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METHOD FOR COLORING NON-DIFFUSIBLY PHOTOGRAPHIC LAYERS BY MEANS OF AN AMINO-GUANIDIZED DIALDEHYDE STARCH MORDANT

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ABSTRACT OF THE DISCLOSURE

A photographic layer can be made completely non-diffusibly colored by incorporating into a binder of the photographic layer, a mordant which is a reaction product of aminoguanidine with dialdehyde starch, and coloring the photographic layer with an anionic dye.

This invention relates to a novel method in which a photographic layer constituting a color material is colored completely non-diffusibly with an anionic dye containing carboxylic acid groups or sulfonic acid groups which is the most common dye known as the acid dye or direct dye, and the method which give such excellent characteristics that the colored layer is stable to such necessary and ordinary photographic treatments as development, fixing, bleaching, washing and the like, and maintains the strength of the photographic layer during said treatments.

The photographic layer referred to herein includes, in addition to silver halide emulsion layers constituting ordinary light-sensitive photographic materials, such auxiliary layers as over layers or protective layers, intermediate layers in multi-layered materials, silver image transfer layers for silver complex diffusion transfer method, color image accepting layers for imbibition transfer or dye transfer method, backin layers, anti-halation layers, anti-irradiation layers and filter layers, and is a general term for those which have been directly or indirectly applied in the form of layers onto such supports as film bases, papers and the like, chiefly by means of a water-soluble or hydrophilic binder such as gelatine, polyvinyl alcohol, starch or ethyl cellulose, and the like

As the colloidal binder for forming the above-mentioned photographic layers, gelatine is most predominantly employed, in general. In addition thereto, however, there are used as binders of natural occurrence not only such protein type binders as casein, zein and albumin but also such polysaccharide type binders as starch, dextran, gum arabic, guar gum and alginic acid. Recently, there have appeared in succession such water soluble synthetic polymers as polyvinyl pyrrolidone, polyvinyl pyridine, polyvinyl alcohol, hydroxyethylated polyvinyl alcohol, polyacrylic acid, polyacrylamide, vinyl acetate-acrylic acid copolymer, styrene-maleic anhydride copolymer and vinyl methyl ether-maleic anhydride copolymer. On the other hand, there have been proposed not only semi-synthetically obtainable cellulose derivatives such as methyl cellulose, ethyl cellulose, carboxymethyl cellulose, hydroxyethy cellulose, cyanoethyl cellulose and the like, and starch derivatives such as hydroxypropyl starch, carboxymethyl starch, oxidized starches (including dialdehyde starch), dextrin and the like, but also even such gelatine derivatives as gelatine phthalate and benzyl gelatine. These may be used alone as in the case of gelatine, but in most cases, they are mixed with each other or are blended with gelatine or polyvinyl alcohol.

The present invention is chiefly concerned with a method for coloring photographic layers with acid- or direct-type azo dyes, which are frequently used in a photographic process known as the silver dye bleach process. The method of the present invention, however, can be advantageously applied to make filter layers or anti-halation layers, etc. Further, the present method is applicable to dye accepting layers of transfer papers employed for the imbibition (or dye transfer) process or for the dye-developer process such as "Pola color" dye, which developer is used in "Pola color" (a product of Polaroid Co., U.S.A.).

The explanation of the invention, however, is restricted mainly to the aforesaid silver dye bleach process and an improvement thereof invented by the present inventors (Japanese Patent No. 598,532). And heretofore, it has been an ordinary practice in this process for binders of photographic layers to be dyed under acidic conditions chiefly with anionic azo dyes known as acid dyes or direct dyes and the colors are made diffusion-fast by use of heavy metal salts. And if a suitable dye is used, the method is practicable in the case where a film base is used, but in the case where a baryta paper is used as the base, the base is stained heavily with the dye which has diffused out from the photographic layers during the processing. It has therefore been considered impossible to prepare a sensitized material having a paper base. This point has been improved to a considerable extent by virtue of the invention of reactive dyes. Yet, the suitable cyan color dye which is easily bleached to pure white is not obtainable in reactive dyes, and the actual state is such that anionic azo dyes should necessarily be used. Since the anionic azo dyes have negative carboxylic acid groups (—COOH) or sulfonic acid groups ($—SO_3H$), it is natural that they have electrically strong affinity for compounds having such positive groups as amino groups, and it is also well known that they react with organic amines, pyridines or guanidines to cause precipitation. Accordingly, there has been proposed a method to fix the anionic azo dyes by incorporating these precipitants, for example, such guanidine derivatives as diphenylbiguanide, 1,1,3-triphenylguanidine, anhydro biguanido-benzyl alcohol and the reaction product of dicyandiamidine with formalin into binders of the layer previously. These substances, however, are originally low in molecular weight although the latter two are considered to have been polymerized to a certain extent, and are readily soluble in water and have insufficient affinity for such binders as gelatine. Accordingly, the resulting precipitates themselves still retain diffusibility in the binder and are not sufficient to make the dye stuff non-diffusible in the layer. Thus, they are effective as mordants for fibers but are not suitable as mordants for the coloration of photographic layers.

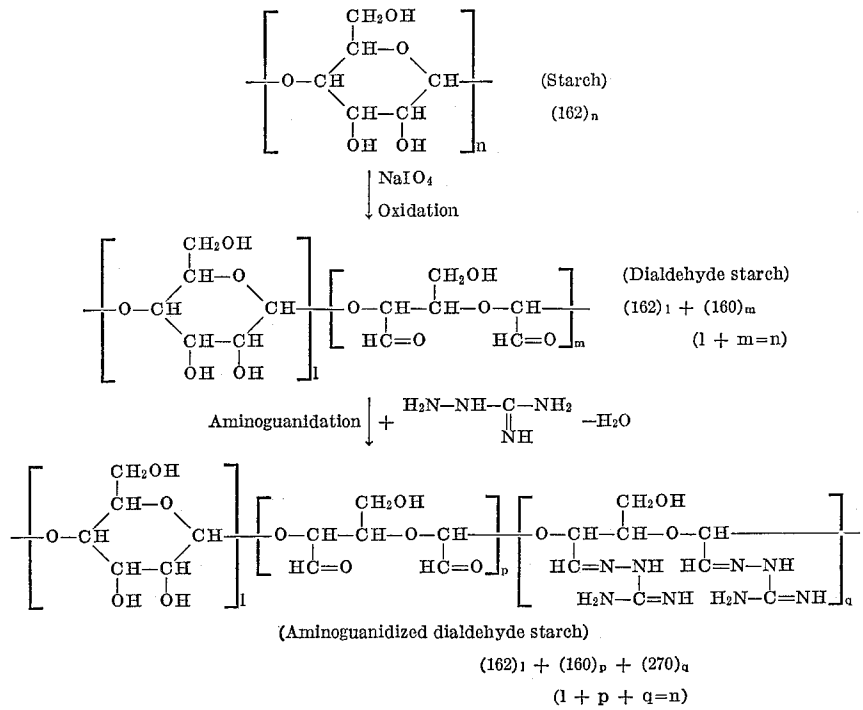
Monochloroaminotriazine or dichloroaminotriazine derivatives, e.g. 2,4-dichloro-6-phenylamino-1,3,5-triazine-3'-sulfonic acid and the like, which are known as hardening agents for photographic layers, contain guanyl groups in the molecules and hence are effective as mordants for the aforesaid dyes. These derivatives are low in molecular weight but have high reactivity to bond with molecules of such binders as gelatine or polyvinyl alcohol to make the compounds non-diffusible. In this case, however, they greatly increase the viscosity of the binder solution. It is difficult to incorporate into photographic layers the said compounds in amounts sufficient to make the dye stuff completely non-diffusible to the extent required in the silver dye bleach process.

Polyvinyl pyridine is high in molecular weight and has a function as a mordant. However, said compound is insoluble in water under neutral and alkaline conditions, and being brought into the form of a quaternary salt so as to be soluble in water, said compound has insufficient compatibility with gelatine, polyvinyl alcohol and the like binders, and has a tendency to separate undesirably at a low temperature. Generally, synthetic vinyl

polymers have the disadvantage that they are poor in compatibility with gelatine, starch or the like natural products and derivatives thereof.

The reaction product of aminoguanidine with dialdehyde starch, i.e. aminoguanidized dialdehyde starch, which is used in the present method, is high in molecular weight and is non-diffusible, in photographic layers. Since said reaction product still retains aldehyde groups, it advantageously bonds directly to the molecules of gelatine and the like binders, and acts also as a hardener. And said product can be incorporated into photographic layers in an amount large enough to sufficiently enhance the mordanting properties thereof to dyes without any fear of a decrease in swelling properties or embrittlement of photographic layers due to an increase in viscosity or excessive hardening, because, the number of aldehyde groups to be introduced into the molecules of starch and the proprtion of the aminoguanidized portion (in the form of guanylhydrazone) in the starch can be freely varied by controlling the degree of the two reactions of periodic acid oxidation and aminoguanidation. This is a particularly excellent feature of said aminoguanidized aldehyde starch. Another feature thereof is that it is prepared by processing a natural product and hence is excellent in miscibility with a natural colloid employed for the binder. It is considered that to make dialdehyde starch cationic by aminoguanidation might have advantageously increased the compatibility thereof with gelatine and the like protein-type binders. Generally, aminoguanidized starch retains aldehyde groups therein and hence acts as hardener. This is quite useful in preventing the undesirable side effect of coloring binders with anionic dyes, which is frequently encountered and results in lowering the resistance of the photographic layer in water. It is considered that the lowering in resistance of photographic layers in water due to anionic dyes is probably ascribable to the fact that such functional groups as amino, imino or hydroxy groups in the molecule of binders which take part in hardening of layers are used up for the bonding to dye molecules. By the addition of aminoguanidized dialdehyde starches, however, the dyes strongly bond to said starches, whereby the binders themselves liberate the above-mentioned functional groups taking part in the hardening of layers and, at the same time, the aldehyde groups bond thereto, and hardening efficiencies are far more improved.

Oxidation and aminoguanidation reactions of starch may be diagrammatically shown by chemical formulas set forth below (where n is the total number of units in one molecule of the modified starch and also l, m, p and q are the number of glucose, dialdehyde glucose and aminoguanidized dialdehyde glucose units respectively).



All these reactions do not go to completion and it is desirable to control the reaction to make the above-mentioned mordanting property and hardening property be suitably balanced.

In the present invention, an aqueous dispersion of a commercially available dialdehyde starch oxidized with a periodic acid salt is reacted with a required amount of a water-soluble aminoguanidine salt and the reaction product is obtained as a white powder after filtration, washing and drying. But the liquid obtained after the reaction is over by heating and dissolving the reaction product in the reaction vessel may be used as it is. Alternatively, it is possible to use a paste prepared by the following procedure, i.e., white powder aminoguanidized starch is dyed by dispersing in an aqueous dye solution, then washing with water, making weakly alkaline and heating. Thus, various modifications are possible according to the purpose of utilization.

The present invention is illustrated in further detail below with reference to examples.

EXAMPLE 1

250 g. of a commercially available dialdehyde starch (Sumstar-175 produced by Miles Chemical Co., U.S.A.; oxidaiton degree about 75%) is dispersed in 750 ml. of water. To the dispersion is added under stirring a solution of 25 g. of a commercially available aminoguanidine bicarbonate in 250 ml. of water which has been adjusted to pH 3 by addition of a small amount of hydrochloric acid, and the mixture is reacted at below 40° C. for 2 hours. After filtration and water-washing, the reaction mixture is washed with methanol and is dried at a low temperature to obtain a white powder containing about 3% of nitrogen and 13% of water. In view of the amount of nitrogen, the amount of aminoguanidized aldehyde groups is only about 6% of the total aldehyde groups, but the white powder is excellently dyed with an anionic dye.

EXAMPLE 2

100 g. of a commercially available dialdehyde starch (Sumstar-150 produced by Miles Chemical Co.; oxidation degree about 50%) is dispersed in 300 ml. of water. To the dispersion is added at pH 2 a solution of 45 g. of aminoguanidine hydrochloride in 450 ml. of water, and the mixture is reacted at room temperature for 20 hours. After filtration and water-washing, the reaction mixture is washed with methanol and is dried at below 40° C. to obtain as a white powder a starch oxide in which about one half of the total aldehyde group has been aminoguanidized. This starch oxide is considerably weaker in hardening power than the starch obtained in Example 1 but is much higher in bonding power to an anionic dye.

EXAMPLE 3

30 g. of a specially-made dialdehyde starch (oxidation degree 10%) is dispersed in 100 ml. of water. To the dispersion is added under stirring a solution of 5 g. of aminoguanidine bicarbonate in 50 ml. of water which has been adjusted to pH 2.5 by addition of a small amount of hydrochloric acid, and the mixture is reacted at below 40° C. and 3 hours. The reaciton liquid is adjusted to pH 7–7.5 by addition of a small amount of caustic soda and is then heated to 90° C. to form a 20% solution. This solution is low in both oxidation degree and aminoguanidization degree but can be incorporated in a large amount into a binder. When the solution is incorporated in an amount of 10–20% by volume into a 5% gelatine solution and the mixed solution is applied into a baryta paper, there is obtained a transfer paper for imbibition transfer.

EXAMPLE 4

To 100 g. of the aminoguanidized dialdehyde starch obtained in Example 2 is added a solution of 20 g. of Chicago Blue 6B (CI 24410) in 5 l. of water. After stirring, the mixture is allowed to stand at room temperature for more than 10 hours, and is then suctioned, filtered, water-washed and dried to obtain a blue-colored powder.

EXAMPLE 5

Example 4 is repeated, except that Diamine Rose (CI 15080) is used as the dye, to obtain a reddish pink powder.

EXAMPLE 6

Example 4 is repeated, except that Brilliant Yellow (CI 24890) is used as the dye, to obtain a yellow powder.

These 3 kinds of colored powders of Examples 4, 5 and 6 are extremely effective for coloring emulsions of color films and color print materials of silver dye bleach process, and are preferably incorporated in an amount of 25–50 g. per kg. of emulsion (the amount should be controlled depending on color density of the layer). Further, in the case of color materials as disclosed in Japanese Pat. No. 584,700, the said colored powders are applicable, to the coloration of diffusion transfer positive layers adjacent to emulsion layers.

EXAMPLE 7

Gelatine—120 g.
Polyvinyl alcohol—60 g.
Copolymer of vinyl methyl ether and maleic anhydride—20 g.
Half amide of said copolymer—10 g.
Aminoguanidized dialdehyde starch of Example 2—90 g.
Water—6 l.

A solution comprising the above components is applied in an amount of 100 g./m.^{2} onto a paper of high water-resistance and dried to obtain a transfer paper of the highest quality for preparing color photograph, so called imbibition- or dye transfer-color.

EXAMPLE 8

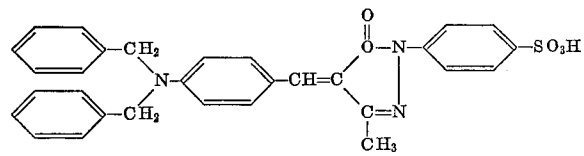
0.8 g. of a colloidal fine precipitate of cadmium sulfide is dispersed in a solution having the composition mentioned in Example 7 to obtain a coating material for a transfer layer of the silver complex diffusion transfer process which is suitable for the invention of Japanese Patent No. 584,700. The coating material thus obtained can be completely dyed with an anionic azo dye.

The preparation of a color paper according to the process of the above-mentioned invention is as follows.

On one side of a baryta paper having both sides coated with polyethylene is applied the aforesaid coating material to form a colorless transfer layer. Onto said transfer layer is applied about 50 cc./m.^{2} of a 1% solution of Chicago Blue 6B which has been purified and freed from purple impurities. After drying, only the uppermost layer of the transfer layer is colored to blue. Onto the above-mentioned top blue colored and underpart colorless transfer layer is applied a chlorobromide emulsion layer sensitized to red and a colorless transfer layer as above, and then the composite is dried. After or during the drying, the said composite is coated on the surface with a 1% solution of Diamine Rose, which has thoroughly been purified by recrystallization, and only the uppermost layer thereof is colored and is then dried. In the same manner as above, an emulsion layer sensitized to green and a colorless transfer layer are applied. In the drying step, the composite is coated on the surface with a 1% solution of Brilliant Yellow and then dried. Finally, a non-color sensitized chlorobromide emulsion and a common colorless protective layer are applied onto the said surface, and the composite is dried to obtain a desired color paper.

EXAMPLE 9

A colored powder is obtained in the same manner as in Example 4 by adding 30 g. of a decolorizable yellow acid dye of the formula



to 100 g. of the aminoguandized dialdehyde starch obtained in Example 2. This powder is suitable for the coloration of a yellow filter layer, which is disposed between the uppermost yellow layer of a multi-layered color material, and a Magenta and/or a blue layer and is decolored during treatments of developing and fixing.

EXAMPLE 10

To 7 liter solution of the composition shown in Example 7, 15 g. of Palatine Fast Black RRN and 10 g. of Palatine Fast Yellow 6 GEN are added. The solution is suitable as an anti-halation layer, which is disposed between a multi-layered light-sensitive emulsion layer and a support. The layer is not dischargeable during photographic treatments but is so complete in non-diffusion property that the dyes do not diffuse out into the emulsion layer or baryta-paper base.

What we claim is:

1. A method for coloring a photographic layer composed mainly of gelatine or the like hydrophilic binder, characterized in that in order to color the photographic layer with an anionic dye and to make it completely non-diffusible, an aminoguanidized dialdehyde starch is incorporated into the binder as a mordant.

2. A transfer material for producing color photographs having incorporated in a hydrophilic binder in the transfer layer an aminoguandized dialdehyde starch as a mordant for an anionic dye.

3. A composition for coloring a sensitive emulsion layer, a filter layer and/or an antihalation layer of color materials which comprises an aminoguanidized dialdehyde starch and an anionic dye.

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8—29, 30; 96—77, 84; 260—233.3A