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IMBIBITION ANIONIC DYE IMAGE MORDANTED WITH N-HETERO HOMOPOLYMER

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No Drawing. Continuation of abandoned application Ser. No. 768,530, Oct. 17, 1968. This application May 14, 1971, Ser. No. 143,635

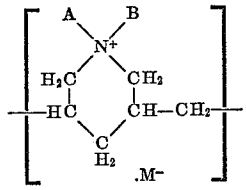
Claims priority, application Great Britain, Oct. 17, 1967, 47,310/67

Int. Cl. G03c *1/72, 1/84;* B41m *5/00*

U.S. Cl. 96—114 7 Claims

ABSTRACT OF THE DISCLOSURE

An imbibition dye image is produced by imagewise applying an anionic dye solution to a hydrophilic colloid layer mordanted with a homopolymer containing the following recurring units:



wherein each of A and B represents a hydrogen atom, a C_1–C_5 lower alkyl group unsubstituted or substituted with a hydroxyl, cyano, acetate or carbonamide group, or A and B represent together the necessary atoms to close a morpholine, a piperidine or a pyrrolidine nucleus, and M^- represents a photographically inert anion.

This application is a continuation of Ser. No. 768,530 filed Oct. 17, 1968, now abandoned.

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 colour copies by the imbibition printing process.

In the manufacture of colour films according to the imbibition process, a first step comprises the formation of a 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 non-hardened 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. Multi-

colour images can be obtained by preparing relief images which correspond with the colour separation images to be reproduced in register. Thus, monochrome separation images can be printed in register forming on one blank a multicolour image. This process of producing multicolour images by imbibition is described, e.g. by P. Glafkidès Photographic Chemistry, Fountain Press, London (1960) vol. II, pp. 696–699.

The sharpness of the transferred dye images has been improved by counteracting the lateral diffusion of the dyes in the colloid layer with mordanting agents.

For obtaining high quality transfer imbibition 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 re-immersing the matrix in the dye solution, the dye will precipitate also on non image areas and on subsequent printing a more or less uniform colour fog will result on the blank film. This harmful colour-fog formation will be repeated and evidently increased during the production of further prints.

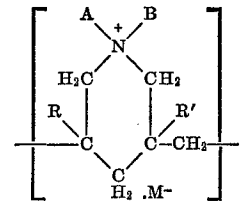
When used in combination with a light-sensitive silver halide emulsion layer, which is e.g. the case when a silver sound track has to be produced, the mordanting agent should not cause a substantial fog in the light-sensitive silver halide emulsion.

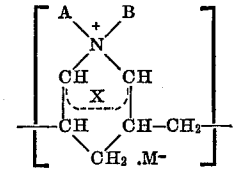
A further requirement for a useful mordant is to effect a sufficient colour absorption.

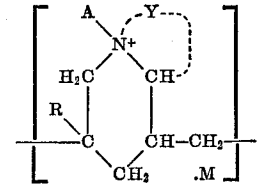
By colour absorption is meant the maximum colour density obtainable in any given combination of time and temperature under which the dye-immersed matrix is brought into close contact with the blank. Said conditions are determined by the apparatus ensuring the contact between the matrix and the blank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

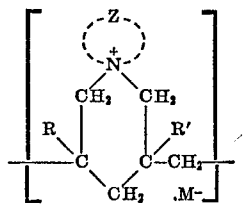
As mordanting agents more or less successfully meeting the above requirements for fixing anionic dyes more particularly acid dyes, several groups of polymers containing free amino groups, tertiary amino groups in salt form, or quaternary salt groups have been proposed.

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 addition polymers containing at least 50% of structural units selected from the class consisting of:









wherein:

each of A and B represents hydrogen or an organic substituent, e.g. a hydrocarbon radical such as an alkyl radical preferably a C_1–C_5 alkyl radical, a cycloalkyl radical, e.g. cyclohexyl, an aralkyl radical e.g. benzyl, an aryl radical e.g. phenyl or a heterocyclic radical including said radicals in substituted form, e.g. substituted with hydroxyl, acyl, an acyloxy group, e.g. acetoxy, alkoxy e.g. methoxy, aryloxy, thialkoxy, thiophenoxy, sulphamyl, carbamyl, alkoxycarbonyl or cyano,

each of R and R′ represents hydrogen, an alkyl radical preferably a lower alkyl radical (C_1–C_5), a phenyl radical including said radicals in substituted form e.g. contain these radicals substituted as stated for the radicals defined under A,

X represents a divalent radical of the formula:

$$—CH_2—(O)_{n-1}—(CH_2)—_{m-1}$$

Y represents a divalent radical of the formula:

$$—(CH_2)_{p-1}—(O)_{n-1}—CH_2—$$

Z represents the necessary atoms to close a nitrogen-containing heterocyclic 5- or 6-membered ring, e.g. represents a divalent radical of the formula:

$$—(CH_2)_{p-1}—(O)_{n-1}—(CH_2)_2—$$

forming a 5- or 6-membered heterocyclic ring including such ring in substituted form and/or forming part of a condensed ring system e.g. a morpholine, a piperidine or a pyrrolidine nucleus,

n represents 1 or 2,

m represents 2 or 3, and

p represents 3 or 4,

M^- represents an anion, preferably a photographically inert anion, e.g. a halogen anion such as Cl^- or Br^-, an anion derived from an oxyacid, e.g. a monomethyl sulphate group, a p-tolusulphonate group or a perchlorate group.

The preparation of homopolymers containing quaternary structural units as described above is mentioned, e.g., in the Canadian patent specification 687,942.

The present invention includes. however, also the use of copolymers containing preferably at least 50% of the above described structural units. Suitable copolymers for the purpose of the present invention contain in their structure sulphonyl groups, e.g. derived from SO_2 as a comonomer, although the copolymers may be derived from compounds other than SO_2 which are capable of copolymerizing with the structural units hereinbefore described.

The polymers and copolymers used according to the present invention are preferably of such a structure that they are water-soluble and can be mixed in dissolved state with a hydrophilic colloid dissolved in water. The effectiveness in mordanting action or diffusion hindering is directly proportional to the intrinsic viscosity [η] of the mordanting polymers containing structural units as described above.

The synthesis of monomers for the production of homo- and copolymers used according to the present invention is illustrated hereinafter.

PREPARATION A

(a) N-allylmorpholine

In a 5 litre reaction flask equipped with a mechanical stirrer, a thermometer, a reflux condenser and a separatory funnel, both the funnel and the condenser being provided with a calcium chloride guard tube, were placed 790 g. of morpholine, 1590 ml. of benzene and 990 g. of anhydrous sodium bicarbonate.

With stirring 1100 ml. of allyl bromide were gradually added to this mixture. The reaction was exothermic and cooling in a water-bath was necessary in order to keep the reaction under control. After the addition of the allyl bromide (lasting 90 minutes) the temperature of the reaction medium rose to 55° C. The reaction mixture was stirred for further 2 h. and heated to maintain refluxing. Thereupon the reaction mixture was cooled, and the formed sodium bromide and residual sodium bicarbonate separated by filtering. The salt residue was washed with approximately 2 litres of benzene. The filtrates were poured together and after drying overnight over anhydrous sodium sulphate distilled through a fractionating column. After the removal of the greater part of the benzene, the remaining sodium bromide was filtered and the fractional distillation of the filtrate continued. The N-allylmorpholine distilled between 156 and 158° C.

Yield: 950 g.

Density at 25° C.: 0.9267.

Refractive index: 1.458 (23° C.).

(b) N-diallylmorpholinium chloride

In a 2 litre reaction flask equipped with a mechanical stirrer, a separatory funnel and a reflux condenser, both the funnel and the reflux condenser, being provided with a calcium chloride guard tube, were placed 207 g. of N-allylmorpholine and 700 ml. of acetophenone. The mixture was heated on an oil-bath, the temperature of which was maintained at 100° C., whereupon 125 g. of allyl chloride were added with stirring. The reaction was not exothermic and heating on the oil bath was continued for 8 h. in order to maintain the temperature at 100° C.

Gradually N-diallylmorpholinium chloride crystals formed in the hot solution.

After cooling and standing at room temperature for 1 week, the crystals were sucked off and washed with 1 l. of acetone.

Yield: 253 g.

Melting point: 185° C.

PREPARATION B

N-dimethyl-N-diallylammonium chloride

In a one litre reaction flask equipped with a mechanical stirrer, a thermometer, a reflux condenser and a separatory funnel, were placed 175 g. of a 40% solution of dimethylamine in water. During stirring 116.6 g. of allyl chloride were dropwise added within 1 h. The reaction was exothermic and the temperature rose to 55° C. The reaction mixture was kept for 1 h. at 55° C. and during this period a solution of 62.1 g. of sodium hydroxide in 62 g. of water was added. Then, for 3 h. the reaction mixture was maintained at room temperature with stirring.

The aqueous solution of N-allyl-N-dimethylamine was heated to 45° C. and 240 g. of allyl chloride were added within 1 h. under continuous stirring. During and after the addition of the allyl chloride the reaction mixture was maintained at 45° C.

The reaction mixture was refluxed for 16½ h. and at the end of this period a few drops of hydrochloric acid were added for adjusting the pH at 5. The excess of reactants was removed by heating on a water-bath under reduced pressure maintained by a water-jet pump.

After adding twice 100 ml. of water to the residue and after removing it again and again, the dry powder obtained was dissolved in about 175 ml. of water. In the solution crystalline sodium chloride separated. It was filtered and the filtrate freeze-dried. A powder consisting of 5.75 g. of sodium chloride and 109.25 g. of N-dimethyl-N-diallylammonium chloride was obtained.

PREPARATION C

(a) N-allyl-N-di-β-hydroxyethylamine

In a reaction flask of 250 ml. equipped with a mechanical stirrer, a thermometer, a reflux condenser and a separatory funnel, both the funnel and the condenser being provided with a calcium chloride tube, was placed a mixture of 26.62 g. of allyl bromide and 30.36 g. of anhydrous potassium carbonate. At room temperature 21 g. of anhydrous diethanolamine were added. The reaction was exothermic and when the temperature in the flask reached 80° C. refluxing started whilst carbon dioxide escaped. Thereupon, the reaction mixtures was heated for 2 h. at 90° C. and filtered after 15 g. of dry magnesium sulphate were added. The solids on the filter were washed with 30 ml. of ethanol and the filtrates obtained poured together and subjected to fractional distillation.

The fraction boiling at 92° C. under a pressure of 0.7 mm. Hg was collected.

Yield: 24.2 g.

Refractive index: 1.4770 (23° C.).

I.R. spectrography analysis confirmed that N-allyl-N-di-β-hydroxymethylamine was obtained.

(b) N-diallyl-N-di(β-hydroxyethyl)-ammonium chloride

In a reaction flask of 1.0 l. equipped with a mechanical stirrer, a reflux condenser and a thermometer 72.5 g. of N-allyl-N-diethanolamine and 200 ml. of acetophenone were heated till 100° C. on an oil bath.

To the solution obtained were gradually added 76.5 g. allyl chloride.

The reaction was not exothermic and heating on the oil-bath was continued for 16 h. to maintain refluxing.

Thereupon, the reaction mixture was heated to 120° C. and not reacted allyl chloride collected.

By I.R. spectrography was found that the dried residue contained 96.1% by weight of N-diallyl-N-di(β-hydroxyethyl)-ammonium chloride and 4.3% by weight of N-di-(β-hydroxyethyl)-N-allylamine.

PREPARATION D

N-diallyl-N-methyl-N-β-hydroxyethylammonium chloride was prepared by a method analogous to that described in Preparation C.

PREPARATION E

N-diallyl-N-β-cyanoethylamine

In a reaction flask of 250 ml. equipped with a mechanical stirrer, a thermometer and a reflux condenser provided with a calcium chloride guard tube were subsequently placed 53 g. of acrylonitrile, 250 mg. of copper (II) acetate, 97 g. of diallylamine and 500 mg. of sodium methanolate as a catalyst. The homogeneous mixture was stirred and during 15 h. heated on an oil-bath, the temperature of which was maintained at 100° C. The obtained solution was distilled through a fractionating column and the fraction boiling between 112–118° C. under a pressure of 20 mm. Hg collected.

After redistilling the distillate, 120.0 g. N-diallyl-N-cyanoethylamine were obtained boiling at 74–76° C. under a pressure of 1 to 2 mm. Hg.

$n_D^{23° C.} = 1.4648$.

PREPARATION F

N-β-diallyl methoxy carbonyl ethylamine is prepared analogously to N-diallyl-N-β-cyanoethylamine but by starting from 1 mole of diallylamine and 1 mole of methylacrylate.

PREPARATION G

N-diallyl-N-β-carbamylmethylamine is prepared analogously to N-diallyl-N-β-cyanoethylamine but by starting from 1 mole of diallylamine and 1 mole of acrylamide.

PREPARATION H

N-diallyl-N-β-acetylethylamine

In a reaction flask of 250 ml. equipped with a mechanical stirrer, a thermometer and a reflux condenser provided with a calcium chloride guard tube were subsequently placed 250 mg. of copper (II) acetate, 97 g. of diallylamine and 35 g. of vinyl methyl ketone.

The reaction started exothermically and the temperature of the solution reached 82° C. The reaction mixture was cooled to 50° C. and again 35 g. of vinylmethylketone were added. By the heat produced in the exothermic reaction the temperature rose now to 95° C.

The reaction mixture was kept for 16 h. at 95° C. and then distilled through a fractionating column of 30 cm. filled with glass beads. The fraction distilling between 90 and 108° C. under a pressure of 18 mm. Hg was collected.

After drying on sodium hydroxide pellets 97.0 g. N-diallyl-N - β-acetylethylamine boiling at 60–61° C./1.5 mm. Hg were obtained.

PREPARATION J

N-diallyl-N-β-hydroxyethylamine

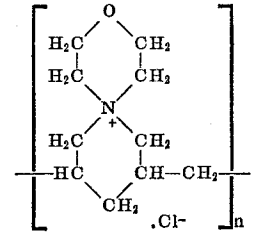
In a reaction flask of 250 ml. equipped with a mechanical stirrer, a thermomer, a reflux condenser and a separatory funnel were placed subsequently 97 g. of diallylamine, 80.5 g. of ethylenechlorohydrin and 250 mg. of copper(II) acetate. The temperature of the reaction mixture attained 33° C. and heat was supplied for 8 h. in order to maintain the temperature at 100° C. Thereupon, a solution of 50 g. of sodium hydroxide in 90 ml. of water was dropwise added.

The N-diallyl-N-β-hydroxyethylamine separated as a supernatant oil layer. The underlaying water-layer was extracted twice with 50 ml. of benzene. The benzene extracts were added together, mixed with the crude oily N-diallyl-N-β-hydroxy-ethylamine and thereupon distilled through a fractionating column of 30 cm. The fraction collected between 90 and 100° C. under a pressure of 20 mm. Hg was redistilled and the purified N-diallyl-N-β-hydroxyethylamine boiling betwen 55–56° C. under a pressure of 1.5 to 2 mm. mg collected. Yield: 90.0 g.

The production of homopolymers for use according to the present invention is illustrated by the following typical polymerization reactions.

PREPARATION 1

Poly(N-cyclodiallylmorpholinium chloride).—Compound 1



In a 500 ml. reaction flask equipped with a mechanical stirrer, a gas-inlet tube and a reflux condenser were placed 210 g. of N-diallylmorpholinium chloride dissolved in 92 ml. of distilled water at 50° C.

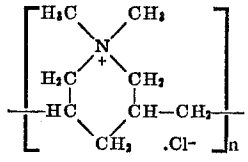
To the homogeneous solution were added 2.1 ml. of butyl hydroperoxide as a catalyst and the reaction mixture was maintained at 50° C., while a stream of nitrogen was bubbled through the solution. After a reaction period of 20 h., 45 ml. of water were added and the very viscous solution maintained for 8 h. at 75° C.

The polymerization was completed and the viscous solution was diluted with water up to a volume of 1020 ml. In 100 ml. of solution 21 g. of polymer were present.

The intrinsic viscosity of the obtained polymer measured in 0.1 N sodium chloride solution at 25° C. amounted to 1.00 dl. $g.^{-1}$.

PREPARATION 2

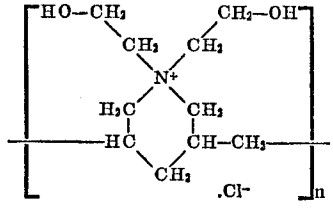
Poly(N-cyclo-diallyl-N-dimethylammonium chloride).—Compound 2



25 g. of N-diallyl-N-dimethylammonium chloride containing 5% of sodium chloride dissolved in 14 ml. of demineralized water were placed in a pressure reaction tube. Through the homogeneous mixture nitrogen was bubbled for 5 minutes. Thereupon, 0.50 ml. of Trigonox A 75 (trade name for text.-butylhydroperoxide sold by Noury & Van der Lande, Deventer, Holland) were added and the reaction mixture kept for 16 h. at 50° C. and for 64 h. at 75° C. The partially precipitated polymer was dissolved in water and purified by pouring the solution over an ion-exchanger IR 120 and IRA 45 (sold by Rohm & Haas, Philadelphia, Pa., U.S.A.). After freeze-drying, the yield amounted to 40%.

PREPARATION 3

Poly(N-cyclo-diallyl-N-di-β-hydroxyethyl-ammonium chloride).—Compound 3



The polymerization was carried out analogously to the polymerization according to Preparation 2. The temperature of polymerization was 100° C. and the yield 100%. The polymer had the consistency of an oil and was completely soluble in water.

The production of copolymers for use according to the present invention is illustrated by typical copolymerization reactions. In Table 1 following the Preparations I and II the structural formulae of said copolymers are listed as well as particulars about the copolymerization conditions and intrinsic viscosity.

PREPARATION I

Copolymer of N-cyclodiallyl-N-β-cyano-ethylammonium chloride and sulphur dioxide.—Compound 4

15 g. of N-cyclo-diallyl-N-β-cyanoethylamine was dissolved in 120 ml. of 1 N hydrochloric acid. Under reduced pressure maintained by a water-jet pump, the liquid

was concentrated till an oily residue of N-diallyl-N-cyanoethylammonium chloride was obtained. This residue was further dehydrated by dissolving it in 500 ml. of acetone and 200 ml. of benzene, and by evaporating the solution till dryness. A clear oil was obtained, which was further dried by keeping it for 1 h. at 30° C. under a reduced pressure of 1 mm. Hg. From this N-diallyl-N-cyanoethylammonium chloride an amount of 18.6 g. was dissolved in anhydrous dimethylsulfoxide till a volume of 50 ml. Through the said solution dry air was bubbled for 10 min., whereupon 50 ml. of dimethylsulfoxide containing 2 moles of sulphur dioxide were added. Thereupon 246 mg. of ammonium persulphate as polymerization catalyst were introduced. The reaction flask was closed and kept for 24 h. on a water-bath at 40° C. After a reaction time of 12 h. another portion of 123 mg. of ammonium persulphate was added.

A very viscous solution was obtained, which after being diluted with 100 ml. of dimethylsulfoxide was poured into methanol with stirring.

The copolymer of N-cyclo-diallyl-N-β-cyanoethylammonium chloride and sulphur dioxide precipitated as a white powder. After washing the precipitate with methanol it was sucked off till dryness.

PREPARATION II(a)

Copolymer of N-cyclodiallylmorpholinium chloride and sulphur dioxide.—Compound 5

In a 1 litre reaction flask equipped with a mechanical stirrer, a thermometer and a gas-inlet tube were placed 122 g. of N-diallylmorpholinium chloride and sufficient dimethylsulfoxide so as to obtain a suspension of 300 ml.

For 5 min. dry air was bubbled through the said suspension whereupon 1.6 g. of ammonium persulphate and 308 ml. of dimethylsulfoxide containing 1.95 moles of sulphur dioxide were added subsequently. The closed reaction flask was heated to 35° C. and after 15 minutes a clear solution was obtained.

The copolymerization was not exothermic and the copolymer of N-diallylmorpholinium chloride and sulphur dioxide precipitated gradually.

After 30 minutes of reaction, stirring was stopped, and the reaction mixture was still heated for 16 h. at 35° C. till all of the copolymer was precipitated. Then the precipitate was sucked off and washed with 1 l. of methanol. Finally the copolymer was dried under reduced pressure of 1 mm. Hg at 50° C. till constant weight.

PREPARATION II(b)

Copolymer of N-cyclodiallylmorpholinium chloride and sulphur dioxide.—Compound 5

In a 500 ml. reaction flask equipped with a mechanical stirrer and a thermometer were placed 20.35 g. of N-diallyl morpholinium chloride and sufficient methanol so as to obtain 100 ml. of solution.

To this solution 50 ml. of methanol, containing 6.4 g. (0.1 mole) of sulphur dioxide, were added subsequently.

Thereupon 1.34 g. of di-tert.-butyl peroxide, dissolved in 19 ml. of methanol were added.

The clear solution was stirred and gradually warmed till 27° C. Suddenly the reaction became exothermic and cooling in a water-bath was necessary in order to keep the reaction under control at 25° C.

After 5 minutes the exothermic period was over and the copolymer of N-cyclo-diallylmorpholinium chloride and sulphur dioxide precipitated gradually.

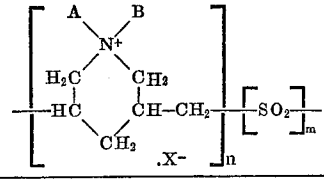
The reaction mixture was again heated and for 8 h. kept at 30° C. till all the copolymer was precipitated. Then the precipitate was sucked off and washed with 200 ml. of methanol. Finally the copolymer of N-cyclodiallylmorpholinium chloride and sulphur dioxide was dried under reduced pressure (1 mm. Hg) at 25° C. till constant weight.

Yield: 26.5 g.

Viscosity: In an 0.1 N aqueous sodium chloride solution at 25° C.: $[\eta]=0.50$ dl. g.$^{-1}$.

tact of the mordanting agent with the light-sensitive silver halide grains.

TABLE 1



Compound	Model of preparation	Starting monomer	A	B	X⁻	Reaction temperature, ° C.	[ε] dl. g.$^{-1}$ at 25° C.
6	I	N-diallyl-N-cyanoethylammonium chloride	$-(CH_2)_2-CN$	H	Cl⁻	40	0.30 in DmSO.
7	I	N-diallylammonium chloride	H	H	Cl⁻	35	0.24 in S.
8	I	N-diallyl-N-β-hydroxyethylammonium chloride	$-(CH_2)_2-OH$	H	Cl⁻	40	0.52 in DmSO.
9	I	N-diallyl-N-methoxycarbonyl ethylammonium chloride	$-(CH_2)_2-\overset{\overset{O}{\|}}{C}-OCH_3$	H	Cl⁻	40	0.40 in DmSO.
10	I	N-diallyl-N-acetylethyl ammonium chloride	$-(CH_2)_2-\overset{\overset{O}{\|}}{C}-CH_3$	H	Cl⁻	35	
11	I	N-diallyl-N-carbamylethyl ammonium chloride	$-(CH_2)_2-CONH_2$	H	Cl⁻	35	0.28 in DmSO.
12	II	N-diallylmorpholinium chloride	CH_2-CH_2 / O \ CH_2-CH_2	.....	Cl⁻	35	0.61 in S.
13	II	N-diallyl-N-methyl,N-β-hydroxyethyl ammonium chloride	$-(CH_2)_2-OH$	CH_3	Cl⁻	40	0.060 in S.

NOTE.—DmSO=dimethylsulfoxide; S=0.1 N aqueous sodium chloride; $n=m$.

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

Anthtracene Yellow GR
Fast Red S Conc.—C.I. Acid Red 88—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, or softening agents improving the flexibiity and also when necessary to some extent hardening agents 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 onto a silver halide emulsion layer.

The reason why such structure of the blank film is preferred has to be found in the fact that most of the mordanting polymers particularly those containing a free amino group produce a substantial fog in the developed photographic emulsion when incorporated in the silver halide emulsion layer. Therefore, it is preferred to apply the mordanting agent in a colloid layer covering the silver halide emulsion layer, thus preventing direct con-

In order to further prevent an interaction of the mordanting agent with the silver halide grains it has been proposed in the French patent specification 1,453,062 to incorporate into the silver halide emulsion layer cyclic ketones containing an acid radical such as a carboxylic acid radical or a sulphonic acid radical in free acid or salt form.

Those cationic polymers applied in the present invention, which are not completely inert in respect of light-sensitive silver halide and may cause fog can be used in silver halide materials the silver halide of which is shielded for direct contact with said polymers by anionic surfactants hindering the diffusion of said polymers in hydrophilic colloids. These surfactants are preferably incorporated in the emulsion layer of a blank film but can be incorporated in an interlayer between the emulsion layer and dye receptor layer of the blank film as well. Among said anionic compounds those are preferred containing at least one sulphonic acid group in acid or salt form. Anionic surfactants contain a rather large organic molecular part substituted with an anionic substituent, the anionic part of which is directly bound to the organic rest. Commercial anionic surfactants are known for use as detergents, wetting agents and dispersants or emulsifiers. In photographic materials they have been used, e.g., as spreading agents or wetting agents improving the spreading of coated colloid layers to each other or to their support.

However, when applied in a silver halide emulsion layer in order to inhibit the fogging of said layer the surfactants are used in an amount surpassing the quantity normally selected for wetting or spreading purposes, e.g., in an amount of 0.3 to 0.7 g. per sq. m.

When used in a light-sensitive material suited as receptor material in the imbibition printing process, these surfactants are preferably applied in the emulsion layer itself but may be present in an interlayer being in water-permeable relationship with the receptor layer and the emulsion layer.

Particularly effective anionic surfactants for inhibiting the fogging of light-sensitive silver halide by the cationic polymers, used in the present invention are the dialkyl (C_5–C_{20}) esters of sodium sulfosuccinic acid and compounds corresponding to the formula: $R—CH_2—SO_3Me$, wherein R represents a higher (C_{10}–C_{20}) hydrocarbon

radical and Me a metal cation, e.g., a sodium cation. Products within the scope of the latter general formula are sold under the trade name Mersolat by Farbenfabriken Bayer A.G., Leverkusen, Germany.

For inhibiting the fogging of a light-sensitive silver halide emulsion layer by the said mordanting polymers the anionic surfactants are preferably used in an amount of 20% to 100% by weight in respect of the amount of mordanting polymer in the final material. The mordanting polymers and copolymers containing structural units as described above when applied in a blank film 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 or 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 colour couplers, anionic masking compounds, and different kinds of dyes used in silver halide photographic materials e.g. anionic coloured colour couplers, anti-halation 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 multicolour film which contains normally three differently spectrally sensitive silver halide emulsion layers. Particulars regarding these special applications are disclosed in the United Kingdom patent specification 830,189.

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

Colour couplers used in silver halide colour photography and containing water-solublizing groups e.g. anionic groups such as carboxylic acid or sulphonic acid salt groups are when incorporated in the photographic material itself made more fast to diffusion e.g. by incorporating in the molecule structure of the colour coupler a large organic radical, a so-called ballasting group, which is normally an aliphatic radical containing from 5 to 20 carbon atoms in straight line. "Non-diffusing" colour couplers forming on colour development indophenol or azamethine dyes with a p-phenylene diamine type colour developing agent are described e.g. by P. Glafkidès—Photographic Chemistry—vol. II—Fountain Press—London (1960), pp. 606–615.

According to the present invention anionic colour 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 colour couplers produce on colour development colour images the sharpness of which is markedly better even if the colour couplers contain the so-called ballasting group.

The following examples illustrate the present invention without, however, limiting it thereto.

EXAMPLE 1

Onto a subbed cellulose triacetate support a gelatino silver halide emulsion of the type used for producing positive prints or a sound track was applied. The said emulsion contained in parts by weight the following ingredients:

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

The emulsion was coated pro rata of 7 g. of gelatin per sq. m.

Onto the emulsion layer of colloid layer containing a mordanting agent was applied from a solution containing the following ingredients in parts by weight:

6% aqueous gelatin solution	845
10% aqueous solution of the Compound 1 (Preparation 1)	125
40% aqueous formaldehyde solution	7.5
2% aqueous solution of Adjupal A (a wetting agent containing isononylphenoxypoly(ethyleneoxy)ethanol sold by Adjubel N.V., Belgium)	22.5

The coating of this solution was carried out in such a way that the said colloid layer contained 3.5 g. of gelatin per sq. m.

The thus obtained blank film was used in hydrotype printing and very sharp high density colour prints were obtained therewith.

EXAMPLE 2

A blank film as described in Example 1, was made with the difference, however, that the dioctyl ester of sodium sulphosuccinic acid was replaced by 4.7 parts by weight of Mersolat H (an anionic wetting agent of the structure $R—CH_2—SO_3Na$ wherein R represents a mixture of saturated and unsaturated hydrocarbon radicals derived from Kogasin II, ref. Römpp Chemie-Lexikon 3 ed. p. 946, manufactured by Farbenfabriken Bayer A.G., Leverkusen, Germany).

EXAMPLE 3

A blank film as described in Example 1 was made with the difference however, that the Compound 1 prepared according to Preparation 1 was replaced by Compound 12 listed in Table 1.

EXAMPLE 4

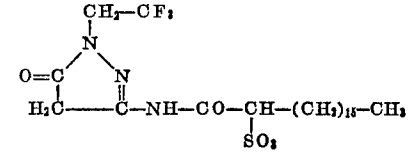
A blank film as described in Example 2 was made with the difference however, that the Compound 1 prepared according to Preparation 1 was replaced by the Compound 12 listed in Table 1.

EXAMPLE 5

A silver bromide iodide emulsion (containing 3 mole percent of iodide) was prepared using the following ingredients:

23 g. of gelatin, an amount of silver bromide iodide (3 mole percent of iodide) equivalent to 5.5 g. of silver nitrate

1/600 mole of the magenta colour coupler with following general formula:



the preparation of which is described in the United Kingdom patent specification 1,069,533.

After the addition of the usual hardening agents, stabilizing agents and wetting agents 1 g. of the mordanting polymer listed as Compound 12 in Table 1 was added to the emulsion composition in the for mof a 10% aqueous solution having a pH 7. The emulsion composition ready for coating was diluted to 720 ml. and the pH adjusted to 6.5.

The silver halide emulsion was coated pro rata of 125 g. per sq. m. onto a cellulose triacetate support having an antihalation backing layer.

After image-wise exposure and colour development in the usual way the developed image was compared with one obtained in a same photographic material but containing no mordanting polymer. The increase in image sharpness was clearly detectable in the photographic material containing the mordanting polymer. By increasing the amount of mordanting polymer from 1 to 4 g. a still better image-sharpness was obtained.

EXAMPLE 6

Coating solutions of the following compositions were prepared:

Inert gelatin ----------g-- 100
Saponine ----------g-- 2.5
4% aqueous solution of formaldehyde ----------ml-- 2.5
Dyestuffs and mordanting polymers to obtain the amounts in mg. per sq. m. as indicated in the Table 2 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 discolour completely in their gelatin layer during conventional photographic processing.

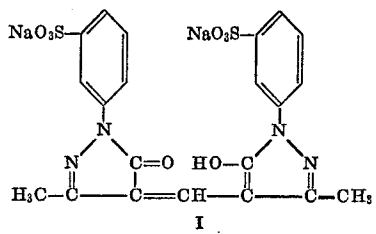
In the presence of a mordanting polymer applied according to the present invention the dyestuffs obtained a high fastness to diffusion, which is needed in antihalation and filter layers.

The relative diffusion values listed in Table 2 were obtained by comparing the spectral density obtained in a colourless thick gelatin layer (100 times as thick as the coloured gelatin layer) after keeping the different coloured gelatin layers in contact with said colourless gelatin layer for the same time under identical conditions of relative humidity. The values of the optical densities (log 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 coloured gelatin layer containing no mordanting agent and being identically coloured as those layers containing a mordanting agent being given the arbitrary value 100.

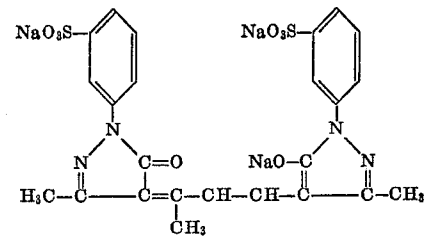
TABLE 2

Dyestuff		Mordanting polymer		Relative diffusion (arbitrary values)
No.	Mg./m.²	Compound	Mg./m.²	
I	300			100
I	300	1	300	15
I	300	5	1,500	20
I	300	11	300	54
I	300	7	300	28
II	120			100
II	120	7	200	10

The dyestuffs used have the following structures:



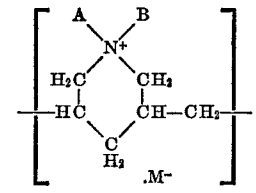
I



II

What is claimed is:

1. In an improved imbibition process for producing a dyed image in a hydrophilic colloid layer of a reception material comprising the steps of impregnating the relief image of a matrix film with a solution of an anionic dye compound, and bringing the impregnated relief image into contact with a hydrophilic colloid layer of a reception material to thereby transfer said dye compound from said relief image to said hydrophilic colloid layer to produce a dye image therein, the improvement comprising incorporating in said colloid layer to mordant said dye a homopolymer containing the following recurring units:



wherein each of A and B represents a hydrogen atom, a C_1–C_5 lower alkyl group unsubstituted or substituted with a hydroxyl, cyano, acetate or carbonamide group, or A and B represent together the necessary atoms to close a morpholine, a piperidine or a pyrrolidine nucleus, and M^- represents a photographically inert anion.

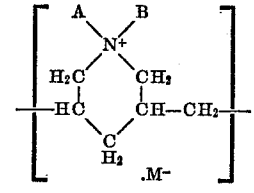
2. The process according to claim 1 wherein the homopolymer is present in an amount of 15 to 35 g. per 100 g. of said hydrophilic colloid.

3. The process of claim 1 wherein said reception material includes a light-sensitive silver halide emulsion layer in effective contact with said colloid layer.

4. The process of claim 3 wherein emulsion layer is a gelatin emulsion layer.

5. The process of claim 3 wherein said emulsion layer contains an anionic surfactant.

6. A photographic reproduction material comprising a light-sensitive silver halide emulsion layer and a hydrophilic colloid layer in effective contact with said emulsion layer, at least one of said layers having incorporated therein a homopolymer containing the following recurring units:



wherein each of A and B represents a hydrogen atom, a C_1–C_5 lower alkyl group unsubstituted or substituted

with a hydroxyl, cyano, acetate or carbonamide group, or A and B represent together the necessary atoms to close a morpholine, a piperidine or a pyrrolidine nucleus, and M^- represents a photographically inert anion.

7. The material of claim 6 wherein said homopolymer is present in said colloid layer in an amount of about 15–25 g./100 gm. of said colloid.

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96—114; 101—464