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COLORED PHOTOGRAPHIC MATERIALS AND METHOD OF PRODUCING THEM

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This invention relates to a method of producing colored photographic materials.

It is already known for the purpose of producing color photographs to incorporate dyestuffs in photographic layers, and to fix these by a mordanting process or by the formation of a deposit. In this connection, however, it has been found that various dyestuffs reveal the tendency to separate again subsequently from the mordant. Beyond this, the inorganic salts proposed for this purpose are very disturbing in the layer, as the same may readily react with the photographic bath or take effect on the silver halide.

It has been found that diffusion of the dyestuffs in the layer may be prevented to a very considerable extent if salts of the fast acid dyestuffs, and more particularly of the sulphonic acids of these dyestuffs, are introduced into the layer with nitrogenous organic bases. These substances also have no detrimental effect on the silver halide.

The salts in question may be incorporated in finished state in the layers or emulsions in fine suspension or by way of addition in a suitable solvent, for example alcohol, or these deposits may be produced in the layer itself by double decomposition. These non-diffusing salts of the dyestuff may be incorporated in those layers, which consist of a plurality of part-layers poured one on to the other, or of a plurality of particles, such as result from the known re-emulsifying action of differently colored emulsions. They may also be formed by applying, atomizing or impressing the dyestuff on to a colloidal layer, whereby there is employed either a solution of the dyestuff salts, or the same may be employed together with the organic bases for coloring the arrangements as described, or the dyestuff deposit may be formed in the layer itself by way of double decomposition. This method of fixing dyestuffs may also be employed for other purposes, for example in the transfer method, in which, for example, an organic base is introduced into the colloid used for the transfer, and an insoluble non-diffusing salt of the dyestuff there formed after the transfer has taken place. In this method the transfer images are extremely sharp, owing to prevention of the diffusion. This method is also extremely useful for the production of antihalation layers.

Layers containing, for example, dyes, which may be removed entirely from the gelatin by washing, may be applied to the emulsion carrier on the front or the rear side of a film or plate or immediately above or below the emulsion.

In my prior application 645,312 dated December 1, 1932, matured into Patent No. 2,046,067, of June 30, 1936, I have already described a method as set forth in the above making use of a difficultly soluble non-diffusing salt of an organic base, which is not a dyestuff, and an acid dyestuff.

The invention relates to an additional development of this process. It has been found that the quaternary salts of heterocyclic bases are very suitable for the purpose in question. These salts are remarkable for extremely good solubility in water, and do not have a detrimental effect of any kind in the emulsion. The salts of these bases result together with the acid dyestuffs in salts which are soluble only with extreme difficulty.

An additional advantage resides in the fact that the insoluble dyestuff salts may be produced in the photographic emulsion directly, in which connection a subsequent washing is usually unnecessary.

Suitable salts are the quaternary salts of the higher homologues of pyridine, for example alkylnaphthoquinolinium salts, anthraquinolinium salts, thiazolium salts, benzothiazolium and naphthothiazolium salts, whereby the 3–4 carbon atoms of the pyridine ring may be substituted by sulphur, selenium or oxygen. Other suitable substances are halogen alkylates, perchlorates, alkyl sulphates and alkyl toluene sulphonates. It has been found that alkyl sulphates are particularly suitable.

Example 1.—A silver bromide emulsion containing 2 grammes Diamine Pure Blue FF per litre has admixed therewith, prior to pouring, a solution comprising .5 gramme 1-ethylquinoline ethylsulphate in 20 cm^3 water.

Example 2.—To an emulsion colored with Chloramine Light Red 7BL at the rate of 3 grammes per litre there is added a solution of .5 gramme 1-methylbetanaphthoquinoline perchlorate in 100 cm^3 water.

What I claim as new and desire to secure by Letters Patent is:

1. A method of producing colored photographic materials which comprises producing in a light sensitive silver halide emulsion a substantially water insoluble, non-diffusing compound by the addition of a quaternary salt of a substantially colorless organic base and an acid dyestuff, and pouring the said emulsion having the dyestuffs incorporated therein on a support.

2. A method of producing colored photographic materials which comprises producing in a light sensitive silver halide emulsion a substantially water insoluble, non-diffusing compound by the addition of alkylsulphates of a quaternary organic base and an acid dyestuff, and pouring the said emulsion having the dyestuff incorporated therein on a support.

3. A method of producing colored photographic materials which comprises producing in a colloidal solution a substantially water insoluble, non-diffusing compound by the addition of a substantially colorless quaternary salt of an organic base and an acid dyestuff, pouring a light sensitive silver halide emulsion on a support, and pouring the said colloidal solution on the said emulsion.

4. A method of producing colored photographic materials which comprises producing in a colloidal solution a substantially water insoluble, non-diffusing compound by the addition of a substantially colorless quaternary salt of an organic base and an acid dyestuff, pouring the said colloidal solution on a support, and pouring a light sensitive silver halide emulsion on the said colloidal solution.

5. A method of producing colored photographic materials which comprises producing in a light sensitive silver halide colloidal emulsion by double decomposition a substantially water insoluble, non-diffusing compound by the addition of a substantially colorless quaternary salt of an organic base and an acid dyestuff, and applying the said emulsion and dyestuff to a support.

6. A method of producing colored photographic materials which comprises producing in a light sensitive silver halide emulsion a substantially water insoluble, non-diffusing compound by the addition of quaternary salts of the higher homologues of pyridine and an acid dyestuff, and pouring the said emulsion having the dyestuff incorporated therein on a support.

7. A method of producing colored photographic materials which comprises producing in a light sensitive silver halide emulsion a substantially water insoluble, non-diffusing compound by the addition of any of the following quaternary salts of organic bases: alkyl halides, perchlorates, alkyltoluene sulphonates, alkylsulphates, and an acid dyestuff, and pouring the said emulsion having the dyestuff incorporated therein on a support.

8. In a method of producing colored light sensitive silver halide colloids, the step which consists in adding to the said colloids a quaternary salt of a substantially colorless organic base and an acid dyestuff to form a substantially water insoluble non-diffusing compound.

9. In a method of producing colored photographic materials, the steps which comprise adding to the light sensitive silver halide emulsion a quaternary salt of a substantially colorless organic base, applying the said emulsion to a support and thereupon applying an acid dyestuff to form a substantially water insoluble non-diffusing compound.

10. A photographic material comprising a colored, light sensitive silver halide emulsion layer containing a substantially water insoluble, non-diffusing compound of an acid dyestuff with a substantially colorless salt of a quaternary organic base.

11. A photographic material comprising a colored light sensitive silver halide emulsion layer containing a substantially water insoluble, non-diffusing compound produced by the addition of an acid dyestuff and a substantially colorless salt of a quaternary organic base to the light sensitive emulsion.

12. A photographic material comprising a light sensitive silver halide emulsion layer containing a substantially water insoluble, non-diffusing compound of an acid dyestuff and a quaternary salt of a higher homologue of pyridine.

13. A photographic material comprising a colored light sensitive silver halide layer on a support, said layer containing substantially water insoluble, non-diffusing reaction-products resulting from the addition to the light sensitive emulsion of an acid dyestuff and any of the following quaternary salts of heterocyclic organic bases: alkyl halides, perchlorates, alkylsulphates, and alkyltoluene sulphonates.

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