

## UNITED STATES PATENT OFFICE

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## PHOTOGRAPHIC SILVER HALIDE EMULSION LAYERS

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Our present invention relates to the manufacture of photographic silver halide emulsion layers.

One of its objects is the provision of photographic silver halide emulsion layers for color development. Further objects will be seen from the detailed specification following hereafter.

It is known that with the aid of color development (chromogenic development) color pictures can be obtained photographically as described, for instance, in U. S. Patent No. 1,102,028. Attempts have been made to produce multi-color pictures by the process of the said patent by superimposing a number of suitably sensitized films capable of being developed in the color they are sensitized for. This process must, however, remain without practical application since all the compounds capable of color development recommended in the prior art are soluble in alkali even when incorporated in the layer and diffuse from the layer of selective sensitivity to which they are allotted into the adjacent layers or into the developing bath.

According to this invention it has been found that several superimposed layers can be developed in color without the fault of diffusion. This is possible if the components used in the colors are of such character that in spite of good solubility in water they are so firmly held by the gelatin that diffusion from the layer is not possible. This property is secured by using products of reaction of certain derivatives of highly polymeric carboxylic acids with bodies adapted by known reactions to form dyestuffs, for example, amines, phenols, aminophenols, naphthols, aminonaphthols and bodies with the reactive methylene groups. Reaction between the derivatives of the highly polymeric carboxylic acid and the amine, etc., yields a compound, generally an acid amide, which is thoroughly soluble and in consequence without difficulty may be uniformly distributed in gelatin, or other binding agent, but, being colloidal, cannot be separated from the layer by simple extraction. The reaction is carried out with molecular proportions of the compounds at ordinary or at a raised temperature. Suitable solvents are preferably water, but organic solvents such as alcohol, acetone and dioxane also may be used, particularly if the solubility in water is not sufficient. Thus, layers containing these bodies are suitable for forming the required multi-layer material, since diffusion from one layer to another cannot occur.

The aforesaid phenols and compounds having

reactive methylene groups yield a color picture by simple development or may be converted by a diazo-process coupled with the photographic process into an azo-dyestuff picture. Substances such as leuco bodies may be caused to react with the highly polymeric substances which then yield a dyestuff picture by the photographic process. Two or more such layers combined are specially suitable for making pictures in color.

Suitable highly polymeric carboxylic acids and substances like polyglycuronic acids, proteinamino acids or synthetic compounds from unsaturated organic acids such as polyvinylcarboxylic acids (polyacrylic acid alone or as a mixed polymerizate with styrene, vinylchloride, vinyl ether or nitrogenous vinyl compounds such as vinylcarbazole or the like), polymerizates of maleic acid, fumaric acid, methylene-malonic acid, alone or as mixed polymerizates with vinyl compounds. These polycarboxylic acids are caused to react in the form of their acid chlorides or anhydrides or esters or other reactive derivatives with the aforesaid reactive amines, phenols and bodies with active methylene groups, for example with aminophenols, phenylenediamines, aminonaphthols, aminoacetic acid anhydrides, aminobenzoylacetic acid esters, aminophenylmethylpyrazolones, hydroxynaphthoic acid aminoarylates, diazo-bodies, leuco-dyestuffs, or the like.

The following examples illustrate the invention:

*Example 1.*—1 gram of a condensation product from metaaminophenylmethylpyrazolone and the mixed polymerizate from vinylchloride and maleic acid anhydride are ground with 5 cc. of caustic soda lye of 5 per cent strength and then dissolved in water. The solution is added to 100 cc. of silver bromide emulsion. A layer of this emulsion may be developed with para-aminodimethylaniline to a picture which consists of a red dyestuff after the separation of the silver.

*Example 2.*—The procedure is as described in Example 1, but instead of a pyrazolone and a condensation product there is used one made from 1.5-aminonaphthol and the mixed polymerizate named in Example 1; the layer made yields a picture in a blue dyestuff.

What we claim is:

1. A photographic silver halide gelatin emulsion containing a dyestuff component fast to diffusion with respect to the gelatin, said dyestuff component being an amide of a color former with a highly polymeric carboxylic acid capable of forming a dye at the places of the

silver image upon being contacted with a color forming developer.

2. A photographic silver halide gelatin emulsion containing a dyestuff component fast to diffusion with respect to the gelatin, said dyestuff component being an amide of a color former with a highly polymeric carboxylic acid capable of forming a dye at the places of the silver image upon being contacted with a color forming developer, said highly polymeric carboxylic acid derivative consisting of a chain-molecule wherein the color forming group recurs periodically linked to recurring carboxylic acid groups.

3. A photographic silver halide gelatin emulsion containing a dyestuff component fast to diffusion with respect to the gelatin, said dyestuff component being an amide of a color former with a highly polymeric carboxylic acid capable of forming a dye at the places of the silver image upon being contacted with a color forming developer, said dyestuff component being an acid amide from meta-aminophenylmethylpyrazolone and an interpolymers from vinyl chloride and maleic acid anhydride.

4. A photographic silver halide gelatin emulsion containing a dyestuff component fast to diffusion with respect to the gelatin, said dyestuff component being an amide of a color former with a highly polymeric carboxylic acid capable of forming a dye at the places of the silver image upon being contacted with a color forming developer, said dyestuff component being an acid

amide from 1,5-aminonaphthol and an interpolymers from vinyl chloride and maleic acid anhydride.

5. A photographic silver halide gelatin emulsion containing a dyestuff component fast to diffusion with respect to the gelatin, said dyestuff component being an amide of a color former with a highly polymeric carboxylic acid capable of forming a dye in situ with the reduced silver image.

6. A photographic silver halide gelatin emulsion containing a dyestuff component fast to diffusion with respect to the gelatin, said dyestuff component being an amide of a color former with a highly polymeric carboxylic acid in which the color former group recurs periodically, and being capable of forming a dye at the places of the silver image upon being contacted with a color forming developer.

7. A photographic silver halide gelatin emulsion containing a dyestuff component fast to diffusion with respect to the gelatin, said dyestuff component being an amide of a color former with a highly polymeric carboxylic acid, said highly polymeric carboxylic acid derivative consisting of a carbon chain molecule wherein the color forming group recurs periodically in pairs, each group of a pair being united by an acid amide linkage to adjacent carbon atoms of said chain.

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