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3,353,956

PHOTOGRAPHIC DIFFUSION TRANSFER PROCESSES UTILIZING AN IMIDAZOLE AND AN IMAGE-RECEIVING ELEMENT CONTAINING A POLYMERIC ACID LAYER

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9 Claims. (Cl. 96—29)

This invention relates to photography and, more particularly, to improvements in processes for obtaining color images by diffusion transfer.

U.S. Patent No. 2,983,606, issued May 9, 1961, to Howard G. Rogers, discloses processes employing dye developers to form color transfer images and products useful therein. The copending application of Edwin H. Land and Howard G. Rogers, Ser. No. 565,135, filed Feb. 13, 1956, discloses the use of such dye developers in integral multilayer negatives to give multicolor transfer images. The copending application of Milton Green and Howard G. Rogers, Ser. No. 50,851, filed Aug. 22, 1960 (now U.S. Patent No. 3,173,786 issued Mar. 16, 1965), discloses and claims as improvement in the aforesaid dye developer processes wherein development and transfer are effected in the presence of a quaternary ammonium compound. The copending application of Edwin H. Land, Ser. No. 234,864, filed Nov. 1, 1962, discloses and claims still another improvement in said dye developer transfer processes, wherein the image-receiving element contains a layer of polymeric acid and the pH of the image-receiving layer is substantially reduced prior to separation of said layer at the end of the imbibition period. This invention is particularly concerned with an improvement in such diffusion transfer processes and, in particular, with the provision of novel diffusion transfer processes wherein processing is effected in the presence of an imidazole.

It is a further object of this invention to provide novel image-receiving elements for use in diffusion transfer processes employing dye developers whereby the resulting color image exhibits superior and unobvious optical and physical properties.

A further object of this invention is to provide diffusion transfer processes and products for performing such processes wherein the color transfer image is only slightly alkaline when it is separated from the exposed and developed photosensitive layers.

Yet another object of this invention is to provide novel image-receiving elements adapted to effect a substantial reduction in the alkalinity of the color transfer image without interfering in the formation of said color transfer image.

Still another object of this invention is to provide novel processing compositions for use in diffusion transfer processes employing dye developers, whereby the optical properties, e.g., gloss, of the transfer image are improved.

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 products and compositions possessing

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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.

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

As is now well known in diffusion transfer processes of the type contemplated herein and set forth in detail in the aforementioned issued U.S. patent and copending U.S. applications, a processing composition is applied to an exposed photosensitive emulsion to effect development thereof, and an imagewise distribution of diffusible, unoxidized dye developers is formed as a function of development. At least a portion of each such imagewise distribution of diffusible dye developer is transferred imagewise to an image-receiving layer positioned in superposed relationship with said photosensitive emulsion. At the end of the appropriate imbibition period, the image-receiving layer is separated from its superposed relationship with the developed photosensitive emulsion.

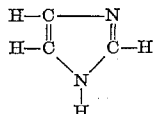
10 In carrying out the process of this invention, a photosensitive element containing a silver halide emulsion is exposed and wetted with a fluid processing composition, for example by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed, prior to, during or after wetting, on an image-receiving element. In one preferred embodiment, the photosensitive element contains a layer of dye developer, and a liquid processing composition is applied to the photosensitive element in a thin, substantially uniform layer as the photosensitive element is brought into superposed position with an image-receiving element. The liquid processing composition permeates the emulsion to provide a solution of dye developer substantially uniformly distributed therein. As the exposed silver halide emulsion is developed, the oxidation product of the dye developer is immobilized or precipitated in the developed areas, thereby providing an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition. This immobilization is apparently due, at least in part, 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 the oxidized developing agent. At least part of each such imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer which layer receives a depthwise diffusion of the transferred, unoxidized dye developer, without appreciably disturbing the imagewise distribution thereof, to provide a reversed or positive, colored image of the image developed in each silver halide emulsion. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. The transfer image is revealed by separating the image-receiving layer from the photosensitive element at the end of the imbibition period. In an especially useful embodiment, the dye developers are dissolved in a water-immiscible solvent and the resulting solution is then dispersed in gelatin to provide the dye developer layers. Numerous examples of suitable dye developers are disclosed in said U.S. Patent No. 2,983,606 and copending applications noted therein. As set forth therein, a dye developer is a compound which is both a dye and a silver halide developing agent. Particularly useful and

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preferred dye developers are azo and anthraquinone dyes which contain one or more hydroquinonyl groups.

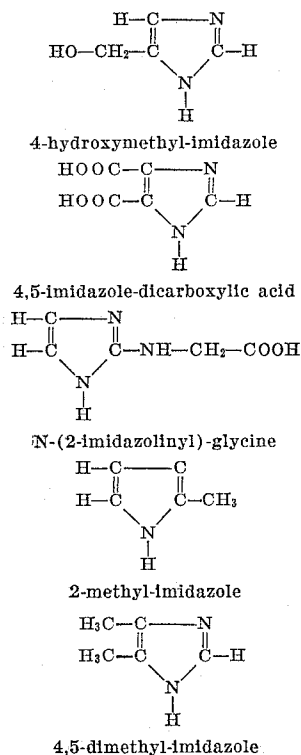
It now has been found that if such dye developer processes are performed in the presence of an imidazole, a number of unexpected and desirable results are obtained. The imidazole may be present initially as a component of the processing composition or it initially may be contained in the image-receiving element.

As used herein, the expression "an imidazole" refers to compounds based upon imidazole, i.e.,



and derivatives thereof which do not provide additional rings. Imidazole itself is the simplest member of the class of compounds contemplated herein. It should be noted that imidazole derivatives containing additional, fused rings, e.g., benzimidazoles, are not within the scope of this invention as they do not provide the unique results obtained with the single ring imidazoles herein contemplated. The imidazoles with which this invention is concerned are soluble in aqueous alkali, and may contain groups such as alkyl, hydroxyalkyl, alkylamino, carboxyl, carboxymethylamino, etc., as substituents on the imidazole ring, provided that the resulting imidazole is alkali soluble.

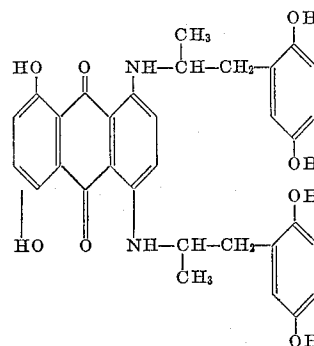
As examples of other imidazoles contemplated as useful in accordance with this invention, mention may be made of:



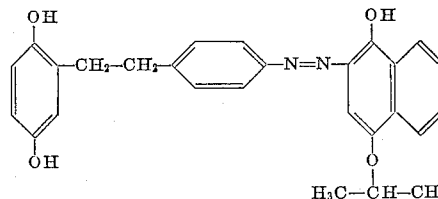
In the examples set forth below, reference to a multicolor negative is to a multilayer negative in which the blue-sensitive, green-sensitive, and red-sensitive silver iodobromide emulsion layers have positioned behind them, respectively, a yellow dye developer, a magenta dye developer, and a cyan dye developer. A gelatin interlayer is positioned between the yellow dye developer layer and the green-sensitive emulsion, and between the magenta dye developer and the red-sensitive emulsion. Multilayer negatives of this type are disclosed, for example, in FIG. 9 of the previously mentioned U.S. Patent No. 2,983,606.

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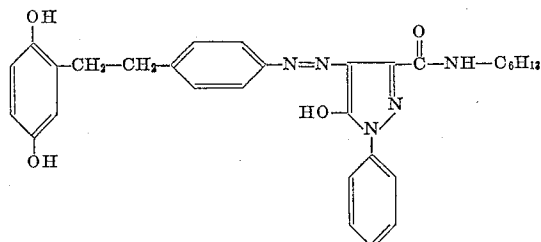
The dye developer layers are prepared by dissolving each dye developer in a water-immiscible solvent and dispersing the resulting solution in gelatin. The particular dye developers employed, unless otherwise indicated, were:

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cyan:10
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1,4-bis-[α -methyl- β -hydroquinonyl-ethylamino]-5,8-dihydroxy-anthraquinone

magenta:

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30
2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-isopropoxy-1-naphthol

yellow:

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40
1-phenyl-3-N-n-hexylcarbonyl-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone

The following examples are given for purposes of illustration and are not intended to be limiting:

Example 1

An image-receiving element was prepared by coating a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine on cellulose acetate-subcoated baryta paper to provide an image-receiving layer approximately 0.40 mil thick. A multilayer, multicolor negative as described above was exposed and a thin layer of processing composition comprising:

Water	-----cc--	100
NaOH	-----g--	5.17
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington 99, Delaware, under the trade name Natrasol 250]	-----g--	4.03
Sodium thiosulfate	-----g--	1.15
Benzotriazole	-----g--	2.3
N-benzyl- α -picolinium bromide	-----g--	2.3
Imidazole	-----g--	1.0

was spread between said image-receiving element and said exposed multicolor negative as they were brought into superposed relationship. After an imbibition period of approximately 2 minutes, the image-receiving element was separated and contained a good quality multicolor transfer image. This transfer image was noticeably more glossy than a control transfer image formed in the same manner except that no imidazole was present in the processing composition.

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Example 2

The procedure described in Example 1 was repeated, except that the imidazole was omitted from the processing composition and the image-receiving layer was formed by coating a solution comprising, by weight, 6% polyvinyl alcohol, 3% poly-4-vinylpyridine and 2% imidazole. The image-receiving layer was noticeably glossier than a control which did not contain imidazole.

Image-receiving elements containing a layer of a non-diffusible acid-reacting reagent, e.g., polymeric acid, whereby the pH of the image-receiving layer is substantially reduced prior to separation of the image-receiving element from superposed relationship with the negative and subsequent exposure to air, are disclosed and claimed in the aforementioned copending application of Edwin H. Land, Ser. No. 234,864. The following examples illustrate the use of imidazoles in conjunction with such image-receiving elements.

Example 3

300 g. of high viscosity poly-(ethylene/maleic anhydride) [commercially available from Monsanto Chemical Company, St. Louis, Mo., under the trade name DX-840-31 Resin] was dissolved in 1500 cc. of acetone. 150 g. of n-butyl alcohol and 1 cc. of 85% phosphoric acid were added and the mixture was refluxed for 14 hours. The resulting solution comprising the partial half-butyl ester of poly-(ethylene/maleic anhydride) was allowed to cool, and 10% imidazole was then added to the solution and the resulting mixture coated on a cellulose nitrate-subcoated baryta paper to give a layer about 0.8 mil thick. An image-receiving layer about 0.3 mil thick of polyvinyl alcohol and poly-4-vinylpyridine (2:1 by weight) was then applied. This image-receiving element gave an excellent multicolor transfer when diffusion transfer processed for 1½ minutes with an exposed multilayer, multicolor negative and a processing composition comprising:

Water	-----cc--	100
NaOH	-----g--	5.17
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington 99, Delaware, under the trade name Natrasol 250]	-----g--	4.03
Sodium thiosulfate	-----g--	1.15
Benzotriazole	-----g--	2.3
N-benzyl- α -picolinium bromide	-----g--	2.3

The presence of the imidazole appeared to increase the rate of pH reduction without decreasing the transfer image density.

Example 4

The procedure described in Example 3 was repeated, except that a layer of polyvinyl alcohol approximately 0.5 mil thick was coated between the layer of the partial butyl ester of the ethylene/maleic anhydride copolymer and the image-receiving layer. The polyvinyl alcohol was applied using a solution of 7 parts by weight polyvinyl alcohol, 100 parts by weight of water, and a small amount of wetting agent.

Example 5

Image-receiving elements were prepared as described in Examples 3 and 4 except that the imidazole was omitted from the polymeric acid layer. The thus-coated image-receiving elements were then passed between a pair of squeeze rolls, a solution containing 10 parts by weight of imidazole to 100 parts of water being maintained in the nip between the image-receiving layer and one of the squeeze rolls. This imidazole solution appeared to soak into the image-receiving layer. After drying, the image-receiving layer was free of haze and glossier than a control image-receiving element prepared in the same manner but without the imidazole. Use of these image-re-

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ceiving layers in the diffusion transfer process of Example 3 gave similar good results.

Example 6

The procedure described in Example 3 was repeated except that the layer of the partial butyl ester of poly-(ethylene/maleic anhydride) was replaced by a layer approximately 1 mil thick coated from a solution comprising a 1:1 mixture, by weight, of cellulose acetate and cellulose acetate hydrogen phthalate (approximately 35% phthalyl and 18% acetyl content) and 10%, by weight, of the polymers, of imidazole. Similar good transfer images were obtained. The presence of the imidazole appeared to increase the rate of pH reduction without decreasing the transfer image density.

Example 7

An image-receiving element was prepared as described in Example 4 except that the imidazole was omitted from the polymeric acid layer. An exposed multilayer, multicolor negative was then processed with a processing composition comprising:

Water	-----cc--	100
NaOH	-----g--	5.17
Hydroxyethyl cellulose (high viscosity)	-----g--	4.5
Sodium thiosulfate	-----g--	1.15
N-benzyl- α -picolinium bromide	-----g--	2.3
Imidazole	-----g--	1.5

and the prepared image-receiving element. After an imbibition period of 2 minutes, the image-receiving element was separated. Measurement of the pH of the surface of the separated image-receiving element, using pH paper wetted with distilled water, showed that the pH dropped to approximately pH 7-8 within 15 to 30 seconds after the image-receiving element was separated. In a control experiment employing the processing composition set forth in Example 3, it was found that the pH of the surface of the image-receiving layer was approximately 12 immediately after separation, and dropped to approximately pH 8-9 three minutes after separation.

Example 8

Use of a processing solution comprising:

Water	-----cc--	100
NaOH	-----g--	4.08
Hydroxyethyl cellulose (high viscosity)	-----g--	4.25
N-2',5'-dimethyl-benzyl- α -picolinium chloride	-----g--	2.1
Benzotriazole	-----g--	1.0
Imidazole	-----g--	1.0
Sodium thiosulfate	-----g--	0.75
Cesium hydroxide	-----g--	0.5

with an image-receiving element similar to that prepared in Example 7 gave a good multicolor transfer image, the surface of which exhibited a pH of 8 two minutes after the image-receiving element was separated.

Example 9

The procedure described in Example 8 was repeated employing the following processing composition:

Water	-----cc--	100
Sodium hydroxide	-----g--	5.17
Potassium hydroxide	-----g--	3.75
Cesium hydroxide	-----g--	0.5
Hydroxyethyl cellulose (high viscosity)	-----g--	4.03
N-benzyl- α -picolinium bromide	-----g--	2.3
Benzotriazole	-----g--	2.3
Sodium thiosulfate	-----g--	0.5
4,5-imidazole-dicarboxylic acid	-----g--	2.0

After an imbibition period of approximately 1¼ minutes, the surface of the separated image-receiving layer exhibited a pH of 10, which pH dropped to 8.5 within 3 minutes after separation.

In addition to the previously noted advantages ob-

tained by the use of an imidazole, xenon arc accelerated light fading tests of dye developer transfer images obtained in accordance with the procedures described in Example 5 unexpectedly showed a beneficial effect on light stability, particularly of the magenta component.

It will be understood that the imidazole may be present in the image-receiving element in the form of a salt of an acid, e.g., of the acetic acid frequently used to dissolve poly-4-vinylpyridine to facilitate coating thereof, or of the polymeric acid exemplified in Examples 2 and 5. The term "an imidazole" as used herein is intended to include such salts.

Although the preferred image-receiving layer is a mixture of polyvinyl alcohol and poly-4-vinylpyridine (such receiving layers are disclosed and claimed in the copending application of Howard C. Haas, Ser. No. 50,848, filed Aug. 22, 1960, now U.S. Patent No. 3,148,061 issued Sept. 8, 1964), the invention is not limited thereto. Other image-receiving layers are known in the art and may be employed. Similarly, while the preferred embodiment effects development in the presence of a quaternary ammonium compound (as disclosed and claimed in the copending application of Milton Green and Howard G. Rogers, Ser. No. 50,851, filed Aug. 22, 1960, now U.S. Patent No. 3,173,786 issued Mar. 16, 1965), and particularly a quaternary ammonium compound capable of forming an active methylene base in alkali, the invention is not so limited, even though in the preferred embodiment such an active methylene quaternary ammonium salt is used.

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'-methylphenylhydroquinone, 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; the negatives employed in the examples set forth above contained 4'-methylphenylhydroquinone in a layer of gelatin over the blue-sensitive emulsion layer.

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 emulsion.

Suitable hardening agents may be employed in the image-receiving layer coating solution. Particularly useful hardening agents are acrolein condensates, such as that sold by Shell Development Corporation under the trade name Aldocryl Resin X-12, and disclosed in the copending application of Lloyd D. Taylor, Ser. No. 229,194, filed Oct. 8, 1962, now abandoned.

This invention is especially useful in composite film units intended for use in a Polaroid Land camera, made by Polaroid Corporation, Cambridge 39, Massachusetts, or a similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717, issued to Edwin H. Land on Feb. 10, 1948. In general, such composite film units comprise a photosensitive element, an image-receiving element and a rupturable pod containing an aqueous alkaline processing solution, and may take the form of roll film, sheet film, or film packs. The elements and pod are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pod may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of such pods is well known to

the art. See, for example, U.S. Patents Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

It will be noted that other materials useful in the diffusion transfer processes may be incorporated into the image-receiving layer or one of the other layers of the image-receiving element. As an example of such a material, mention may be made of development restrainers such as 1-phenyl-5-mercaptotetrazole.

Several examples of useful image-receiving elements have been noted above and in the noted patent and copending applications, e.g., polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine. Another particularly useful image-receiving layer is a partial acetal of polyvinyl alcohol with a trialkyl ammonium benzaldehyde quaternary ammonium salt, as disclosed and claimed in the copending application of Howard C. Haas, Ser. No. 71,424, filed Nov. 25, 1960 (now U.S. Patent No. 3,239,337 issued Mar. 8, 1966). The image-receiving element also may contain a development restrainer, e.g., 1-phenyl-5-mercaptotetrazole, as disclosed in the copending application of Howard G. Rogers and Harriet W. Lutes, Ser. No. 50,849, filed Aug. 22, 1960 (now U.S. Patent No. 3,265,498 issued Aug. 9, 1966).

Since certain changes may be made in the above products, compositions 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 sense.

What is claimed is:

1. In a process for forming a color image by diffusion transfer, wherein an exposed photosensitive element comprising a silver halide emulsion and a dye developer is developed to provide an imagewise distribution of diffusible dye developer which is transferred by diffusion to a superposed image-receiving layer to impart to said image-receiving layer a positive color image, wherein the image-receiving element containing said image-receiving layer also contains a layer of a polymeric acid positioned between the support and said image-receiving layer, the improvement wherein said development and transfer are effected in the presence of an imidazole which is soluble in aqueous alkali, said imidazole being selected from the group consisting of imidazole and imidazoles containing substituents selected from the group consisting of alkyl, hydroxylalkyl, alkylamino, carboxy and carboxymethylamino, said imidazole being free of rings other than the imidazole ring.

2. The process of claim 1, wherein said development and transfer is effected in the presence of a quaternary ammonium compound.

3. The process of claim 1, wherein said development and transfer are initiated by application of a processing composition containing imidazole.

4. The process of claim 1, wherein a layer of said image-receiving element contains imidazole.

5. The process of claim 1, wherein said imidazole is imidazole.

6. The process of claim 1, wherein said imidazole is 4,5-imidazole-dicarboxylic acid.

7. The process of claim 1, wherein said imidazole is 2-methyl-imidazole.

8. The process of claim 1, wherein said imidazole is 4-hydroxymethyl-imidazole.

9. The process of claim 1, wherein said imidazole is 4,5-dimethyl-imidazole.

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J. TRAVIS BROWN, *Primary Examiner*.