

1

3,075,841

MORDANT TREATING PROCESS AND ELEMENTS CONTAINING SAME

Roland James Lehman, Sayreville, and Gustave William Moessen, New Brunswick, N.J., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware
No Drawing. Filed June 19, 1956, Ser. No. 592,245
6 Claims. (Cl. 96-77)

This invention relates to photography and more particularly to a process for improving photographic polymeric acid dye mordants useful in dye imbibition or dye transfer printing elements. Still more particularly, it relates to film elements containing improved polymeric acid dye mordants. More specifically, this invention relates to photographic silver halide emulsions containing polymeric acid dye mordants which have been admixed in solution with polyvalent metal ions. The invention further relates to a process for reducing the back transfer properties of metal ion-mordant solutions by aging and to water-permeable colloid emulsions and film elements containing the resultant solutions.

It is well known that the dye mordant used in mordanted films in dye imbibition or dye transfer printing operations tends to diffuse out of the mordanted image receiving element and into the image bearing gelatin matrix. This migrating or diffusion of the mordant is called "back transfer" and is highly objectionable in dye imbibition or dye transfer printing. Specially, upon repeated transfer of successive dye applications from the same matrix in routine printing operations, the matrix becomes infused with dye mordant, accumulated from the premordanted image receiving element with each successive printing, and the efficiency and usefulness of the matrix is thus impaired. In addition, the dye mordant may typically spread into the areas of the matrix which should not contain the transfer dye and thus ultimately cause lack of sharpness and objectionable dye density in highlight areas of the final print.

An object of this invention is to provide a process for improving the back transfer properties of a photographic acid dye mordant. A further object is to provide a process for treating acid dye mordants which results in reduction in the amount of back transfer of the mordant during dye imbibition or dye transfer printing. A still further object is to provide such a process for treating a polymeric mordant for inclusion in a dye print receiving film element, and particularly in a light-sensitive silver halide photographic emulsion without causing any deleterious effect to either the emulsion or the polymeric mordant. Another object is to provide such a process for obtaining improved dye mordants which exhibit reduced back transfer and do not harmfully affect the photographic properties of the emulsion, such as sensitometric gamma, fog and fog stability.

An additional object of this invention is to provide improved film elements, including gelatin blanks, light-sensitive silver halide emulsions and photographic films having light-sensitive layers, which elements contain polymeric acid dye mordants which exhibit negligible back transfer when used in dye imbibition or dye transfer processes. Yet another object is to provide such mordanted elements in which mordanted acid dye images of good resolution may be formed. A further and more specific object of the invention is to provide photographic silver halide emulsions which contain non-fogging polymeric acid dye mordants which have been admixed in aqueous solution with polyvalent metal ions. A still further object is to provide such emulsions containing such metal ion-treated mordants which are non-diffusing in water-permeable colloid layers and have no deleterious action on light-

2

sensitive silver halides. Still other objects will be apparent from the following description of the invention.

It has been found that a decrease in back transfer of dye mordant in dye transfer processes results when a polymeric acid dye mordant is used in the image receiving film element in the dye transfer printing operation, which mordant has been treated by admixing the mordant in solution with polyvalent metal ions each having a valence of two or more. The undesired characteristics of back transfer are further markedly decreased if the treated mordant is given an aging treatment as described below prior to inclusion of the mordant in the water-permeable colloid, e.g., gelatin, binder, the coated layer of which is to ultimately receive the transfer dye.

The invention in its broadest aspects comprises a process for reducing the diffusing or back transfer tendencies of a polymeric acid dye mordant of the type having recurring extralinear amino groups by admixing the mordant, prior to inclusion in the image receiving element, in solution with polyvalent positive metal ions each having a valence of two or more, said metal ions being present in an amount of at least 0.006 mol per 100 grams of mordant present. The metal ions may conveniently be introduced by adding a corresponding metal salt to a solution already containing the mordant, or by adding the mordant to a solution of the metal salt, or by admixing two separate solutions, one of which contains the mordant and the other of which contains the metal ions which may have been introduced as a metal salt. After mixing, the mordant-metal ion solution can then be added to a water-permeable colloid binder for making a film element.

In a more specific aspect, the invention comprises a process for reducing the diffusing or back transfer tendencies of a polymeric mordant for acid dyestuffs, said mordant being of the type having recurring extralinear amino groups, which process comprises mixing the mordant, prior to inclusion in the image receiving element, in solution with polyvalent positive metal ions each having a valence of 2 or more, said metal ions being present in an amount of at least 0.006 mol per 100 grams of mordant present, followed by an aging step. The aging step comprises subjecting the solution to certain conditions of time and temperature which can be varied over wide limits to suit the particular conditions. It has been found that suitable aging with its subsequent reduction in back transfer can even be carried out at refrigeration temperatures of about 45° F. if the aging period is allowed to take place for a sufficiently long time. Temperatures as low as 32° F. and as high as 212° F. are considered satisfactory. Further, there is no required minimum or maximum period of time necessary for aging of the mordant-metal ion solution; the longer the aging period, the greater the reduction of back transfer. For example, an approximately equal reduction in back transfer occurs by carrying out the aging process for 264 hours at 45° F., 48 hours at 95° F. for 2½ hours at 140° F. More or less aging treatment at any given temperature results respectively in a higher or lower degree of improvement in back transfer reduction.

The invention also comprises the water permeable colloid emulsions and photographic emulsions containing the mordant which has been improved as described above, and film elements made from such emulsions. The emulsions are made by simply mixing the polymers treated according to the process of this invention with a dispersion of a colloid, e.g., gelatin, which acts as a binder for the mordant. Such an emulsion, which may or may not be light sensitive, can be coated onto a suitable support or layer to make a film element, which may be used as the image receptive element in a dye imbibition transfer process.

In a preferred embodiment of this invention, a photographic emulsion can be made by simply mixing the mordant treated according to the above described processes of this invention with an aqueous dispersion or emulsion of light-sensitive silver halide in a water-permeable colloid, which may contain the usual emulsion adjuvants, e.g., sensitizing dyes, stabilizers, hardeners, anti-foggants, etc., prior to coating onto a suitable support or layer to form a photographic element. In general, the amount of mordant used is about 25 to 55 grams per mol of silver halide. The resulting products have excellent mordanting properties with respect to acid dyes, and are particularly distinguishable by the superior non-diffusing properties of the polymeric mordant.

The polymeric mordants within the scope of this invention include polymeric acid dye mordants having recurring extralinear amino groups. By amino groups we mean either an amino group itself or an acid salt or quaternary salt thereof. The polymers may be substituted or unsubstituted and may include polymers of amines, amine acid salts and quaternary ammonium salts, and copolymers of two or more said amines, amine acid salts and quaternary ammonium salts with each other or with other polymerizable ethylenically unsaturated compounds in an amount not exceeding about 50% of the latter. Preferably, the polymeric mordants of this invention are selected from the group consisting of (a) vinyl copolymers of monoethylenically unsaturated compounds having tertiary amine salt groups and monoethylenically unsaturated compounds having quaternary ammonium salt groups, (b) vinyl copolymers of said unsaturated compounds with up to 50% by weight of another monoethylenically unsaturated compound, and (c) quaternary salts of polyvinylpyridine. Suitable polymeric mordants for the processes and products of this invention include the polymeric polyamine mordants disclosed in Gray U.S. application Serial No. 379,467, filed September 10, 1953, now U.S. Patent 2,753,263, issued July 3, 1956, the quaternary salt products of polyvinylpyridine disclosed in Minsk et al. U.S. Patent No. 2,484,420, and the alkyl amine polymers disclosed in Carroll et al. U.S. Patent No. 2,675,316. The especially preferred mordants are the copolymeric alpha-alkacrylic acid esters of amino alcohols having tertiary and quaternary salt groups in the proportion of 35 to 75 mol percent of the former to 65 to 25 mol percent of the latter, which are disclosed in Gray and Webers U.S. application Serial No. 478,544, filed December 29, 1954, now U.S. Patent 2,839,401, issued June 17, 1958. Polymeric mordants having molecular weights above 10,000 are preferred.

The metal ions useful in this invention include those which are well known in the photographic art as gelatin hardening agents. Such hardening or cross-linking of gelatin or other proteinaceous material is well known. Suitable metal ions which may be introduced, as stated above, in the form of an appropriate ionizable salt include chromic, cupric, aluminum and ferric ions. Suitable salts containing suitable metal ions include chromic bromide, chromic sulfate, aluminum chloride, potassium aluminum sulfate, ferric chloride, ferric sulfate, ferric ammonium sulfate, cupric chloride, cupric sulfate, etc. Of the useful salts, those which contain ionizable trivalent metal ions are preferred, and, in particular, the preferred metal salt is chrome alum.

It has been found that the range of concentration of metal ions, when used in the processes and products of this invention, is limited to a minimum amount of at least about 0.006 mol per 100 grams of mordant present. It has been found that below the stated range the amount of metal ion added is insufficient to effect any significant improvement in the back transfer properties of the mordant. The upper limit is not as critical but it has been found that larger amounts of metal ions cause brittleness of the water-permeable colloid emulsion or film product. The upper limit will therefore be determined

by the amount of brittleness which can be tolerated in the film product, and brittleness is also affected by other factors, e.g., emulsion additives and ambient conditions of temperature and humidity. Metal ions in an amount as great as 0.085 mol and more per 100 grams of mordant are considered satisfactory. The preferred range of iron concentration is from 0.02 to 0.055 mol per 100 grams of mordant.

Surprisingly, it has been found that it is essential to admix the metal ions with the polymeric mordant prior to the inclusion of the mordant in the photographic emulsion or film element. Mere addition of the metal ions to the photographic emulsion, or to the water-permeable colloid as is done when the ions are used as colloid hardening agents does not attain the outstanding improvement in reduction of the diffusion tendencies of dye mordants.

The colloids used as the binders in the emulsions according to this invention may be of any of the usual colloids used by photographic manufacturers. They are generally water-permeable and may be of natural or synthetic composition. Thus, the colloid, which is preferably gelatin, may be agar-agar, albumin, zein, colloidion, polyvinyl alcohol, partly hydrolyzed polymeric acetals, and hydrophilic copolymers thereof with ethylenically unsaturated monomers such as ethylene, vinyl chloride, etc.; polyvinyl acetals, e.g., the acetals of polyvinyl alcohols with acetaldehyde or benzaldehyde; or water soluble or hydrophilic cellulose derivatives. Suitable binders or water-permeable colloids of the above types are described in U.S. Patents Nos. 2,110,491, 2,211,323, 2,276,322, 2,276,323, 2,286,215 and 2,397,866.

To form a film element, which may be done according to well known means, the emulsion containing the metal ion-mordant solution according to this invention is coated on a suitable support. Such supports include paper, which may be baryta coated, cardboard, or water-proofed or transparentized paper or other film. The support may be composed of any suitable hydrophilic sheet or pellicle, e.g., cellulose derivatives such as cellulose nitrate, cellulose triacetate, cellulose propionate, cellulose acetate butyrate; polyvinyl chloride, polyvinyl chloride/acetate; hydrophilic acetals, e.g., from formaldehyde and acetaldehydes, superpolymers, e.g., polyamides, polyesters such as polyethylene terephthalate, polystyrene, etc. The film supports may be clear or may contain dyes or pigments. The coated polyester film base described in Alles and Saner U.S. Patent No. 2,627,088 is especially useful as a support material.

In admixing the polymeric mordant with the metal ions in a solution, the solvent must be a common solvent for both the mordant and the metallic salt. Particularly when the usual water-permeable colloids listed above are used as a binding material, the solvent is typically and preferably water.

The processes and products of this invention will be further described but are not intended to be limited by the following examples.

EXAMPLE I

A washed positive-type light-sensitive iodo-bromide gelatin photographic emulsion was given a customary second digestion treatment and divided into four equal parts. To the first part was added a 5% aqueous solution of diethylaminoethylmethacrylate tertiary salt-diethylaminoethylmethacrylate quaternary salt copolymer having a mol ratio of 60% tertiary salt to 40% quaternary salt copolymer made according to the procedures described in Gray et al. application Serial No. 574,593, filed March 29, 1956, in the amount of 22.0 grams of copolymer per 100 grams of emulsion gelatin. To the second part of the emulsion there was added an equal amount of copolymer mordant solution which had been aged at 140° F. for 21 hours. To third part of the emulsion there was added an equal amount of copolymer mordant solution to which had been

5

added chrome alum in an amount of 0.041 mol per 100 grams of mordant, the mixed polymer mordant chrome alum solution having been aged for 24 hours at 75° F. prior to incorporating into the emulsion. To the fourth part of emulsion was added an equal amount of polymer mordant-chrome alum mixture as in part three, except the mixture was aged at 140° F. for 21 hours prior to use. To emulsion portions one and two there was then added an amount of chrome alum which was equal to that contained in the mordant-chrome alum mixtures used in portions three and four. The usual post-digestion additives of stabilizers, coating aids, etc., were added to each portion and the emulsions were coated on a thin cellulose acetate film support and dried in the customary manner.

Sample strips of each coating were then processed without exposure in a positive-type metol-hydroquinone developing solution and fixed in a non-hardening type hypo fixing bath to eliminate the silver halide.

The film samples were then dried and tested by an imbibition transfer procedure for the degree of mordant migration which approximates the level of mordant back transfer that normally accrues during the commercial operation from 20 successive dye imbibition transfers from a single matrix. The aqueous dye solution used was adjusted to a pH of 2.4 to 3.0 and contained approximately 1.6 grams of Pontacyl Carmine 6B Extra Concentrated (Colour Index No. 57) magenta dyestuff per liter of water. The spectral density of residual dye stain on the film used to test the level of back transfer was read on a color densitometer (as described in J.S.M.P.T.E., 56, page 23, 1951) at a wavelength of 540 millimicrons. The spectral density of such residual dye stain is a direct measure of the degree of back transfer. The greater the amount of mordant adsorbed from the mordanted blank during the imbibition transfer test, the greater is the density of residual stain. For example, if a control film containing no mordant is used in place of the mordanted film in the test procedure described above, the spectral density of residual dye stain as read at a wavelength of 540 millimicrons is zero to within the accuracy of the density determination.

Sensitometric testing of the four light sensitive silver halide emulsion coatings containing the mordants which had been variously treated as described above was carried out as follows: Samples of each coating were given a 1b sensitometric exposure and developed for 3½ minutes in a positive-type metol-hydroquinone developer at 68° F. Fixing, washing, drying and determination of speed, gamma, and fog were carried out in the customary manner. Duplicate samples of each coating were subjected to an incubation treatment at a temperature of 120° F. and 65% relative humidity for 48 hours and processed together with the non-incubated samples. For the incubated samples, only the fog values were recorded. The data are given in Table I.

Table I

Coating No.	Mordant treatment	Density of residual dye stain	Fresh test			Incubated test Fog
			Speed	Gamma	Fog	
1-----	None-----	1.26	100	3.07	.01	.13
2-----	Aged 21 hrs. at 140° F. without chrome alum.	1.19	102	3.23	.01	.13
3-----	Aged 21 hrs. at 75° F. with chrome alum.	.77	100	3.18	.01	.10
4-----	Aged 21 hrs. at 140° F. with chrome alum.	.06	66	3.18	.01	.06

6

The results of Example I show that the process of metal ion treatment and aging, as in coating Nos. 3 and 4, gives a reduction in back transfer of, respectively, about 38.9% and 95.2% over the untreated mordant. There has been no deleterious affect on the photographic properties of the emulsion. The slight indicated reduction in speed is not critical in positive type emulsions and can be compensated for by means well known in the art.

EXAMPLE II

In this example the reduction of back transfer as a function of variation of the aging time of polymeric mordant-metal ion mixtures at elevated temperature is illustrated. To a 5% aqueous solution of diethylaminoethylmethacrylate tertiary salt-diethylaminoethylmethacrylate quaternary salt copolymer mordant was added chrome alum as described in Example I. The copolymeric mordant-chrome alum mixture was divided into seven equal parts and each portion was subjected to the aging treatment indicated in Table II. A washed positive-type light-sensitive iodo-bromide gelatin photographic emulsion was divided into seven equal portions after the customary second digestion treatment. To each portion of emulsion was then added one of the pre-aged mordant-chrome alum mixtures. The quantities of various ingredients were so calculated that after combination each emulsion portion contained 22.0 grams of copolymer per 100 grams of emulsion gelatin and 0.041 mol of chrome alum per 100 grams of mordant. Equal quantities of the usual post digestion adjuvants were added to each emulsion portion and the emulsions were then coated and dried. Samples of each coating were then tested for back transfer, and sensitometric speed, gamma, and fog as described in Example I. The mordant-chrome alum mixture pre-treatment and the results of the tests are given in Table II.

Table II

Coating No.	Mordant treatment	Density of residual dye stain	Fresh test			Incubated test Fog
			Speed	Gamma	Fog	
1-----	21 hrs. at 75°-----	.44	100	2.86	.02	.09
2-----	15 Min. at 140° F. + 20½ hrs. at 75° F.	.33	96	3.04	.02	.07
3-----	1 hr. at 140° F. plus 20 hrs. at 75° F.	.15	75	2.97	.02	.08
4-----	2½ hrs. at 140° F. plus 18½ hrs. at 75° F.	.08	68	3.26	.02	.11
5-----	5 hrs. at 140° F. plus 16 hrs. at 75° F.	.06	68	2.97	.02	.16
6-----	10 hrs. at 140° F. plus 11 hrs. at 75° F.	.05	64	3.00	.02	.10
7-----	21 hrs. at 140° F-----	.05	66	2.93	.02	.11

EXAMPLE III

This example serves to illustrate the effect of varying both the time and the temperature of mordant-metal ion solution aging treatment as a means of reducing the undesirable effects of back transfer during imbibition dye transfer printing operation.

To seven equal quantities of the tertiary-quaternary copolymeric mordant compositions previously described in Examples I and II were added equal amounts of chrome alum at proper time intervals so that the varying aging treatments noted in Table III could be carried out immediately in advance of the emulsion preparation, coat-

ing and drying operations. A washed positive-type light-sensitive iodo-bromide gelatin photographic emulsion was given a customary second digestion treatment and divided into seven equal portions. One of the pre-aged polymeric mordant-chrome alum mixtures was added to each of the emulsion portions. The quantities of ingredients were such that each of the final emulsion portions contained 22.0 grams of copolymeric mordant per 100 grams of gelatin and 0.041 mol of chrome alum per 100 grams of mordant. After addition of the usual post digestion adjuvants, the seven emulsions were coated and dried in a manner similar to that employed in Examples I and II. Samples of each coating were then tested for back transfer and sensitometric values as described in Example I. Details of the mordant-chrome alum mix-

mixed at such times that aging at varying time and temperature conditions as outlined in Table IV were completed immediately before the carrying out of the final emulsion preparation. One of the above pretreated mordant-chrome alum mixtures was then added to a portion of washed positive-type light-sensitive iodo-bromide gelatin photographic emulsion which had been given a customary second digestion treatment. The remaining operations of addition of post-digestion adjuvants, coating, drying, test for back transfer, sensitometric test, etc., were carried out as described in the preceding Examples. The concentrations of chrome alum employed, the conditions of the aging treatment, the nature of the mordant-chrome alum mixture treatment and the results of the tests are presented in Table IV.

Table IV

Coating No.	Mols of Chrome alum per 100 g. of mordant	Mordant-chrome alum treatment	Density of residual dye stain	Fresh test			Incubation test
				Speed	Gamma	Fog	
1-----	0.041	24 hrs. at 80° F-----	.42	100	3.27	.02	.10
2-----	0.0615	24 hrs. at 80° F-----	.32	93	3.30	.01	.10
3-----	0.041	24 hrs. at 95° F-----	.14	84	3.13	.01	.10
4-----	0.0615	24 hrs. at 95° F-----	.12	67	2.87	.01	.07
5-----	0.041	48 hrs. at 95° F-----	.09	67	3.08	.01	.09
6-----	0.0615	48 hrs. at 95° F-----	.06	60	2.77	.01	.05
7-----	0.041	11 days at 45° F-----	.10	72	3.17	.01	.07

ture aging used in each case and results of the tests are shown in Table III.

Table III

Coating No.	Mordant-chrome alum treatment	Density of residual dye stain	Fresh test		
			Speed	Gamma	Fog
1-----	Fresh solutions-----	0.57	100	3.28	.02
2-----	1 day at 75° F-----	0.58	105	3.37	.02
3-----	4 days at 75° F-----	0.23	95	3.41	.01
4-----	5 days at 75° F-----	0.22	90	3.34	.01
5-----	6 days at 75° F-----	0.20	82	3.27	.01
6-----	1 day at 95° F-----	0.27	85	3.25	.01
7-----	4 days at 95° F-----	0.15	72	3.34	.01

It can be seen from the data presented in Table III that one day's aging treatment of the polymeric mordant-chrome alum mixture at 95° F. effects the same reduction in back transfer as would occur for approximately three days' aging at 75° F. It is also evident from the data that 4 days' aging treatment at 95° F. is superior to 6 days' aging treatment at 75° F. insofar as reduction in back transfer is concerned.

EXAMPLE IV

In this example illustration is made that reduction in back transfer by the aging treatment of polymeric mordant and metal ion combinations can also be effected by the use of temperatures substantially below ordinary room conditions, e.g., such as found in ordinary refrigeration systems, as well as by the employment of temperatures substantially above ordinary room conditions. Illustration is also made that metal ion concentrations other than those used in the preceding examples will serve equally well.

Amounts of chrome alum were added to seven equal quantities of the tertiary-quaternary copolymer mordant solutions as set forth in Example I such that the concentration of chrome alum in the final photographic emulsion composition would correspond as indicated in Table IV to either 0.041 mol or 0.0615 mol of chrome alum per 100 grams of mordant and the amount of copolymer mordant would be 22.0 grams per 100 grams of emulsion gelatin. These mordant-chrome alum mixtures were

It can be seen from the data in Table IV that variation in the amount of chrome alum present in the polymeric mordant-chrome alum mixture within the range of the invention does not markedly affect the efficacy of the aging treatment. It is also apparent that a sizable reduction in back transfer can be accomplished by carrying out the polymeric mordant-metal ion mixture aging treatment of the invention even at temperatures substantially below ordinary room conditions as well as at elevated temperatures as described in this and in the preceding examples.

EXAMPLE V

A 5% aqueous solution of diethylaminoethylmethacrylate tertiary salt-diethylaminoethylmethacrylate quaternary salt copolymer mordant as described in Example I was prepared and divided into 8 equal portions. To portion No. 1 was added 0.041 mol of chrome alum per 100 g. of mordant; to portion No. 3 was added 0.041 mol of potassium aluminum sulfate per 100 g. of mordant; to portion No. 5 was added 0.041 mol of ferric ammonium sulfate per 100 g. of mordant, and to portion No. 7 was added 0.041 mol of cupric sulfate per 100 g. of mordant. Portions numbered 1, 3, 5 and 7 were then aged for 24 hours at 140° F. The remaining mordant portions numbered 2, 4, 6 and 8 were kept at 75° F. without further addition or treatment. After a customary second digestion, a washed positive-type light-sensitive iodobromide gelatin photographic emulsion was divided into eight equal portions and one of the eight mordant compositions variously treated as described above was combined with one of the emulsion portions. To emulsion-mordant admixture No. 2 was then added the same quantity of chrome alum as had previously been employed in the mordant-chrome alum pre-aging treatment for mordant portion No. 1. Similarly, like molar quantities of potassium aluminum sulfate, ferric ammonium sulfate, and cupric sulfate were added to emulsion-mordant admixtures Nos. 4, 6 and 8 respectively. The addition of post digestion adjuvants, coating, drying, test for back transfer, sensitometric test, etc. was completed as described in the preceding examples. Test results are presented in Table V.

Table V

Coating No.	Metal salt added to mordant	Mordant aging treatment	Metal salt added to emulsion after mordant	Density of residual dye stain	Fresh test		
					Speed	Gamma	Fog
1.....	Chrome alum.....	24 hrs. at 140° F.....					
2.....		24 hrs. at 75° F.....	Chrome alum.....	.10	44	2.30	.01
3.....	Potassium aluminum sulfate.....	24 hrs. at 140° F.....		.57	100	3.20	.02
4.....		24 hrs. at 75° F.....	Potassium aluminum sulfate.....	.43	119	3.04	.01
5.....	Ferric ammonium sulfate.....	24 hrs. at 140° F.....		.72	133	3.51	.01
6.....		24 hrs. at 75° F.....	Ferric ammonium sulfate.....	.39	95	2.91	.01
7.....	Cupric sulfate.....	24 hrs. at 140° F.....		.52	118	3.34	.01
8.....		24 hrs. at 75° F.....	Cupric sulfate.....	.48	26	3.42	.01
				.62	30	3.52	.01

The data in Table V indicate that substantial reduction in back transfer is effected by the use of any of a variety of metal ions in the mordant treatment process of this invention. It is also apparent that chromic ions are more efficacious in the polymeric mordant-metal ion preaging treatment for minimizing back transfer than the other metal ions illustrated and are therefore to be preferred.

EXAMPLE VI

5% aqueous solutions of each of diethylaminoethyl-

dant companions. After the additions of post digestion adjuvants, and the usual operations of coating, drying, etc., tests for back transfer and sensitometric values were made as previously described. The type of mordant used for each case, the mordant aging treatment and type of hardening agent used, as well as back transfer and sensitometric results are given in Table VI. The fog values reported for the incubated test were determined after subjection to 120° F. and 65% relative humidity for 48 hours.

Table VI

Coating No.	Mordant	Metal salt added to mordant	Mordant aging treatment	Metal salt added to emulsion after mordant	Density of residual dye stain	Fresh test			Incubated test
						Speed	Gamma	Fog	
1.....	Copolymer ¹	Chrome alum.....	24 hrs. at 140° F.....						
2.....	do ¹		24 hrs. at 75° F.....	Chrome alum.....	.08	48	3.21	.01	.05
3.....	PMe2VP ²	Chrome alum.....	24 hrs. at 140° F.....		.83	100	3.18	.03	.13
4.....	PMe2VP ²		24 hrs. at 75° F.....	Chrome alum.....	.58	97	3.32	.01	.03
5.....	P2Me5VP ³	Chrome alum.....	24 hrs. at 140° F.....		.79	110	3.15	.03	.04
6.....	P2Me5VP ³		24 hrs. at 75° F.....	Chrome alum.....	.06	13	1.76	.01	.02
7.....	P2Me5VP ³	Ferric ammonium sulfate.....	24 hrs. at 140° F.....		.18	11	1.77	.01	.02
8.....	P2Me5VP ³		24 hrs. at 75° F.....	Chrome alum.....	.43	10	1.77	.01	.01
9.....	PMe2VP ²	Potassium aluminum sulfate.....	24 hrs. at 140° F.....		.92	6	1.58	.01	.01
10.....	PMe2VP ²		24 hrs. at 75° F.....	Potassium aluminum sulfate.....	.56	138	3.33	.03	.04
					1.48	130	3.24	.04	.04

¹ Diethylaminoethylmethacrylate tertiary salt-diethylaminoethylmethacrylate quaternary salt copolymer.

² Poly-1-methyl-2-vinylpyridinium cyclohexanesulfonate.

³ Poly-2-methyl-5-vinylpyridine hydrochloride.

methacrylate tertiary salt-diethylaminoethylmethacrylate quaternary salt copolymer mordant, poly-1-methyl-2-vinylpyridinium cyclohexanesulfonate mordant, and poly-2-methyl-5-vinylpyridine hydrochloride were prepared. Chrome alum, ferric ammonium sulfate or potassium aluminum sulfate to the extent of 0.041 mol of metal ion per 100 g. of polymer material was added to selected portions of these solutions followed by aging of the mordant-metal ion mixtures for 24 hours at 140° F. Duplicate portions of the polymeric solutions were reserved as controls without metal ion admixture and held at 75° F. during the 24 hour aging process of the treated polymer materials. Details of the treatment followed for each case is tabulated in Table VI. The treated and untreated polymer mordant solutions were then added to equal quantities of a washed positive-type light-sensitive iodobromide gelatin photographic emulsion which had been given a customary second digestion treatment. To those emulsion-mordant mixtures which contained the untreated mordant solutions controls, an amount of chrome alum, ferric ammonium sulfate, or potassium aluminum sulfate, respectively, was added which was equal to the amount of metal ion previously present in each of the respective treated and aged polymeric mor-

EXAMPLE VII

A 5% aqueous solution of poly-1-methyl-2-vinylpyridinium cyclohexanesulfonate was prepared and divided into six equal portions. To portions numbered 2, 3, 4 and 5 were added respectively 0.0068, 0.0205, 0.041 and 0.082 mol of chrome alum per 100 g. of vinylpyridine polymer mordant. No additions were made to portions numbered 1 and 6. The first five portions of mordant were then aged for 24 hours at 140° F. and the sixth portion which served as a control was aged for 24 hours at room temperature of 75° F. At the conclusion of the aging treatment, the six resultant solutions were added to separate identical amounts of a positive-type digested emulsion similar to that described in the preceding examples. Additional chrome alum was then added to emulsion-mordant admixtures containing the first three and the sixth mordant portions so as to bring the total amount of chrome alum to 0.041 mol per 100 grams of vinylpyridine polymer. Emulsion portions numbered 4 and 5 already contained at least this amount of chrome alum introduced via the mordant treatment. After the usual additions of post digestion adjuvants, the six emulsions were coated, dried and tested as described in the previous examples. Test data for the experiment are given in Table VII.

Table VII

Coating No.	Mols ch. alum/100 g. mordant before treatment	Mordant aging treatment	Mols ch. alum/100 g. mordant to emulsion	Density of residual dye stain	Fresh test			Incubated test fog
					Speed	Gamma	Fog	
1		24 hrs. at 140° F.	0.041	0.98	93	3.27	.01	.04
2	0.0068	do.	0.0342	0.73	97	3.23	.01	.03
3	0.0205	do.	0.0205	0.79	103	3.21	.01	.03
4	0.041	do.		0.74	103	3.35	.01	.04
5	0.082	do.		0.72	104	3.29	.04	.04
6		24 hrs. at 75° F.	0.041	1.39	100	3.01	.03	.04

EXAMPLE VIII

To five equal portions of a 5% aqueous diethylaminoethylmethacrylate tertiary salt-diethylaminoethylmethacrylate quaternary salt copolymer mordant solution were added respectively 0.041 mol of chrome alum, 0.0273 mol of potassium aluminum sulfate, 0.082 mol of potassium aluminum sulfate, 0.0273 mol of ferric ammonium sulfate, and 0.082 mol of ferric ammonium sulfate respectively.

then added to each of five equal portions of a digested positive-type silver halide emulsion such as has been described more fully in the preceding examples. The necessary steps for completion of the emulsions and the test operations of the completed films were carried out in a manner analogous to that employed in Example VIII. The results of sensitometric and back transfer tests are tabulated in Table IX.

Table IX

Coating No.	Metal salt added per 100 g. mordant before treatment	Mordant treatment	Density of residual dye stain	Fresh test			Incubated test fog
				Speed	Gamma	Fog	
1	0.041 mol chrome alum	24 hrs. at 140° F.	0.21	100	1.95	.01	.01
2	0.273 mol potassium aluminum sulfate	do.	0.36	111	1.96	.01	.01
3	0.082 mol potassium aluminum sulfate	do.	0.13	111	2.01	.01	.01
4	0.0273 mol ferric ammonium sulfate	do.	0.19	78	1.76	.01	.01
5	0.082 mol ferric ammonium sulfate	do.	0.05	78	1.66	.01	.01

These five mordant solutions thus treated were then aged at 140° F. for 24 hours. A sixth control solution of mordant received no additions and was retained at 75° F. for 24 hours. After completion of the aging process, the five treated and the sixth untreated mordant solutions were added to equal portions of a digested positive-type silver halide emulsion as described in the preceding examples. To the sixth control emulsion containing the untreated mordant was then added chrome alum in the amount of 0.041 mol per 100 g. of copolymer mordant. The remaining operations of addition of post digestion adjuvants, coating, drying, etc. were carried out and the usual tests made on the films thus prepared. The results of the tests are given in Table VIII.

EXAMPLE X

A 5% aqueous solution of diethylaminoethylmethacrylate tertiary salt-diethylaminoethylmethacrylate quaternary salt copolymer mordant was prepared and divided into six equal portions. To portions numbered 3, 4, 5 and 6 were added respectively 0.0068, 0.0205, 0.041 and 0.0615 mol of chrome alum per 100 g. of copolymer mordant. Portion No. 1 served as a room temperature aged (75° F.) untreated control and portions numbered 2 through 6 were aged at 140° F. for 24 hours. At the conclusion of the aging treatment, the six mordant solutions were added to a 5.5% aqueous gelatin solution such that each gelatin solution-mordant admixture contained

Table VIII

Coating No.	Metal salt added per 100 g. mordant before treatment	Mordant treatment	Metal salt added to emulsion per 100 g. mordant	Density of residual dye stain	Fresh test			Incubated test fog
					Speed	Gamma	Fog	
1	0.041 mol chrome alum	24 hrs. at 140° F.		0.08	95	3.12	.01	.12
2	0.0273 mol potassium aluminum sulfate	do.		0.28	102	3.40	.01	.20
3	0.082 mol potassium aluminum sulfate	do.		0.19	105	3.46	.01	.17
4	0.0273 mol ferric ammonium sulfate	do.		0.22	98	3.29	.01	.13
5	0.082 mol ferric ammonium sulfate	do.		0.13	94	3.23	.01	.14
6		24 hrs. at 75° F.	0.041 mol chrome alum	0.42	100	3.41	.01	.19

EXAMPLE IX

A 5% aqueous solution of poly-2-methyl-5-vinylpyridine hydrochloride was prepared and divided into five equal portions. To these were added respectively 0.041 mol of chrome alum, 0.0273 mol of potassium aluminum sulfate, 0.082 mol of potassium aluminum sulfate, 0.0273 mol of ferric ammonium sulfate, and 0.082 mol of ferric ammonium sulfate. The five mordant-metal ion admixtures were then aged for 24 hours at 140° F. After aging treatment, one of the treated mordant solutions was

22.0 g. of mordant per 100 g. of gelating. To each of the gelating solutions containing mordant portions numbered 1, 2, 3 and 4 sufficient chrome alum was added to make the concentration 0.041 mol of chrome alum per 100 g. of mordant.

The usual coating aids were added to each of the above six gelatin-mordant compositions and coatings were made from each and dried. Since these coatings were not light-sensitive and contained no silver halide, back transfer tests could be made immediately. The same procedure for back transfer test was followed as was used in the earlier

examples, except that the silver halide bearing samples underwent suitable development, fixation, etc., prior to the actual back transfer test operation. The results are shown in Table X.

Table X

Coating No.	Mols chrome alum per 100 g. mordant before treatment	Mordant aging treatment	Mols chrome alum per 100 g. mordant added to mordant-gelatin admixture	Density of residual dye stain
1		24 hrs. at 75° F.	0.041	.45
2		24 hrs. at 140° F.	0.041	.50
3	0.0068	do.	0.0342	.24
4	0.0205	do.	0.0205	.08
5	0.041	do.		.06
6	0.0615	do.		.10

EXAMPLE XI

Example X was repeated except that the mordant used was poly-1-methyl-2-vinylpyridinium cyclohexanesulfonate. The results are shown in Table XI.

Table XI

Coating No.	Mols chrome alum per 100 g. mordant before treatment	Mordant aging treatment	Mols chrome alum per 100 g. mordant added to mordant-gelatin admixture	Density of residual dye stain
1		24 hrs. at 75° F.	0.041	.38
2		24 hrs. at 140° F.	0.041	.36
3	0.0068	do.	0.0342	.14
4	0.0205	do.	0.0205	.11
5	0.041	do.		.15
6	0.0615	do.		.06

Among the acid dyes which can be mordanted by means of the polymeric mordants having the improved diffusing characteristics according to this invention are:

Anthracene Yellow GR (400% pure Schultz No. 177)
 Fast Red S Conc. (Colour Index 176)
 Pontacyl Green SN Ex. (Colour Index 737)
 Acid blue black (Colour Index 246)
 Acid Magenta O (Colour Index 692)
 Naphthol Green B Conc. (Colour Index 5)
 Brilliant Paper Yellow Ex. Conc. 125% (Colour Index 364)
 Tartrazine (Colour Index 640)
 Metanil Yellow Conc. (Colour Index 138)
 Pontacyl Carmine 6B Ex. Conc. (Colour Index 57)
 Pontacyl Scarlet R Conc. (Colour Index 487)
 Pontacyl Rubine R Ex. Conc. (Colour Index 179)

An advantage of the invention is that it provides a new and simple process for reducing the diffusing tendencies of polymeric acid dye mordants useful in dye imbibition and dye transfer printing operations. Premordanted films containing the improved polymeric mordants along with a light-sensitive silver halide may be exposed and processed before dye transfer so that the film will bear records of silver, e.g., an optical sound track.

A further advantage of the invention is that the improved polymeric mordants do not fog silver halide layers and can be incorporated directly therein. A still further advantage is that the improved mordants in the dye imbibition blank or image receiving layer produces dye images of increased sharpness. Another advantage of the invention is that a large number of satisfactory prints can be made from the same matrix in routine dye transfer printing. Yet another advantage is the reduction in objectionable dye density in high light areas of the final print.

An additional advantage of the invention is that it provides improved non-diffusing and non-migrating polymeric acid dye mordants which can be incorporated in light-sensitive silver halide emulsions and in photographic elements containing light-sensitive silver halide without deleterious effect on the photographic properties of the light-sensitive material. Still other advantages will be apparent from the above.

The invention claimed is:

1. The process for reducing in a dye transfer receiving element the back transfer tendencies of a water-soluble, photographic polymeric acid dye mordant selected from the group consisting of (a) vinyl copolymers of monoethylenically unsaturated compounds having tertiary amine salt groups and monoethylenically unsaturated compounds having quaternary ammonium salt groups, (b) vinyl copolymers of said unsaturated compounds with up to 50% by weight of another monoethylenically unsaturated compound, and (c) quaternary salts of polyvinylpyridine, which comprises admixing said mordant in aqueous solution with from 0.006 to 0.085 mol per 100 grams of mordant of polyvalent metal ions selected from the group consisting of chromic, cupric, aluminum and ferric ions, subsequently aging said solution at a temperature of from 45° F. to 212° F. for a period of at least 2½ hours, the temperature and time of said aging treatment being selected so that the back transfer tendencies of said mordant are reduced by more than about 40% and coating said aged solution on said dye transfer receiving element.
2. A process as defined in claim 1 wherein said aged solution is impregnated into said dye transfer element.
3. The process set forth in claim 1 wherein the solution is aged at a temperature in the range from 75° F. to 140° F.
4. The process of making a film element comprising admixing in solution (1) a water-soluble, photographic polymeric acid mordant selected from the group consisting of (a) vinyl copolymers of monoethylenically unsaturated compounds having tertiary amine salt groups and monoethylenically unsaturated compounds having quaternary ammonium salt groups, (b) vinyl copolymers of said unsaturated compounds with up to 50% by weight of another monoethylenically unsaturated compound, and (c) quaternary salts of polyvinylpyridine, and (2) polyvalent metal ions selected from the group consisting of chromic, cupric, aluminum and ferric ions, aging said solution of mordant and metal ions at a temperature of from 45° F. to 212° F. for a period of at least 2½ hours, the temperature and time of said aging treatment being selected so that the back transfer tendencies of said mordant are reduced by more than about 40%, after said aging admixing with said solution a water-permeable colloid to form an emulsion, and coating said emulsion onto a film support.
5. A photographic element comprising a water-permeable colloid emulsion containing a light-sensitive silver halide and mordanting amounts of a solution prepared by admixing in aqueous solution a water-soluble photographic polymeric acid dye mordant selected from the group consisting of (a) vinyl copolymers of monoethylenically unsaturated compounds having tertiary amine salt groups and monoethylenically unsaturated compounds having quaternary ammonium salt groups, (b) vinyl copolymers of said unsaturated compounds with up to 50% by weight of another monoethylenically unsaturated compound, and (c) quaternary salts of polyvinylpyridine, and metal ions in an amount of from 0.006 to 0.085 mol per 100 grams of mordant, said metal ions selected from the group consisting of chromic, cupric, aluminum and ferric, and subsequently aging said solution at a temperature of from 45° F. to 212° F. for a period of at least 2½ hours, the temperature and time of said aging treatment being selected so that the back

transfer tendencies of said mordant are reduced by more than about 40%.

6. A dye imbibition transfer element comprising a support and a water-permeable colloid layer which comprises a water-permeable colloid emulsion containing in mordanting amounts a solution prepared by admixing in aqueous solution a water-soluble photographic polymeric acid dye mordant selected from the group consisting of (a) vinyl copolymers of monoethylenically unsaturated compounds having tertiary amine salt groups and monoethylenically unsaturated compounds having quaternary ammonium salt groups, (b) vinyl copolymers of said unsaturated compounds with up to 50% by weight of another monoethylenically unsaturated compound, and (c) quaternary salts of polyvinylpyridine, and metal ions in an amount of from 0.006 to 0.085 mol per 100 grams of mordant, said metal ions selected from the group consisting of chromic, cupric, aluminum and ferric, and subsequently aging said solution at a temperature of from 45° F. to 212° F. for a period of at least 2½ hours, the temperature and time of said aging treatment being selected so that the back transfer tendencies of said mordant are reduced by more than about 40%.

2,182,794
2,215,196
2,256,356
2,474,612
2,527,223
2,527,260
2,548,575
2,635,535
2,675,316
2,753,263
2,768,079
2,813,845
2,821,455
2,839,401
2,857,372
2,897,200

5

10

15

20

References Cited in the file of this patent

UNITED STATES PATENTS

Dawson	Dec. 12, 1939
Schlack	Sept. 17, 1940
Russell et al.	Sept. 16, 1941
Barney	June 28, 1949
Kern	Oct. 24, 1950
Hart et al.	Oct. 24, 1950
Weyerts	Apr. 10, 1951
Jennings	Apr. 21, 1953
Carroll et al.	Apr. 13, 1954
Gray	July 3, 1956
Russell	Oct. 23, 1956
Wesp et al.	Nov. 19, 1957
Delangre	Jan. 28, 1958
Gray et al.	June 17, 1958
Straley et al.	Oct. 21, 1958
Meader et al.	July 28, 1959

FOREIGN PATENTS

330,199	Great Britain	June 12, 1930
344,365	Great Britain	Mar. 12, 1931