PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in and relating to Light-Sensitive Multi-Layer Material for use in Colour Photography or Cinematography

I, Dr. BELA GASPAR, a Subject of the King of Roumania, of 42, Avenue Victor Rousseau, Brussels-Forest, Belgium, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in light-sensitive multi-layer photographic material for use in colour photography or cinematography.

For many purposes in connection with colour photographic and cinematographic processes it is desirable to produce a multi-layer material, the colour or colours of which does or do not bleed or do not diffuse from one coloured layer into an adjacent layer which may be either colourless or may be differently coloured. It has been proposed with the object of preventing this wandering of dyestuffs to mordant the dyestuffs used for dyeing the gelatine by treating the layer after dyeing with metal salts. It has also been proposed to precipitate the dyestuff within the emulsion prior to pouring the same on to the support. Furthermore, for the same purpose it has been proposed to cause mutual precipitation of dyestuffs of contrary reaction or to effect double decomposition of dyestuffs and precipitating agents, a difficultly soluble salt of the dyestuff being formed by this double decomposition (my prior Patents Nos. 415,756 and 428,158). It has also been proposed to prevent diffusion of the dyestuffs present in adjacent layers of a multi-layer material by the formation at the boundary zone of such layers of a finely dispersed dyestuff precipitate produced by mutual precipitation of the dyestuffs contained in each of the layers or of one dyestuff contained in one of the layers and a colourless precipitating agent present within the other layer.

It has been found, however, as the result of experiment which I have made that such dyestuff precipitates in the boundary zone of mutually superimposed layers whilst capable of preventing the diffusion of the dyestuffs already present in the adjacent layers do not prevent the diffusion of dyestuffs from aqueous solutions through the boundary zone into the deeper strata of the gelatine. Even with thick layers of gelatine which contain a precipitating agent and in which a very finely dispersed dyestuff precipitate is formed by treating with the aqueous dyestuff solution it has been proved that there is no difficulty for complete dyeing of the gelatine.

For example, it has been found that a gelatine layer containing diphenyl-guanidine acetate allows penetration of a solution of 1% strength of Diamine Pure Blue (Schultz Farbstofftabellen 5th Ed. No. 426). An insoluble diphenyl-guanidine salt is formed at the surface of the layer, but nevertheless the penetration of the dyestuff solution is not inhibited and further quantities of the dyestuff are precipitated within the deeper strata of the gelatine layer. When the treatment with the solution of the blue dyestuff is interrupted or stopped and is continued, for example, with a solution of Xylene Light Yellow 2G (Schultz, loc. cit. No. 22) the deepest stratum of the gelatine will be dyed yellow. These phenomena may be used for dyeing gelatine layers and more particularly for the selectively dyeing of gelatine layers for photographic purposes.

The light-sensitive photographic multi-layer material according to the present invention is of the known type including one or more uncoloured layers and at least one layer containing a dyestuff in such a form that it is incapable of being washed out of said layer by an aqueous solution but capable of being locally destroyed under the influence of the photographic image, and is characterised in that at least one of said uncoloured layers contains a precipitating agent capable of forming a dyestuff precipitate when treated with an aqueous solution of the dyestuff with which the said layer is to be subsequently coloured.

The precipitating agent is such that it

[Price 1/-]

is not affected by the exposure of the material and, if the layer containing the same is not treated with the dyestuff solution until after the image has been developed, is further such that it is not washed out by the photographic developer.

The said uncoloured layer or layers may also contain one or more dyestuff-forming compounds, the dyestuff or dyestuffs formed from which is or are precipitated by the precipitating agent or agents present in the layers or layer.

The addition of the precipitating agent to the uncoloured layer or layers of the multi-layer material and the subsequent dyeing with a dyestuff, which is precipitated by the agent present within the layer, has many advantages, for example, even a layer which is not situated on the surface of the multi-layer material may be selectively dyed and the colouration so obtained does not diffuse or bleed. Then the dyestuffs are uniformly applied to and precipitated within the layers or part-layers and may be locally destroyed at the image or non-image parts of the layer by the use of the known dyestuff destroying processes (see, for example, my prior Patent No. 397,159).

A plurality of superimposed layers may be dyed with different colours, either by using, for example, in the layers precipitating agents which selectively precipitate the two different dyestuffs or by using successively two dyestuff solutions, the first used solution only reacting with the precipitating agent in the first layer, thereby leaving the precipitating agent in the deeper part layer available to effect the precipitation with the second used dyestuff solution. When using a plurality of precipitating agents the agent for the deeper layer is applied to the gelatine or emulsion prior to coating. The precipitating agent for the top layer may be applied after dyeing the deeper layer and the second dyestuff solution is then applied subsequently.

EXAMPLE 1.

A solution of 5 grms. gelatine in 80 ccs. water is mixed with a solution of 1 grm. beta-naphthoquinolinium-N-ethyl sulphate and is poured as one layer of a multi-layer material on to a support. The layer is subsequently treated with an aqueous solution of 1% strength of Diamine Pure Blue FF (Schultz, loc. cit. No. 424).

EXAMPLE 2.

A layer as described in Example 1 is treated with a solution of ½% strength of Diamine Fast Red F (Schultz loc. cit. No. 343).

EXAMPLE 3.

A silver bromide gelatine emulsion is coloured yellow by adding 2-phenyl-4-amino-quinoline hydrochloride and Metanil Yellow (Schultz loc. cit. No. 134). The emulsion is a sensitized emulsion, containing, for example, pinacyanol. After coating a colourless silver bromide gelatine emulsion containing 3 grm. diphenyl-guanidine-acetate per sq. m. is coated on top of the yellow layer. After exposure, development and fixing, the film is treated with a solution of Diamine Pure Blue FF of 1% strength.

EXAMPLE 4.

A silver bromide gelatine emulsion is dyed with Chloratine Light Yellow (a dyestuff furnished by the Gesellschaft fur Chemische Industrie, Basle, Switzerland) the dyestuff being precipitated by barium nitrate. The emulsion is poured on a support and on top of the yellow layer a colourless silver bromide gelatine emulsion containing 3 grms. of cinchonine hydrochloride per sq. m. is poured. The yellow layer may contain a sensitizer for red light or for green light, the top layer being an ordinary blue-sensitive emulsion layer. After exposure the surface layer is treated with a solution of 1% strength of Diamine Pure Blue or with a solution of Diamine Fast Pink BBF. The film is then developed and fixed and the dyestuff is destroyed, for example, by a thiocarbamide solution at the points where silver is present.

EXAMPLE 5.

A silver halide emulsion containing 0.3% of tannin is poured on to a support of celluloid. On top of this colourless layer is poured a layer containing Diamine Pure Blue precipitated by triphenyl-guanidine acetate. The composite film is treated after exposure with an aqueous solution of ¼% strength of Auramine (Schultz loc. cit. 493) and is washed in water until the upper layer has become pure blue. The film as a whole appears green

Instead of the dyestuffs used in the preceding examples other dyestuffs may be used which are precipitated by the precipitating agent contained in the layer. For dyeing of the deeper layers dyestuffs are used which do not dye the already coloured upper layer but can be removed from the upper layer by washing. For dyeing of the surface layer acid and substantive dyestuffs are preferred and therefore precipitating agents are used which form insoluble salts by double decomposition with acid or substantive dyestuffs. There may be used, for example, the salts of organic bases, such as naphthoquinoline, triphenyl-guanidine, quinine, cinchonine, amino-quinoline. The salts formed by these bases with organic acids

or the quaternary salts derived from the amines may be used. Other precipitating agents which may be used are inorganic bases or salts, such as barium carbonate or magnesium carbonate. For the precipitation of basic dyestuffs, such as chrysoidine (Schultz loc. cit. No. 33) or Janus-red B (Schultz loc. cit. No. 240) antimony salts or zinc-ferrocyanide may be used or acids, such as tannic acids which form insoluble salts with basic dyestuffs. The amount of the precipitating agent and the methods of using the layers are substantially the same as in the foregoing examples.

Instead of the dyestuff solutions described, there may be used solutions which do not contain a dyestuff itself, but which form a dyestuff by interaction with dyestuff-forming substances present in the material. For example, a layer may be used which contains a leuco-derivative of a vat-dyestuff and a precipitating agent for the vat-dyestuffs. When such a layer is treated with an oxidizing agent the dyestuff is precipitated *in situ* by the precipitating agent and there is no possibility for bleeding or diffusion of the dyestuff.

In the process according to the present invention the dyestuff is uniformly applied from aqueous solutions and by the presence of precipitating agents the amount of dyestuff and the selective dyeing of different strata of the material is rendered possible.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A light-sensitive photographic multi-layer material having one or more uncoloured layers and at least one layer containing a dyestuff in such a form that it is incapable of being washed out of the said layer by an aqueous solution but capable of being locally destroyed under the influence of the photographic image, characterised in that at least one of said uncoloured layers contains a precipitating agent capable of forming a dyestuff precipitate when treated with an aqueous solution of the dyestuff with which the said layer is to be coloured.

2. A light-sensitive photographic multi-layer material according to Claim 1, characterised in that the precipitating agent present is capable of precipitating dyestuffs of different colours, for example, purple-red and blue dyestuffs.

3. A light-sensitive photographic multi-layer material according to Claim 1, characterised in that, in addition to the precipitating agent, the said uncoloured layer includes a dyestuff-forming substance which, subsequent to exposure, is converted into a dyestuff to dye the layer, the precipitating agent and the dyestuff-forming substance included in the uncoloured layer being such that the precipitating agent will precipitate the dyestuff when formed.

4. A light-sensitive photographic multi-layer material according to any of the preceding Claims 1 to 3, characterised in that the precipitating agent is an organic base or salt.

5. A light-sensitive photographic multi-layer material according to any of the preceding Claims 1 to 4, characterised in that the precipitating agent or agents present in the one or more uncoloured layers of the material is or are such that it or they are unaffected by the photographic developer with which the same is treated after exposure.

6. The improved light-sensitive photographic multi-layer material, substantially as hereinbefore described.

Dated this 20th day of June, 1936.

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