin.

As hydrophobic macromolecular substance, soluble in organic medium, may be used polymers with good water-permeability as well as less permeable polymers. Indeed, the protective envelope can always be made as thin as to allow the passage of the developer. Sometimes it can be useful to choose a product as little water-permeable that for the development it is necessary to dissolve it partially by a preliminary bath or to make it permeable by the addition of an organic solvent such as alcohol or acetone to the developing bath.

As appropriate hydrophobic products can be cited cellulose derivatives and polyvinyl compounds such as polyvinyl acetals and co-polymers of vinyl compounds and maleic anhydride.

Although the colloid of the inner phase and that of the outer phase can be identical, it may be advantageous that the colloid of the inner phase shows a certain incompatibility towards that of the outer phase. E.g. a photographic gelatino-silver halide emulsion emulsified in polyvinyl alcohol as layer-former, or a photographic emulsion prepared by dispersion of silver halide in polyvinyl alcohol and emulsified in gelatin as layer-former is more stable than a photographic gelatino-silver bromide emulsion emulsified in gelatin as layer-former. This better stability can likewise be obtained in the case where both phases are composed of gelatin by an appropriate addition to the gelatin of the inner phase or to that of the outer phase in order to obtain a certain incompatibility towards the gelatin of the other phase.

Before coating the emulsion with the small drops it may be useful to evaporate wholly or partially the organic solvents. It may also be desirable to evaporate part of the water of the outer phase.

If the transparency of the layer leaves much to desire, this inconveniency can be remedied by e.g. making equal the refraction indices of the inner phase and of the outer phase e.g. by appropriate additions to one or the other phase or by suppressing the irregularities on the surface of the sensitive layer by applying another layer thereto.

For some applications color couplers can be added to the emulsions according to the present invention. No restriction is made as regards the place of these color couplers. Thus, the color couplers may be added to the inner hydrophilic phase, to the outer hydrophilic phase or to the hydrophobic envelope; they can also be added to two of these places or even to all three.

The color coupler can also be replaced by a color developing substance, the coupler itself being added either to a treating bath or to the photographic material too. Indeed, it is also possible to add the color coupler as well as the developing substance to the emulsion or to the envelope or also one to the emulsion and the other to the envelope. The color coupler and/or the color developing substance can be linked in a chemical way to one of the three binding agents.

It is also possible to mix two or more emulsions as described above, which differ among each other e.g. by their photographic properties or by the kind of additions such as the color couplers, before coating them on a support. The binding agents and/or the solvents of these emulsions can be the same or different. Moreover, for the outer phase a colloid optionally containing a color coupler and wherein a photographic emulsion is prepared by dispersion of silver halide, can be used.

It is further possible that two or more emulsions of photographic emulsions in an organic solution of a hydrophobic colloid be consecutively emulsified in the same solution of hydrophilic layer-former.

The uses of such emulsions are widely varying in the field of black-and-white photography as well as in the field of color photography. The great choice of macromolecular products available for the envelope allows to produce it in such a way that it effectively prevents the diffusion of the sensitizers. It can also prevent the diffusion of the color couplers and it is even capable of retarding the development of the surrounded emulsion. E.g. the difference in development rate between silver bromide and silver chloride could be accentuated by surrounding the silver bromide with an envelope. In general, an appropriate choice of the envelope will enable a selective development.

In a more concrete way, the following uses can be cited;

In the field of black-and-white photography by mixing emulsions according to the present invention a photographic material can be produced, which although containing only one sensitive layer gives different gradations in function of the colour of the exposing light.

In the same way, emulsions with other properties can be mixed e.g. a very sensitive emulsion with soft gradation and a little sensitive emulsion with vigorous gradation and sensitized to a region of the spectrum to which the other is not sensitive, in such a way as to obtaining a photographic material capable of giving excellent tone reproduction.

Moreover, the invention allows to obtain a finer granulation. The envelope of insoluble polymer seems to inhibit extension of the grain during development as well as contagious development.

Since not only gelation can be used as soluble polymer of the outer phase, but also polyvinyl alcohol or an other binding agent, the choice of the binder allows to influence to a great extent the physical properties of the layer.

In the field of color photography, the possible uses are very numerous too.

Three photographic silver halide emulsions with different spectral sensitivity and provided each with a color coupler can be emulsified as above and next they can be coated in three superposed layers or mixed and coated in a single layer. Instead of being in the inner phase, the color coupler can be in the envelope or in both. It is also possible to emulsify in the way described above only two of these photographic emulsions, to mix the emulsions thus obtained and to apply the mixture to a photographic support. For trichromatic photography, a layer of a third photographic emulsion must be applied in any way whatever, either over or under the layer of the mixed emulsions. The third photographic emulsion can also form the outer phase of the mixed emulsion.

The layer of the mixed emulsion can contain a simple color coupler giving different color with different developers. One of the emulsions must then selectively be color developed without the other being affected by this first color-development. To this phase effect one of the emulsions can be composed of an other silver halide or be surrounded with a thin envelope having a greater or an other permeability, or also that of the emulsions, containing the color coupler which must react with the first developer, can be used as layer-former wherein the small drops of the other emulsion surrounded with a thin envelope are dispersed. In this way, e.g. a non-sensitized silver bromide emulsion can be emulsified in a green- or red-sensitized silver chloride emulsion. The emulsion thus obtained can contain a color coupler in the photographic emulsions of the inner phases or in the binding agents of the thin envelope or of the outer phase or also this coupler can be dispersed all over the layer. This color coupler must be chosen in such a way that it gives magenta or blue-green in one developer and yellow in another.

If the thin envelopes possess a different permeability, i.e. if they are e.g. permeable to photographic baths containing organic solvents in different concentration or of different kind, two or three photographic emulsions can be selectively treated. In this case, no matter whether the photographic emulsions are coated in different layers or mixed and coated in a single layer, the color coupler if it gives different colors with different developers can be added to the developer or even to the layer-forming binding agent.

Hereinafter follow some examples which illustrate our invention without limiting however, the scope thereof.

Example 1

50 cm.³ of a gelatino-silver bromide emulsion with soft gradation are mixed with 0.6 cm.³ of an aqueous solution 10% of the copolymer of styrene and maleic anhydride obtained from equimolecular quantities of the two monomers.

5 g. of polyvinyl butyral known under the registered tradename "Pioloform BS" and dissolved in 25 cm.³ chloroform, 25 cm.³ amylalcohol and 45 cm.³ carbon tetrachloride.

The photographic emulsion is emulsified in the polyvinyl butyral solution by means of a colloid mill or by a homogenizer.

50 cm.³ of a silver bromide emulsion with vigorous gradation and 50 cm.³ of an aqueous solution of gelatine 6% are mixed; 0.5 cm.³ of an alcoholic solution of bis-2-(3-ethyl-benzoxazol)-trimethine-cyanine bromide 0.1% is added. To this mixture 10 cm.³ of an aqueous solution of the product known under the registered tradename "Ethofat 142/60" is added.

To this emulsion is then added slowly, whilst thoroughly sitrring, the emulsion of the first photographic emulsion in polyvinyl butyral.

The complex emulsion thus obtained is very stable, can repeatedly be solidified and melted and coated and dried as an ordinary emulsion.

On the photographic material produced in this way, images with a softer or more vigorous gradation can be obtained according to whether during exposure the ratio of green-light to blue-light is greater or smaller.

Example 2

5 g. polyvinyl butyral known under the registered tradename "Pioloform BS" are dissolved in 25 cm.³ chloroform, 25 cm.³ amyl-alcohol and 45 cm.³ carbon tetrachloride.

50 cm.³ of a gelatino-silver bromide emulsion with soft gradation are emulsified in this polyvinyl butyral solution.

50 cm.³ of a silver bromide emulsion with vigorous gradation and 50 cm.³ of an aqueous solution of gelatin 6% are mixed; 0.5 cm.³ of an alcoholic solution of bis-2-(3-ethyl-benzoxazol)-trimethine-cyanine bromide 0.1% are added.

To this mixture is added 1.2 cm.³ of an aqueous solution of the copolymer from equimolecular quantity of styrene and maleic anhydride 10%.

10 cm.³ of an aqueous solution of "Ethofat 142/60" 10% are added.

To this emulsion is slowly added whilst thoroughly stirring the emulsion in polyvinyl butyral of the first photographic emulsion.

The complex emulsion thus obtained is very stable,

can be repeatedly solidified and melted and coated and dried as an ordinary photographic emulsion.

On the photographic material produced in this way images with a softer or more vigorous gradation can be obtained according to whether during the exposure the ratio of green light to blue light is greater or smaller.

Example 3

50 cm.³ of a slow gelatino-silver bromide emulsion with vigorous gradation and 0.6 cm.³ of a copolymer solution as in Example 1 are mixed and as in said example 5 g. of a polyvinyl acetal is dissolved but this time the polyvinyl acetal known under the registered trade-name "Alvar 17/70" is used and in the solution obtained the photographic emulsion is emulsified.

50 cm.³ of a very sensitive gelatino-silver bromide emulsion with soft gradation and 50 cm.³ of an aqueous gelatin solution 6% are mixed, 0.50 cm.³ of an alcoholic solution of bis-2-(3-butyl-5-methyl-1,3,4-thiodiazol)-trimethine-cyanine iodide 0.1% are added.

10 cm.³ of an aqueous solution of saponine 10% are added. To this emulsion is slowly added whilst thoroughly stirring the emulsion of the first photographic emulsion.

The complex emulsion obtained in this way possesses the same physical properties as that of Example 1.

By exposure to light of different colour the photographic material obtained from such an emulsion allows to obtain fine tone reproduction and is particularly interesting for the graphic arts.

Example 4

As in Example 1, 50 cm.³ of a gelatino-silver bromide emulsion are emulsified in a solution of polyvinyl acetal by means of a colloid mill or of a homogenizer. Whilst thoroughly stirring, this emulsion is emulsified in 150 cm.³ of an aqueous solution of polyvinyl alcohol 5% to which 10 cm.³ of an aqueous solution of "Ethofat 142/60" 2% has been added. After coating the complex emulsion thus obtained on a photographic support, a layer quite resisting to friction is obtained.

Example 5

5 g. polyvinyl butyral known under the registered trade-name "Pioloform BS" are dissolved in 25 cm.³ chloroform, 25 cm.³ amyl alcohol and 45 cm.³ carbon tetrachloride. In this solution 50 cm.³ of a silver bromide emulsion in polyvinyl alcohol are emulsified. Whilst thoroughly stirring, the new emulsion thus obtained is emulsified in 150 cm.³ of an aqueous solution of gelatin 5% to which 10 cm.³ of an aqueous solution of the product known under the registered trade-name "Ethofat 142/60" 10% have been added. The complex emulsion finally obtained can be coated, solidified and dried in the usual manner.

Example 6

To 50 cm.³ of a silver bromide emulsion with normal gradation, mixed with a copolymer of styrene and maleic anhydride as in Example 1, 0.5 of color coupler, e.g. F 546 described in "Fiat Final Report" 943, p. 68, are added. This mixture is emulsified in 100 cm.³ of a solution in chloroform of 10 g. of the product known under the registered trade-name "Hostalit CAM" which is a copolymer of vinyl chloride, vinyl acetate and maleic anhydride. The emulsion thus obtained is emulsified in 150 cm.³ of an aqueous solution of gelatin 5% After coating, exposure and color-development, a cyan image is obtained.

Example 7

From photographic emulsions with normal gradation, two emulsions as described in Example 1 are prepared, one being green-sensitized and containing a magenta color coupler and the other being red-sensitized and containing a cyan color coupler. Each emulsion thus obtained is emulsified in 150 cm.³ of an aqueous solution of gelatin 5% and next the two complex emulsions are thoroughly mixed. After coating and drying, a yellow filter-layer is applied, unless a filter dyestuff has been incorported already in one of the phases of the sensitive layer. An ordinary non-sensitized photographic emulsion containing a yellow color coupler is coated on the yellow filter or occasionally on the sensitive layer. After exposure to light and color development three different colors are obtained.

Example 8

From photographic emulsions with normal gradation, three emulsions as described in Example 1 are prepared, which are sensitive to different regions of the visible spectrum and contain different color couplers. The red-sensitized photographic emulsion and the green-sensitized one are silver chloride or silver chlorobromide emulsions. Each emulsion thus obtained is emulsified in 150 cm.³ of an aqueous solution of gelatin 6% and next the three new and complex emulsions thus produced are mixed. After coating, drying, exposure to light and color-development, a different color in each of the three inner phases is obtained.

Example 9

From photographic silver chloride emulsions with normal gradation two emulsions are prepared as described in Example 1, one green-sensitized and containing a magenta color coupler and the other red-sensitized and containing a cyan color coupler. Each emulsion thus obtained is emulsified in a photographic emulsion only sensitive to blue and containing a yellow color coupler. Next, the two new complex emulsions thus produced are mixed. After coating, drying, exposure to light and color development, three different colors are obtained in the three distinct sensitive phases.

Example 10

Three emulsions are prepared as in Example 1 from photographic emulsions with normal gradation, sensitive to different regions of the visible spectrum. The polyvinyl acetal solution, however, contains a different color coupler for each emulsion. The red-sensitized photographic emulsion and the green-sensitized one are silver chloride or silver chlorobromide emulsions. Each emulsion thus obtained is emulsified in 150 cm.³ of an aqueous solution of gelatin 6%, and the three new complex emulsions thus produced are mixed. After coating, drying, exposure to light and color-development, a different color is obtained in each of the three inner phases.

We claim:

1. A process for making a composition for use in the manufacture of light-sensitive photographic material, which comprises the steps of preparing a solution of a copolymer of vinyl chloride, vinyl acetate and maleic anhydride in a water-immiscible organic solvent, mixing an aqueous gelatin silver halide dispersion with said solution for the purpose of emulsifying said dispersion, and mixing the emulsion thus obtained, for the purpose of emulsifying said emulsion, with an aqueous solution of a hydrophilic layer-forming binding agent selected from the group consisting of gelatin and polyvinyl alcohol.

2. A light-sensitive photographic material containing at least one emulsion layer prepared by mixing a light-sensitive emulsion into a hydrophilic layer-forming binding agent selected from the group consisting of gelatin and polyvinyl alcohol, thereby emulsifying the light-sensitive emulsion, a said light-sensitive emulsion being prepared by mixing an aqueous gelatin silver halide dispersion with a solution of a copolymer of vinyl chloride, vinylacetate, and maleic anhydride in a water-immiscible organic solvent and thus emulsifying said dispersion.

3. A light-sensitive photographic material containing at least one emulsion layer prepared by mixing a light-sensitive emulsion with a hydrophilic layer-forming binding agent selected from the group consisting of gelatin and polyvinyl alcohol, thereby emulsifying said light-sensitive

emulsion, the light-sensitive emulsion being prepared by mixing an aqueous gelatin silver halide dispersion and a copolymer of styrene and maleic anhydride with a solution of a copolymer of vinyl chloride, vinyl-acetate, and maleic anhydride in a water-immiscible organic solvent.

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