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NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

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ABSTRACT OF THE DISCLOSURE

In order to prevent phase separation between poly-4-vinylpyridine and a polymer having functional groups selected from the group consisting of —OH, —NH_2, and —SH, the 4-vinylpyridine may be polymerized first with a vinyl aldehyde and then incorporated with said —OH, NH_2, and/or —SH functional polymer to thereby chemically bond the poly-4-vinylpyridine-vinyl aldehyde copolymer thereto. A film formed from such a composition is useful as a dye image-receiving layer in a diffusion transfer image-receiving sheet.

The present invention relates to photography and, more particularly, to processes for forming photographic diffusion transfer color images and products particularly adapted for employment in such processes.

In processes of the type set forth in U.S. Patent No. 2,983,606, a photosensitive element containing a dye developer and a silver halide emulsion is exposed and wetted by a liquid processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during, or after wetting, on a sheetlike support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid processing composition permeates the emulsion to initiate development of the latent image contained therein. The dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation and especially as regards its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion from the developed emulsion of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable imbibition period.

The dye developers, as noted above, are compounds which contain in the same molecule both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide development function is a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho- and para-amino substituted hydroxyphenyl groups. In general, the development function includes a benzenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized.

Multicolor images may be obtained using color image-forming components such as, for example, the previously mentioned dye developers, in diffusion transfer processes. One technique contemplates the use of a photosensitive silver halide stratum comprising at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen. Transfer processes of this type are disclosed in U.S. Patents Nos. 2,968,554 and 2,983,606. In such an embodiment, each of the minute photosensitive elements has associated therewith an appropriate dye developer in or behind the silver halide emulsion portion. In general, a suitable photosensitive screen, prepared in accordance with the disclosures of said patents, comprises minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer.

Another process for obtaining multicolor transfer images utilizing dye developers employs an integral multilayer photosensitive element, such as is disclosed in the aforementioned copending U.S. application Ser. No. 565,135, filed on Feb. 13, 1956, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion strata. Each set of silver halide emulsion and associated dye developer strata may be separated from other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

Copending U.S. application Ser. No. 234,864, now U.S. Patent No. 3,362,819, filed Nov. 1, 1962, discloses image-receiving elements particularly adapted for employment in the preceding diffusion transfer processes which elements comprise a support layer possessing on one surface thereof, in sequence, a polymeric acid layer; an inert timing or spacer layer; and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substances.

As set forth in the last-mentioned application, the polymeric acid layer comprises polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali

metals, such as sodium, potassium, etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting group is, of course, nondiffusible from the acid polymer layer. In the preferred embodiments disclosed, the acid polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the application, mention may be made of dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives of cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy substituted aldehydes, e.g., o-, m- or p-carboxy benzaldehyde; partial esters of ethylene/maleic anhydride copolymers; partial esters of methylvinyl ether/maleic anhydride copolymers; etc.

The acid polymer layer is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition. As previously noted, the pH of the processing composition preferably is of the order of at least 13 to 14.

It is, of course, necessary that the action of the polymeric acid be so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer is kept at a level of pH 12 to 14 until the positive dye image has been formed after which the pH is reduced very rapidly to at least about pH 11, and preferably about pH 9 to 10, before the positive transfer image is separated and exposed to air. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the quaternary ammonium, sodium or other alkali salt. The diffusion rate of such dye image-forming components is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer. The processing technique thus effectively minimizes changes in color balance as a result of longer imbibition times in multicolor transfer processes using multilayer negatives.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the acid groups are disclosed to be so distributed in the acid polymer layer that the rate of their availability to the alkali is controllable, e.g., as a function of the rate of swelling of the polymer layer which rate in turn has a direct relationship to the diffusion rate of the hydroxyl ions. The desired distribution of the acid groups in the acid polymer layer may be effected by mixing the acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only the acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments are illustrated, respectively, in the above-mentioned copending application, Ser. No. 234,864, by (a) a mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthalyl groups than the first-mentioned cellulose acetate hydrogen phthalate.

It is also disclosed that the layer containing the polymeric acid may contain a water insoluble polymer, such as, for example, a cellulose ester, which acts to control or modulate the rate at which the alkali salt of the polymer acid is formed. As examples of cellulose esters contemplated for use, mention is made of cellulose acetate, cellulose acetate butyrate, etc. The particular polymers and combinations of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry strength and when necessary or desirable, suitable subcoats may be employed to help the various polymeric layers adhere to each other during storage and use.

The inert spacer layer of the aforementioned copending application, for example, a layer comprising polyvinyl alcohol or gelatin, acts to "time" control the pH reduction by the polymeric acid layer. This timing is disclosed to be a function of the rate at which the alkali diffuses through the inert spacer layer. It was stated to have been found that the pH does not drop until the alkali has passed through the spacer layer, i.e., the pH is not reduced to any significant extent by the mere diffusion into the spacer layer, but the pH drops quite rapidly once the alkali diffuses through the spacer layer into the acid polymer layer.

The image-receiving elements used in such processes generally comprise an opaque or transparent support carrying an image-receiving layer of a dyeable material which is permeable to the alkaline aqueous processing solution. In the past, it has been proposed to use film-forming materials, such as polyvinyl alcohol, and nylons, such as N-methoxy-methyl-polyhexamethylene adipamide, as the dyeable materials. A preferred image-receiving element utilizes poly-4-vinylpyridine and, more preferably, a mixture of poly-4-vinylpyridine and polyvinyl alcohol, such as is disclosed in U.S. Patent No. 3,148,061, issued Sept. 8, 1964.

The presence of water-sensitive film-forming materials in the image-receiving layer often results in swelling of the film during processing with a resulting distortion of the image. Such water sensitivity can be minimized or eliminated by hardening or cross-linking the polymer, prior to photographic processing, with aldehydes such as glyoxal as is disclosed in U.S. Patent No. 3,003,872, issued Oct. 10, 1961 to Elkan R. Blout et al. However, while hardening the polymer, such materials may also introduce photographically adverse side effects, such as loss of gloss, reduced image density, and adhesion of the processing composition to the receiving layer. In order to prevent such adhesion of the processing composition, an additional coating or layer may be applied, but this so-called strip coat, as well as introducing an additional step into the fabrication of the image-receiving sheet, may also interfere with the transfer of dye developers to the receiving sheet, as do some of the hardening or cross-linking agents, resulting in an over-all diminution of positive image quality.

The poly-4-vinylpyridine-polyvinyl alcohol mixture disclosed in the above-cited U.S. Patent No. 3,148,061 is applied as the top layer in the receiving sheet (excluding the presence of a strip coat) from aqueous solution. Since poly-4-vinylpyridine is not easily soluble in water the pH of the solution must be made slightly acidic to facilitate complete solvation of the poly-4-vinylpyridine. It is, there-

fore, readily seen that the poly-4-vinylpyridine is present in the stratum in the form of an acid salt. In the above-cited patent, and particularly the examples thereof, the acid utilized is acetic acid. However, any weak acid, e.g., formic acid, lactic acid, etc. may be used. It is preferred to acidify the coating composition with lactic acid thereby placing the polyvinyl pyridine in the form of the lactate—which is completely soluble in the polyvinyl alcohol solution. Since the acids useful herein must be weak, the ionic association between the polyvinyl pyridine and the acid anion is very weak. Hydrolysis is easily facilitated by a humid atmosphere, resulting in the weak acid and polyvinyl pyridine. The weak acid migrates into other layers of the structure leaving the polyvinyl pyridine which is now incompatible in solution with the polyvinyl alcohol. It is theorized that a phase separation takes place which results in a white cast or "milky haze" on the receiving sheet.

Copending U.S. application Ser. No. 605,971, filed Dec. 30, 1966 which is a continuation-in-part of U.S. application Ser. No. 229,194, now abandoned, filed on Oct. 8, 1962 and abandoned on Jan. 8, 1967, teaches that the polyvinyl alcohol of the image-receiving layer may be cross-linked with, for example, an acrolein condensation composition. Functionally, the cross-linked polyvinyl alcohol intersticially traps the poly-4-vinylpyridine and substantially prevents its migration, which would result in "milky haze."

It is a primary object of the present invention to provide a novel method of preventing "milky haze," which probably results from phase separation between the poly-4-vinylpyridine and polyvinyl alcohol in the image-receiving layer of a receiving sheet useful in the well-known diffusion transfer photographic process.

It is a further object of the present invention to provide a print prepared by the well-known photographic diffusion transfer color process with increased stability against fading.

Another object of the present invention is to provide a method for alleviating unsightly yellow stain often found in receiving sheets used in diffusion transfer photographic processes.

Another object of the present invention is to prepare a receiving sheet for use in a photographic diffusion transfer process which contains an image-receiving layer comprising polyvinyl alcohol and poly-4-vinylpyridine and additionally contains a non-extractable, non-volatile cross-linking agent.

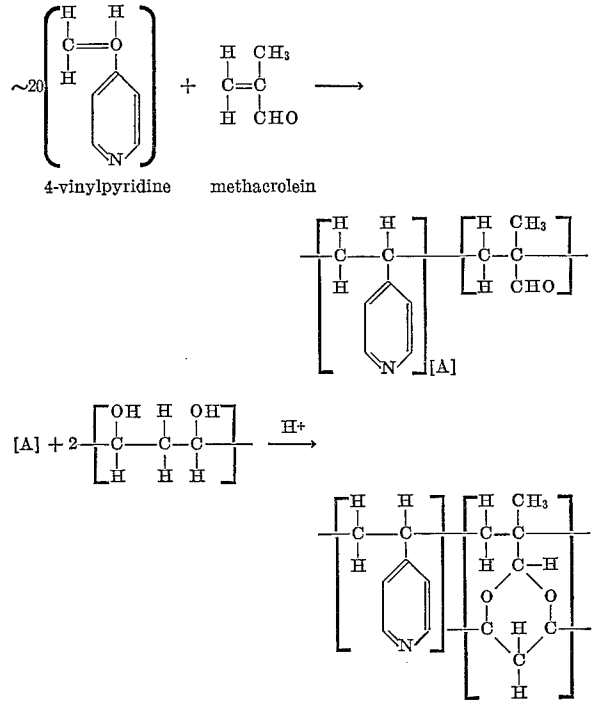
Still another object of the present invention is to provide novel color diffusion transfer processes utilizing the above image-receiving layers.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

As noted above it is of prime importance in preparing an image-receiving sheet for use in a color diffusion transfer photographic process, which sheet comprises an image-receiving layer containing poly-4-vinylpyridine held in a matrix material, to provide a means for preventing phase separation of the poly-4-vinylpyridine from the matrix material. It has been unexpectedly found that if a small amount of a vinyl aldehyde which is capable of condensing with functional groups of the matrix material, is added to the system as a copolymer of the 4-vinylpyridine, phase separation in discouraged since the constituents of the image-receiving layer become chemically associated. Compounds of this class are, for example, acrolein, methacrolein, p-vinyl benzaldehyde, etc. The preferred compound for use in the instant environment is methacrolein in a preferred range of 1 to 10% by weight. The matrix material may comprise any material which will condense with aldehyde groups, such as polyvinyl alcohol; gelatin; partial acetals of polyvinyl alcohols, such as those disclosed in U.S. Patent No. 3,239,337; carbohydrate polymers; etc., which contain varying amounts of functional —OH, —NH_2, and —SH groups. The preferred matrix material is polyvinyl alcohol. The following depicts the method through which, it is theorized, chemical association is effected.



4-vinylpyridine methacrolein

In processes of the prior art and particularly the process described in the above copending application Ser. No. 605,971, a marked yellowing of the image-receiving layer is noted after processing, and particularly after the receiving sheet has aged for some time. This is probably due in large part to the acrolein formaldehyde condensation product. Unexpectedly, the product of the instant invention displays substantially no yellow stain after processing, even after substantial aging. This is due probably to the fact that the acrolein formaldehyde condensation product is deleted from the formulation.

Another surprising benefit achieved by the utilization of the instant invention is a substantial increase in image dye stability when exposed to Florida sunlight. In certain instances stability increases of more than 50% were noted. This phenomenon is both totally unexpected and, at the present, unexplainable.

As pointed out above, a spacer layer is positioned in the composite receiving sheet immediately preceding the image-receiving layer. It is evident that if the material used to formulate said spacer layer contains —OH, —NH_2 or —SH groups, some linking will take place between the spacer layer and image-receiving layer, thereby improving the adhesion therebetween.

After prolonged testing it has been found that the utilization of vinyl aldehydes according to the process of the present invention does not in any way contaminate the photographic system.

The following non-limiting examples illustrate the invention and are to be considered as explanatory rather than as limiting in scope. In all instances where constituents of the image-receiving layer coating mixture are

given in percent by weight, such percents are considered to be on the basis of the weight of the 4-vinyl pyridine.

EXAMPLE 1

An image-receiving element was prepared by coating a cellulose nitrate subcoated baryta paper with the partial butyl ester of polyethylene/maleic anhydride copolymer which may be prepared by refluxing, for 14 hours, 300 gms. of a DX–840–31 resin (trade name of Monsanto Chemical Co., St. Louis, Mo., for high viscosity polyethylene/maleic anhydride), 140 gms. of n-butyl alcohol and 1 cc. of 85% phosphoric acid to provide a polymeric acid layer approximately 0.3 mils thick. The external surface of said acid layer was coated with a 5% solution of polyvinyl alcohol to provide a polymeric spacer layer approximately 0.325 mil thick. The external surface of the spacer layer was then coated with a solution of a 2:1 mixture by weight of polyvinyl alcohol and poly-4-vinyl pyridine-methacrolein copolymers, the latter containing 5% by weight of methacrolein, at a coverage of approximately 600 mg. per square foot to provide a polymeric imate-receiving layer approximately 0.4 mil thick. The thus prepared image-receiving element was then baked at 180° F. for 30 minutes and allowed to cool.

The coating composition for the image-receiving layer was prepared as follows: In a three neck round bottomed flask fitted with a stirrer, condenser, nitrogen inlet, thermometer and heat bath, 75 g. of polyvinyl alcohol is dissolved in 500 ml. of water under a cover of nitrogen. The solution is cooled to 60° F., 1 g. of 2,2'azobis[methyl propionitrile] is dissolved in a solution of 37½ g. of 4-vinylpyridine (freshly distilled, B.P. 59°, at 12 mm.) and 1.88 g. of methacrolein (freshly distilled, B.P. 68.4°, at atmospheric pressure). With as vigorous stirring as possible the 4-vinylpyridine solution is added in a steady stream to the vessel containing the polyvinyl alcohol solution. Copolymerization between the 4-vinylpyridine and methacrolein proceeds by keeping the solution at 60° for 3½ hours after which time the temperature is raised to 90° for a half hour. The solution is subsequently cooled, 15.4 g. lactic acid is added, and the solution is diluted to 6% by weight based on total solids with water. The coating composition prepared in this manner is cast onto the support and allowed to dry.

A multicolor, multilayer photosensitive element was prepared in a manner similar to that disclosed in the aforementioned copending U.S. application Ser. No. 565,135 and detailed hereinbefore. In general, the photosensitive elements comprised a support carrying a red-sensitive halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum. In turn, the emulsions had dispersed behind them in water-immiscible organic solvents and contained in separate gelatin polymeric layers, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. A gelatin interlayer was positioned between the yellow dye developer layer and the green-sensitive emulsion stratum, and also between the magneta dye developer layer and the red-sensitive emulsion stratum. The particular dye developers employed in the photosensitive elements may comprise, for example, 1,4 - bis - (α - methyl - β-hydroquinonyl-ethylamino)-5,8-dihydroxyanthraquinone (a cyan dye developer); 2-(p-[2',5' - dihydroxyphenethyl] - phenylazo) - 4 - isopropoxy-1-naphthol (a magenta dye developer); and 1-phenyl-3-n-hexyl - carbamyl-4-(p-[hydroquinonylethyl]-phenylazo)-5-pyrazolone (a yellow dye developer). The last-mentioned yellow and magenta dye developers are disclosed in U.S. Patent No. 3,134,764, issued May 26, 1964, and the cyan dye developer is disclosed in U.S. Patent No. 3,135,606, issued June 2, 1964. Multicolor photosensitive material may also be commercially procured from Polaroid Corporation, Cambridge, Mass., as it comprises the negative component of the photographic film distributed by that corporation under the trade designation of Polacolor Type 108 Land film.

The photosensitive element was then exposed and processed at various temperatures by spreading an aqueous liquid processing composition at a pH of not less than about 12 which comprised:

Water	cc	100
Potassium hydroxide	gms	11.2
Hydroxyethyl cellulose (high viscosity) [1]	gms	4.03
Potassium thiosulfate	gm	0.5
Benzotriazole	gms	3.5
N-benzyl-α-picolinium bromide	gms	2.3
Lithium hydroxide	gm	0.3

[1] Commercially available from Hercules Powder Co., Wilmington, Del., under the trade name Natrasol 250.

between said image-receiving element and said exposed multicolor element as they were brought into superposed relationship.

After an imbition of 60 seconds or 135 seconds, for tests carried out at 75° and 100° F., or 50° F., respectively, the image-receiving element was separated from the remainder of the film assembly.

For purposes of comparison, an image-receiving element was fabricated in accordance with the above-described procedure with the exception that the image-receiving layer was coated with the composition prepared according to the above-mentioned Patent No. 3,148,061 and contained poly-4-vinylpyridine, polyvinyl alcohol and an acrolein formaldehyde condensation product. The thickness of the thus-prepared image-receiving layer was 0.6 mil.

The last-prepared image-receiving element was then processed, as detailed above, at various temperatures.

Examination of the resultant images showed the following differential maximum densities, which comprise the difference between the maximum and minimum densities recorded for the various colors of the film with a Quantalog MacBeth Densitometer.

	$\Delta D_{max.}$					
	Polyvinyl alcohol, poly-4-vinylpyridine-methacrolein copolymer containing 5% methacrolein image-receiving layer			Polyvinyl alcohol, poly-4-vinylpyridine image-receiving layer containing acrolein-formaldehyde condensation product control		
Temperature, ° F.	Red	Green	Blue	Red	Green	Blue
50	1.42	1.40	1.37	1.22	1.32	1.27
75	1.39	1.63	1.71	1.40	1.68	1.81
100	1.23	1.40	1.63	0.95	1.29	1.49

Substantial improvement in $\Delta D_{max.}$ is evident when using a receiving sheet formulated with an image-receiving layer prepared by the present invention.

Stability tests based on magenta dye fading on sample with original reflection densities between 0.8 and 0.9 were also performed with the image-receiving sheet of the instant example and a control formulated as described above. The test was carried out under Florida sunshine and provided the following results:

Langleys*	Percent fading of polyvinyl alcohol-poly-4-vinyl-pyridine-methacrolein copolymer containing 5% methacrolein image-receiving layer	Percent fading of polyvinyl alcohol poly-4-vinyl-pyridine image-receiving layer containing acrolein-formaldehyde condensation product control
600	4	12
1,200	15	32
2,500	31	64
5,000	65	84

*Gm. cals./cm.² sec.

It is evident that the receiving sheet prepared by the process of the present invention displays substantial increases in stability to intense sunlight over a typical receiving sheet of the prior art. As mentioned before, the reason for this increase in stability is not known at the present time.

EXAMPLE 2

The procedure of Example 1 was carried out using a receiving sheet which comprised a 0.3 mil polyvinyl alcohol spacer layer and an image-receiving layer which was prepared as in Example 1 except that only 1% by weight methacrolein was used. The thickness of the image-receiving layer was 0.425 mil. The control was prepared as in Example 1 except that the thickness of the image-receiving layer was 0.3 mil.

A comparison of the differences in differential dye densities at various temperatures was made and provided the following results:

	$\Delta D_{max.}$					
	Polyvinyl alcohol, poly-4-vinylpyridine-methacrolein copolymer containing 1% methacrolein image-receiving layer			Polyvinyl alcohol, poly-4-vinylpyridine image-receiving layer containing acrolein-formaldehyde condensation product control		
Temperature, ° F.	Red	Green	Blue	Red	Green	Blue
50	1.29	1.43	1.41	1.44	1.44	1.39
75	1.40	1.49	1.57	1.32	1.67	1.82
100	1.46	1.52	1.60	0.89	1.29	1.50

Substantially greater differential dye densities at high temperatures result using the 1% methacrolein copolymer than the differential dye densities of the control.

A comparison of image stability was also made following the format set forth in Example 1 and provided the following results:

Langleys	Percent fading of polyvinyl alcohol-poly-4-vinyl-pyridine-methacrolein copolymer containing 1% methacrolein image-receiving layer	Percent fading of polyvinyl alcohol poly-4-vinyl-pyridine image-receiving layer containing acrolein-formaldehyde condensation product control
600	12	24
1,200	20	40
2,500	43	53
5,000	82	86

EXAMPLE 3

The procedure of Example 1 was carried out using a receiving sheet which comprised a 0.3 mil polyvinyl alcohol spacer layer and an image-receiving layer which was prepared as in Example 1 except that 2% by weight methacrolein was used. The thickness of the image-receiving layer was .7 mil. The control was the same as in Example 2.

	$\Delta D_{max.}$					
	Polyvinyl alcohol, poly-4-vinylpyridine-methacrolein copolymer containing 2% methacrolein image-receiving layer			Polyvinyl alcohol, poly-4-vinylpyridine image-receiving layer containing acrolein-formaldehyde condensation product control		
Temperature, ° F.	Red	Green	Blue	Red	Green	Blue
50	1.34	1.42	1.40	1.44	1.44	1.39
75	1.31	1.47	1.52	1.32	1.67	1.82
100	1.01	1.23	1.33	0.89	1.29	1.50

A comparison of image stability was also made following the format set forth in Example 1 and provided the following results:

Langleys	Percent fading of polyvinyl alcohol-poly-4-vinyl-pyridine-methacrolein copolymer containing 5% methacrolein image-receiving layer	Percent fading of polyvinyl alcohol poly-4-vinyl-pyridine image-receiving layer containing acrolein-formaldehyde condensation product control
600	19	24
1,200	25	40
2,500	41	53
5,000	78	86

EXAMPLE 4

The procedure of Example 1 was carried out using a receiving sheet which comprised a 0.3 mil polyvinyl alcohol spacer layer and an image-receiving layer which was prepared as in Example 1 except that 3% by weight methacrolein was used. The thickness of the image-receiving layer was 0.725 mil. The control was the same as in Example 2.

	$\Delta D_{max.}$					
	Polyvinyl alcohol, poly-4-vinylpyridine-methacrolein copolymer containing 3% methacrolein image-receiving layer			Polyvinyl alcohol, poly-4-vinylpyridine image-receiving layer containing acrolein-formaldehyde condensation product control		
Temperature, ° F.	Red	Green	Blue	Red	Green	Blue
50	1.37	1.52	1.49	1.44	1.44	1.39
75	1.43	1.67	1.80	1.32	1.67	1.82
100	1.38	1.59	1.62	0.89	1.29	1.50

A comparison of image stability was also made following the format set forth in Example 1 and provided the following results:

Langleys	Percent fading of polyvinyl alcohol-poly-4-vinyl-pyridine-methacrolein copolymer containing 3% methacrolein image-receiving layer	Percent fading of polyvinyl alcohol poly-4-vinyl-pyridine image-receiving layer containing acrolein-formaldehyde condensation product control
600	16	24
1,200	29	40
2,500	48	53
5,000	83	86

EXAMPLE 5

The procedure of Example 1 was carried out using a receiving sheet which comprised a 0.3 mil polyvinyl alcohol spacer layer and an image-receiving layer which was prepared as in Example 1 except that 4% by weight methacrolein was used. The thickness of the image-receiving layer was 0.775 mil. The control is the same as in Example 1.

	$\Delta D_{max.}$					
	Polyvinyl alcohol, poly-4-vinylpyridine-methacrolein copolymer containing 4% methacrolein image-receiving layer			Polyvinyl alcohol-poly-4-vinylpyridine image-receiving layer containing acrolein-formaldehyde condensation product control		
Temperature, ° F.	Red	Green	Blue	Red	Green	Blue
50	1.48	1.42	1.33	1.22	1.32	1.28
75	1.36	1.67	1.77	1.40	1.68	1.84
100	1.42	1.45	1.56	0.95	1.29	1.17

Langleys	Percent fading of polyvinyl alcohol-poly-4-vinyl-pyridine-methacrolein copolymer containing 4% methacrolein image-receiving layer	Percent fading of polyvinyl alcohol-poly-4-vinyl-pyridine image-receiving layer containing acrolein-formaldehyde condensation product control
600	9	12
1,200	18	32
2,500	32	64
5,000	63	84

The image-receiving layers to be employed in a photographic diffusion transfer process are required to possess certain critical features if photographic images of excellent quality are to be formed therein. During the diffusion transfer processing of an exposed photosensitive sheet, the image-receiving layer, upon contact with an alkaline processing composition used in diffusion transfer processes, is desired to slightly swell to allow the admittance within the image-receiving layer of the diffusing image-forming material. This slight swelling should be to such a degree that most, if not all, of the diffusing image-

forming material from the exposed photosensitive sheet may enter and be locked within the image-receiving layer so that a print having the highest image density is formed. However, the swelling should not be to such an extent that the gloss of the final print is destroyed or that the processing composition is induced to adhere to the final print. Extensive swelling of the image-receiving layer can also cause distortion of the formed image. It is within this area that the process of the present invention provides its unusual results in that it provides polymeric receiving layers with the desired degree of swellability necessary to provide quality images without loss of gloss or dimensional stability. Most important, this invention provides image-receiving layers to which processing composition does not tend to adhere.

Of primary importance in determining the utility of the instant invention is the ability of the receiving sheet to be peeled away from the photosensitive sheet after imbibition with no reagent adhering to the receiving sheet. It may be stated that the adherence of processing composition to the receiving sheet will render such sheet useless for its intended purpose. In order to determine the ability of sheets prepared by the instant invention to be stripped without the adherence of processing reagent sheets were made up containing various amounts of methacrolein copolymerized with the 4-vinyl pyridine mordant and were drawn in intimate contact with an exposed photosensitive sheet with processing reagent interposed therebetween, between rollers spaced 0.0044 inch apart. In no case was any processing reagent found to adhere to the receiving sheet.

The support layers referred to may comprise any of the various types of conventional rigid or flexible supports, for example, glass, paper, metal, and polymeric films of both synthetic types and those derived from naturally occurring products. Suitable materials include paper; polymethacrylic acid, methyl and ethyl esters; vinyl chloride polymers; polyvinyl acetal; polyamides such as nylon; polyesters such as polymeric films derived from ethylene glycolterephthalic acid; and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate.

Where desired, the support for the image-receiving layer may be transparent or opaque. Suitable opacifying agents may be incorporated in the negative and/or positive to permit imbibition to be completed outside of a camera, i.e., in an area exposed to light actinic to the silver halide emulsions.

Use of the novel image-receiving elements of this invention makes feasible the use, over an extended range of ambient temperature, of image dyes which are pH sensitive, and particularly the use of dye developers having less pH insulation since the final pH of the image layer can be more accurately and reproducibly controlled.

Processing preferably is effected in the presence of an auxiliary or accelerating silver halide developing agent which is substantially colorless, at least in the unoxidized form. Particularly useful are substituted hydroquinones, such as phenylhydroquinone, 4'-methylphenyl-hydroquinone, toluhydroquinone, tertiary-butylhydroquinone, and 2,5-triptycene diol. These hydroquinones may be employed as components of the processing composition or they may be incorporated in one or more layers of the negative. Particularly useful results are obtained when 4'-methylphenylhydroquinone is dispersed in one or more of the gelatin interlayers and/or in a gelatin layer coated over the blue-sensitive emulsion layer.

As noted above, this invention contemplates reduction of the positive image pH to a level substantially precluding aerial oxidation of developer moieties. The provision of antioxidants, such as arbutin, prior to exposure of the image to air to provide additional protection against oxidation also is within the scope of this invention. Since the reduction in pH continues for at least a short time after the positive image is separated from the negative, provision of such an antioxidant permits the positive to be separated at a slightly higher pH than would be otherwise desirable.

It is also contemplated to provide other adjuvants, e.g., ultraviolet absorbers, effective to improve the light stability or other properties of the positive image. Thus, an ultraviolet absorber may be included in the processing composition and deposited on the image-receiving layer during imbibition, or it may be present in a thin overcoat on the image-receiving layer prior to imbibition.

In all preferred embodiments of this invention the polymeric acid layer preferably is thicker than the image-receiving layer and has an appreciably higher mg./ft.^{2} coverage. The image-receiving layer is preferably about 0.25 to 0.4 mil thick, the polymeric acid layer is preferably 0.3 to 1.5 mil thick, and the described spacer layer is preferably about 0.05 to 0.8 mil thick.

Although the invention has been illustrated in connection with dye developers, and the invention is particularly applicable to dye developers because of their susceptibility to aerial oxidation at high pH, the novel image-receiving elements of this invention may be used in other diffusion transfer processes such as those previously described to obtain pH reduction and particularly to obtain transfer images exhibiting great optical clarity and luminosity over an extended range of ambient temperatures.

In addition to the described essential layers, it will be recognized that the image-receiving elements may also contain one or more subcoats or layers, which, in turn, may contain one or more additives such as plasticizers, intermediate essential layers for the purpose, for example, of improving adhesion, etc.

Since certain changes may be made in the above products and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sese.

What is claimed is:

1. A receiving sheet for use in a photographic diffusion transfer process comprising a composite structure comprising a support and an alkali permeable and dyeable polymeric layer comprising the reaction product of a polymer having functional groups selected from the group consisting of —OH, —NH_2, and —SH, and a copolymer of 4-vinyl pyridine and a vinyl aldehyde.

2. The invention of claim 1 wherein said vinyl aldehyde is methacrolein.

3. The invention of claim 2 wherein said methacrolein is present in the range of 1 to 10% based on the weight of the 4-vinyl pyridine.

4. The invention of claim 3 wherein said polymer is polyvinyl alcohol.

5. The invention of claim 4 wherein the polyvinyl alcohol and 4-vinyl pyridine are present in a weight ratio of about 2:1.

6. The invention of claim 5 which additionally contains, in sequence a polymeric acid layer intermediate said support and said dyeable polymeric layer.

7. A process for forming a diffusion transfer color image which comprises the steps of developing an exposed photosensitive element comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers containing a dye, which dye is a silver halide developing agent, by contacting said element with an aqueous alkaline processing solution, immobilizing said dye in said element as a result of development, forming thereby an imagewise distribution of mobile dye as a function of the point-to-point degree of exposure of said element, transferring by imbibition at least a portion of said imagewise distribution of mobile dye to a superposed image-receptive element which comprises a composite structure comprising a support and an alkali permeable and dyeable polymeric layer comprising the reaction product of a polymer having functional groups selected from the group consisting of —OH, —NH_2 and —SH, and a copolymer of 4-vinyl pyridine and a vinyl aldehyde to provide to said dyeable polymeric layer a dye image.

8. The invention of claim 7 wherein said vinyl aldehyde is methacrolein.

9. The invention of claim 8 wherein said methacrolein is present in the range of 1 to 10% based upon the weight of 4-vinyl pyridine.

10. The invention of claim 9 wherein said polymer is polyvinyl alcohol.

11. The invention of claim 10 wherein said polyvinyl alcohol and 4-vinyl pyridine are present in a weight ratio of about 2:1.

12. The invention of claim 11 wherein said composite structure additionally contains, in sequence, a polymeric acid layer intermediate said support and said dyeable polymeric layer.

13. The invention of claim 12 wherein subsequent to substantial positive dye image formation in the dyeable polymeric layer a portion of the hydroxyl ions of said

alkaline solution is transferred by imbibition to said polymeric acid layer to thereby reduce the alkalinity of the processing solution.

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