United States Patent

[11] 3,624,229

[72] Inventors **Daniel Maurice Timmerman**
Mortsel;
August Jean Van Paesschen, Antwerp;
Albert Emiel Van Hoof, Berchem, all of Belgium

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[73] Assignee **Gevaert-AGFA N.V.**
Mortsel, Belgium
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[33] **Great Britain**
[31] **14,523/68**

[54] **FIXATION OF ANIONS IN HYDROPHILIC COLLOID MEDIA**
11 Claims, No Drawings

[52] **U.S. Cl.** **96/84,**
96/11, 96/57, 260/88.3, 101/464
[51] **Int. Cl.** **G03c 1/84**
[50] **Field of Search** 96/57, 84
A, 99; 260/88.3; 101/464

[56] **References Cited**

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Primary Examiner—J. Travis Brown
Attorney—William J. Daniel

ABSTRACT: Process of mordanting a hydrophilic colloid medium with an addition polymer containing 50–95 mole percent of 2-methyl,5-vinyl-pyridinium units or a water-soluble pyridinium salt thereof and the balance of N-aliphatic,2-methyl,5-vinyl-pyridinium units, and a hydrophilic colloid composition containing an acid dye mordanted with such polymer.

FIXATION OF ANIONS IN HYDROPHILIC COLLOID MEDIA

This invention relates to a process for fixing anions, e.g. of anionic dyes, in hydrophilic colloids, and to colloid compositions incorporating polymeric compounds acting as mordanting agents for anions.

Mordanting agents hindering diffusion of acid dyes in colloid layers strongly reduce lateral diffusion of said compounds in said layers and are of great interest in the preparation of cinematographic color copies by the inhibition printing process.

In the manufacture of color films according to the inhibition process, a first step comprises the formation of the relief image suited for absorbing a dye solution. The relief image is commonly prepared in a photographic way, e.g., by hardening development of a gelatino-silver halide emulsion layer and selective removal of the nonhardened portions. The whole is referred to as a matrix or matrix film. The matrix containing the relief image after being immersed into a solution of a dye is brought into close contact with a colloid layer of a receptor material. The receptor material applied for cinematographic purposes contains a transparent film support, at least one colloid layer for absorbing the dye(s) and occasionally a light-sensitive silver halide emulsion layer. Such material is known as the blank or blank film.

During the contact of the dyed matrix with the blank film, dye absorbed in the relief image of the matrix diffuses into the colloid layer of the blank film, on which in this way a monochrome image is formed. In repeating the dye transfer step by using each time a novel blank film, several prints are made with one single matrix. Multicolor images can be obtained by preparing relief images which correspond with the color separation images to be reproduced in register. Thus, monochrome separation images can be printed in register forming on one blank a multicolor image. This process of producing multicolor images by inhibition is described, e.g., by P. Glafkidès Photographic Chemistry, Fountain Press, London (1960) Vol. II, 696–699.

In order to improve the sharpness of the transferred dye images by counteracting lateral diffusion of the dyes in the colloid layer, mordanting agents are incorporated therein.

For obtaining high quality transfer inhibition prints, the mordanting agent has to possess a resistivity to diffusion as high as possible in order to avoid contamination of the matrix. In other words, when a mordanting agent is used, which is insufficiently resistant to diffusion, some of it passes from the blank upon the matrix. On reimmersing the matrix in the dye solution, the dye will precipitate also on nonimage areas and on subsequent printing more or less uniform color fog will result on the blank film. This harmful color-fog formation will be repeated and evidently increased during the production of further prints.

When used in combination with a light-sensitive silver halide emulsion layer, which is e.g. the case when a silver soundtrack has to be produced, the mordanting agent has to be of such a type that it does not cause a substantial fog in the light-sensitive silver halide emulsion.

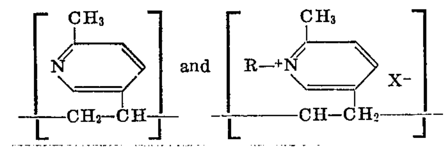
A further requirement for a useful mordant is to effect a sufficient color absorption.

By color absorption is meant the maximum color density obtainable in any given combination of time and temperature under which the dye-immersed matrix is brought into close contact with the blank. Said conditions are determined by the apparatus ensuring the contact between the matrix and the blank film.

As mordanting agents more or less successfully meeting the above requirements for fixing acid dyes, several groups of polymers containing free amino groups, tertiary amino groups in salt form, or quaternary salt groups have been proposed.

It has now been found that in colloid compositions a very effective mordanting action in respect of anionic compounds e.g. acid dyes, can be obtained by the use therein of an addition polymer consisting of structural units of the following structural formulas:

(A) (B)



Wherein X^- represents an anion, e.g. a chlorine or methyl sulfate anion, and R an aliphatic radical including a cycloaliphatic and a substituted aliphatic radical e.g. a C_1–C_5 alkyl radical, preferably a menthyl radical.

The ratio of the structural units (A) and (B) in the polymer is preferably within the ranges 95 to 5 and 50 to 50. For improving the water solubility of the polymer the structural units represented under (A) can be partly or wholly transformed in salt form.

In order to illustrate the preparation of polymers used according to the present invention a detailed preparation recipe is given hereinafter.

preparation of 1,2-Dimethyl-5-Vinylpyridinium Methylsulphate

In a 3-liter reaction flask fitted with a stirrer, a thermometer, a reflux condenser and a separatory funnel 365 g. of 2-methyl-5-vinylpyridine were dissolved in 1,650 cc. of acetone (dried over magnesium sulfate). The solution was cooled to 3° C.

385 g. of dimethyl sulfate neutralized with potassium carbonate were then added dropwise to the solution. The quaternization was exothermic. The temperature in the reaction mass was therefore kept between 0° and 10° C. by cooling.

As soon as all of the dimethyl sulfate had been added, the temperature of the reaction mixture was allowed to rise to 20°–25° C. and the suspension of 1,2-dimethyl-5-vinylpyridinium methylsulphate crystals in acetone was stirred for some 150 minutes more.

Subsequently, the pyridinium salt was filtered, rinsed twice with 150 cc. of dry acetone, and dried at room temperature, till the weight of the crystals remained constant.

Yield: 690 g. Melting point: 143° C.

Preparation of Copoly[2-Methyl-5Vinylpyridine/1,2-Dimethyl- 5-Vinylpyridinium Methylsulphate]

In a 5-liter reaction flask fitted with a stirrer, a thermometer, a reflux condenser, and a nitrogen gas-inlet tube 900 cc. of 5 N nitric acid were added dropwise with stirring to 536 g. of 2-methyl-5-vinylpyridine. The solution was cooled to 10°–15° C.

Subsequently 122.5 g. of 1,2-dimethyl-5-vinylpyridinium methylsulphate and 6.6 g. of potassium persulphate were added to the homogeneous solution.

A slow nitrogen current was allowed to bubble through the clear solution. The heating was then started and as soon as the temperature in the solution reached 75° C., the reaction became exothermic and the heating was switched off.

The temperature rose to 85° C. and solution become more viscous. Then 150 cc. of water were added. The temperature again rose to 85° C. and another 150 cc. of water were added. In this way the exothermic reaction was being controlled. Up to 750 cc. of water (5×150 cc. were added.

After the last addition the reaction was not exothermic anymore. The heating was switched on again to maintain a temperature of 70° C.

The reaction period was 210 minutes.

The resulting solution was diluted with water to a volume of 3 liters. The pH of the resulting solution was 4.3. While stirring 3.1 l of acetone and 6.2 l of dioxan were added thereto. The copolymer precipitated and upon decantation of the supernatant liquid, the residue was washed with 1 liter of acetone, then dissolved in water, and diluted with water to a volume of 3 liters.

Yield: 3.1 l solution (21 percent).

pH of the solution: 4.0.

Intrinsic viscosity $[\eta]=1.88$ dl. $g.^{-1}$, measured at 25° C. in aqueous 0.1 N sodium chloride solution.

The effectiveness in mordanting or diffusion hindering action of the polymers used according to the present invention is directly proportional to their intrinsic viscosity [η].

Acid dyes suited for the inhibition printing process that can be mordanted by means of the polymers and copolymers, the structural units of which are given above, are, e.g.:

Fast Red S Conc. (C.I. Acid Red 80–C.I. 15,620)
Pontacyl Green SN Ex. (C.I. 44,090)
Acid blue black (C.I. 20,470)
Acid Magenta O (C.I. Acid Violet 19–C.I. 42,685)
Naphthol Green B Conc. (C.I. Acid Green 1–C.I. 10,020)
Brilliant Paper Yellow Ex.Conc. (C.I.Direct Yellow 4–C.I. 24,890)
Tartrazine (C.I. Acid Yellow 23–C.I. 19,140)
Metanil Yellow Conc. (C.I. Acid Yellow 36–C.I. 13,065)
Pontacyl Scarlet R Conc. (C.I. Acid Red 89–C.I. 23,910)
Pontacyl Rubine R Extra Conc. (C.I. Acid Red 14–C.I. 14,720)

Suitable supports for the matrix film and the blank film are composed of modified cellulose products such as cellulose esters, e.g. cellulose triacetate, cellulose acetobutyrate, cellulose propionate or synthetic resins such as polycondensation products of the polyester type, e.g. polyethylene terephthalate, polysulphonates and polycarbonates.

Colloids for preparing the receptor layer of blank films containing a silver halide emulsion layer are usually of the same type as those known to one skilled in the art of preparing photographic silver halide materials. Normally the colloid layer contains gelatin and/or polyvinyl alcohol which colloids may be mixed with coating aids such as wetting agents, polymer latices, viscosity reducers, antistatic agents, softening agents improving the flexibility and—if necessary— some amount of a hardening agent improving the mechanical strength. When used in the production of sound film the colloid layer acting as receptor layer in the blank film is usually applied to a silver halide emulsion layer.

The reason why such structure of the blank film is preferred is that when incorporated into the silver halide emulsion layer most of the mordanting polymers, particularly those containing a free amino group, produce a substantial fog in the developed photographic emulsion. Therefore, it is preferred to incorporate the mordanting agent into a colloid layer covering the silver halide emulsion layer, thus preventing direct contact of the mordanting agent with the light-sensitive silver halide grains.

When incorporated into a blank film the mordanting polymers and copolymers containing structural units as described above are preferably used in an amount of 15 to 35 g. per 100 g. of hydrophilic colloid.

The application of the mordanting polymers used in the present invention is not necessarily limited to the use as mordants in blanks for the production of hydrotype prints. Indeed, the mordanting polymers can equally well be applied for substantially increasing the resistance to diffusion in hydrophilic colloid compositions of most different kinds of organic substances containing one or more anionic groups. In that respect the attention is drawn to their use in combination with compounds containing an anionic part selected from the group of anionic color couplers, anionic masking compounds, and different kinds of dyes used in silver halide photographic materials e.g. anionic colored color couplers, antihalation, screening and filter dyes, further anionic antistatic agents, U.V.-absorbing compounds, fluorescing agents and optical bleaching agents. The said polymers can also be used as dispersing agents in aqueous medium, e.g., for the preparation of pigment coatings.

So, apart from their use in blank films the mordanting polymers containing structural units as described herein are particularly advantageously used in the preparation of filter and antihalation layers in photographic silver halide materials. The filter dyes may be applied, e.g., in an antistress layer or in an intermediate layer of a multicolor film, which contains normally three differently spectrally sensitive silver halide emulsion layers. Particulars regarding these special applications are disclosed in the United Kingdom Pat. No. 830,189 filed Aug. 23, 1957 by Gevaert Photo-Producten N.V.

The said mordanting polymers are further particularly useful to prevent the migration of anionic color couplers in hydrophilic colloids, e.g. gelatin used in silver halide photography.

Color couplers used in silver halide color photography and containing water-solubilizing groups, e.g. anionic groups such as carboxylic acid or sulfonic acid salt groups, are made more fast to diffusion when incorporated in the photographic material, e.g. by incorporating into the molecule of the color coupler a large organic radical, a so-called ballasting group, which is normally an aliphatic radical containing from five to 20 carbon atoms in straight line. Nonmigratory color couplers forming on color development with a p-phenylene diamine type color developing agent indophenol or azamethine dyes are described, e.g., by P. Glafkidès—Photographic Chemistry—Vol. II—Fountain Press—London **1960**) p. 606–615.

According to the present invention anionic color couplers are made more resistant to diffusion in a hydrophilic colloid medium by allowing them to adsorb to a mordanting agent as described above.

As a result of the adsorbing or mordanting action of the said addition polymers the said anionic color couplers produce on color development color images the sharpness of which is markedly better even if the color couplers contain the so-called ballasting group.

The following examples illustrate the present invention.

EXAMPLE 1

To a subbed cellulose triacetate support a silver halide gelatin emulsion layer of the type used for producing positive prints of a soundtrack was applied. This emulsion was coated in a proportion of 7 g. of gelatin per sq. m. and contained the following ingredients in parts by weight:

Gelatin	93.5
amount of silver bromide equivalent to 80 parts of silver nitrate	
dioctyl ester of sodium sulphosuccinic acid	4.7
resorcinol	9.8

To this emulsion layer a colloid layer containing a mordanting agent was applied in a proportion of 3.5 g. of gelatin per sq. m. from a solution containing the following ingredients in parts by weight:

6% aqueous gelatin solution	845
10% aqueous solution of the polymer prepared as described above	125
40% aqueous formaldehyde solution	7.5
2% aqueous solution of ADJUPAL A (a wetting agent containing isononylphenoxypoly(ethyleneoxy)$_{9-10}$ ethanol sold by Adjubel N.V., Belgium)	22.5

The obtained blank film was used in hydrotype printing and yielded very sharp high density color prints.

EXAMPLE 2

Coating solutions of the following compositions were prepared:

inert gelatin	100 g.
saponine	2.5 g.
4% aqueous solution of formaldehyde	2.5 ml.

amounts of dyestuffs and mordanting polymers in mg. per sq. m. as indicated in the table below. The pH of the coating solutions was adjusted to 5.9.

The solutions were coated on separate subbed cellulose triacetate supports in a proportion of 10 g. of gelatin per sq. m. The dyes are of such nature that they discolor completely in their gelatin layer during conventional photographic processing.

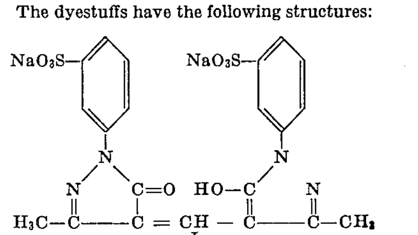
In the presence of a mordanting polymer applied according to the present invention the dyestuffs obtained a high fastness to diffusion, which is needed in antihalation and filter layers.

The relative diffusion values listed in the table were obtained by comparing the spectral density obtained in a thick gelatin layer (100 times as thick as the colored gelatin layer) after keeping that layer in contact with the differently colored gelatin layers for the same time under identical conditions of relative humidity. The values of the optical densities (one e.g. opacity) being directly proportional to the concentration of the dyestuff transmitted by diffusion have been calculated on a procentual basis, the value obtained by the test of a colored gelatin layer containing no mordanting agent and being identically colored as those layers containing a mordanting agent according to the exemplified preparation being given the arbitrary value 100.

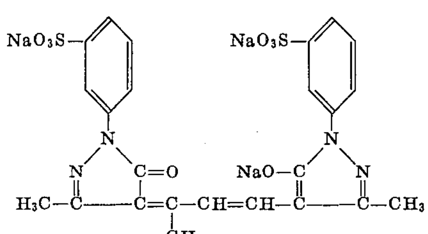
TABLE

Dyestuff No.	Dyestuff Mg./sq.m.	Amount of mordanting polymer in mg./sq.m.	Relative diffusion (arbitrary values)
I	300	----------	100
I	300	500	62
I	300	1,000	20
II	120	----------	100
II	120	500	25
II	120	1,000	15
III	175	----------	100
III	175	500	27
III	175	1,000	4
IV	600	----------	100
IV	600	500	79
IV	600	1,000	40

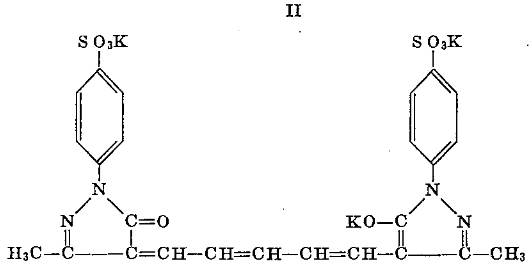
The dyestuffs have the following structures:



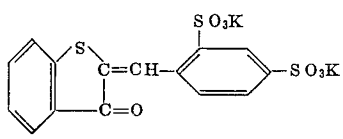
I



II



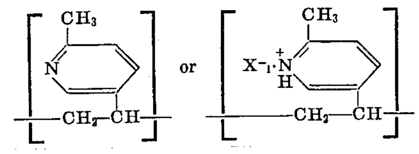
III



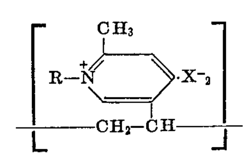
IV

We claim:

1. A process of hindering diffusion of anions in a hydrophilic colloid medium, wherein the diffusion of said anions in said medium is hindered by a mordanting agent, which is an addition polymer containing 50–95 percent structural units having the formulas:



and the balance of structural units having the formula



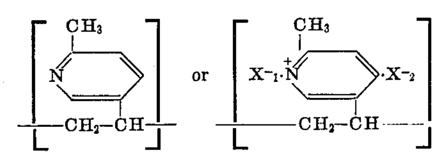
wherein:

X^-_1 and X^-_2 each represents an anion, and R represents an aliphatic group or a cycloaliphatic group.

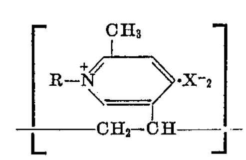
2. A process according to claim 1 wherein the hydrophilic colloid is a dye receptor layer in a gelatin-containing blank film.

3. A process according to claim 1 wherein into the hydrophilic colloid is a dye receptor layer of an imbibition-printing receptor material containing 15 to 35 g. of the addition polymer of claim 1 per 100 g. of hydrophilic colloid.

4. A composition of matter containing a hydrophilic colloid, an organic acid dye compound and as a mordanting agent for said dye an addition polymer containing 50–95 percent of structural units having the formulas:



and the balance of structural units having the formula:



wherein: X^-_1 and X^-_2 each represents an anion, and *R* represents an aliphatic radical including a cycloaliphatic radical.

5. A sheet material comprising a support and a layer containing at least one hydrophilic colloid wherein an addition polymer as described in claim 4 has been incorporated.

6. A sheet material according to claim 6, which sheet material is a blank film containing a dye receptor layer containing at least one hydrophillic colloid, wherein a mordanting

agent has been incorporated, which is an addition polymer as described in claim **4**.

7. A sheet material according to claim **5**, including a light-sensitive silver halide emulsion layer.

8. A sheet material according to claim **5** which is a blank film containing a dye receptor layer comprising at least one hydrophilic colloid, wherein a mordanting agent has been incorporated, which is an addition polymer as described in claim **4** and which layer has been applied to a silver halide emulsion layer.

9. A sheet material according to claim **5**, comprising a hydrophilic colloid layer containing an anionic color coupler and an addition polymer as described in claim **4**.

10. A sheet material according to claim **5**, comprising a hydrophilic colloid layer containing an anionic dye and an addition polymer as described in claim **4**.

11. A sheet material according to claim **5**, containing an anionic antihalation dye, screening dye or filter dye.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,624,229 Dated November 30, 1971

Inventor(s) Daniel Maurice TIMMERMAN et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, Claim 4, lines 45-50, in the second formula in these lines, delete

"X^{-}_{2}".

Column 6, Claim 6, line 1, change "6" to -- 5 --.

Signed and sealed this 2nd day of May 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents