United States Patent [19]

Bush et al.

[11] **3,765,886**

[45] **Oct. 16, 1973**

[54] **IMAGE TRANSFER SYSTEMS WITH 'ONIUM INDOPHENOXIDE IMAGE DYES**

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[73] Assignee: **Eastman Kodak Company**, Rochester, N.Y.

[22] Filed: **Aug. 6, 1971**

[21] Appl. No.: **169,667**

[52] **U.S. Cl.** .... **96/3**, 96/22, 96/29 D, 96/74, 96/76 R, 96/76 C, 96/77

[51] **Int. Cl.** **G03c 5/54**, G03c 7/00, G03c 7/34

[58] **Field of Search** .... 96/3, 22, , 76 R, 96/76 C; 260/78.5

[56] **References Cited**

UNITED STATES PATENTS

3,364,022	1/1968	Barr	96/3
3,557,066	1/1971	Cohen et al.	260/78.5

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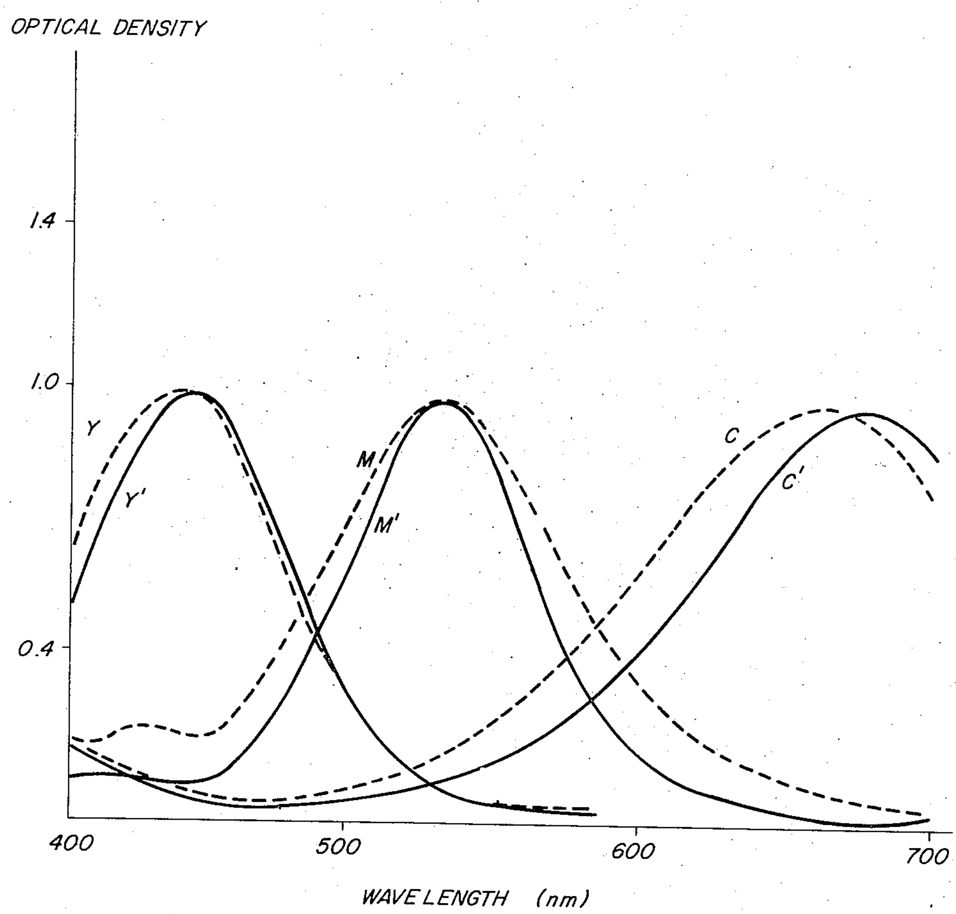
Assistant Examiner—Alfonso T. Suro Pico
Attorney—Robert W. Hampton et al.

[57] **ABSTRACT**

Image transfer systems and processes are disclosed wherein an 'onium indophenoxide image dye is formed during processing after imagewise exposure. In one embodiment, the image transfer systems contain a silver halide emulsion having associated therewith an immobile color coupler which is reacted with p-aminophenol to form a diffusible indophenol which is reacted with an 'onium compound to form an 'onium indophenoxide image dye. In another embodiment, the image transfer system contains a silver halide emulsion having associated therewith a mobile color coupler which is immobilized imagewise during development with portions of the mobile coupler diffusing to an image-receiving layer where it is reacted with oxidized p-aminophenol in association with an onium compound to provide an 'onium indophenoxide image dye.

27 Claims, 1 Drawing Figure



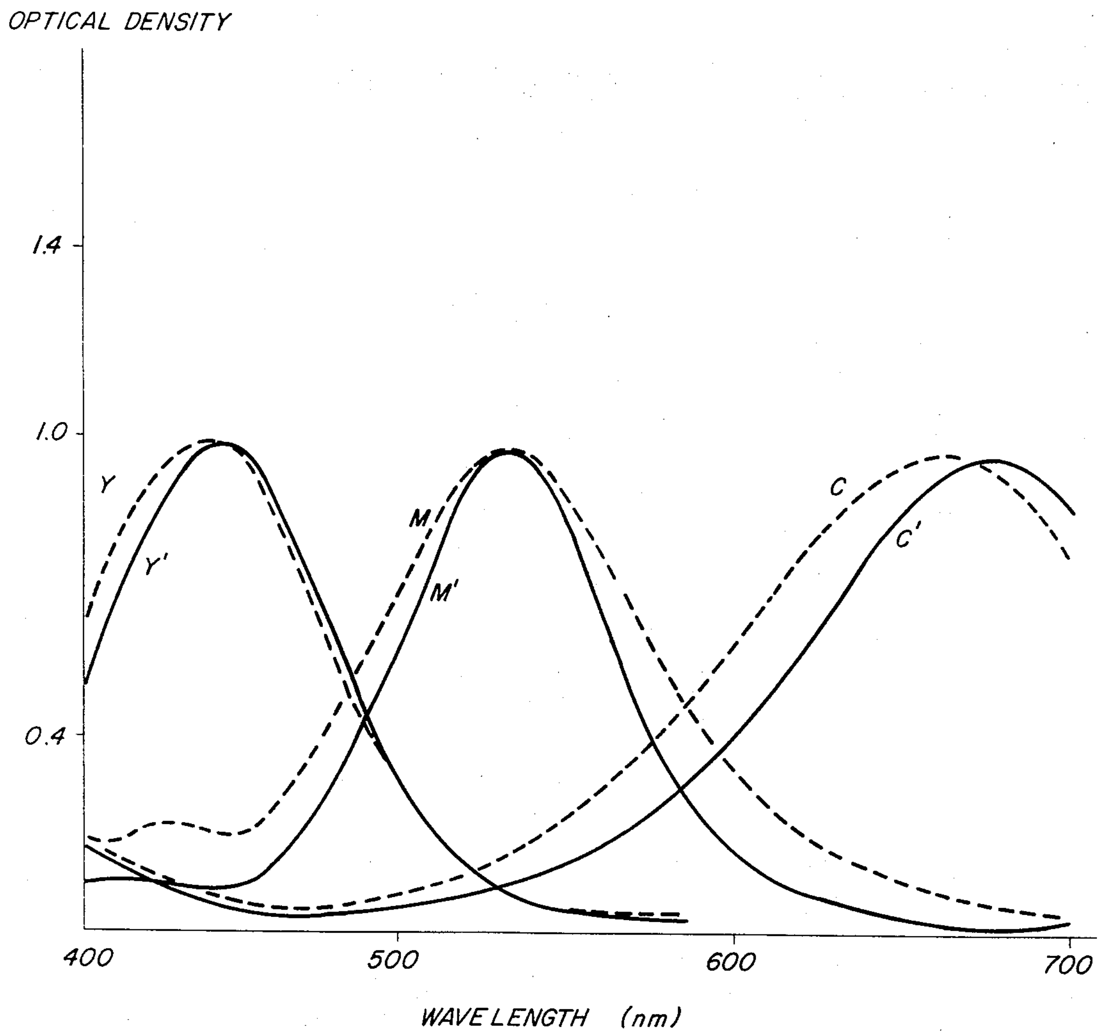


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IMAGE TRANSFER SYSTEMS WITH 'ONIUM INDOPHENOXIDE IMAGE DYES

This invention relates to improved image transfer systems, photographic elements and processes for forming images in photographic elements. In one aspect, this invention relates to systems wherein a photographic element containing a silver halide emulsion and an immobile coupler is developed with a developing composition, wherein the color developing agent is predominantly a p-aminophenol, to form diffusible dye which is then reacted with a positively charged compound such as an 'onium compound to form the image dye. In another aspect of this invention, a photographic element containing a silver halide emulsion and a mobile coupler is developed with a developing composition wherein the color developing agent is predominantly a p-aminophenol to form an immobile dye; in the unexposed regions the mobile coupler and the developer transfer to a receiver where the developer is oxidized and then reacts with the coupler to form a dye in the presence of or with subsequent treatment with a positively charged compound, such as a quaternary compound, to form an image dye.

Transfer systems are known in the art where photographic elements containing silver halide emulsions and mobile or immobile couplers are developed with p-phenylenediamines, as the color developing agent, to provide a transfer image system, as evidenced by U.S. Pat. No. 3,227,552 by Whitmore and 2,559,643 by Land. However, systems having improved image characteristics are desired to provide better image densities, color separation and the like.

We have now found that photographic transfer elements containing color couplers can be developed with developing compositions wherein the color developer is predominantly p-aminophenol, and preferably the color developing agent consists essentially of p-aminophenol, in the presence of or with subsequent treatment with a positively charged compound such as a quaternary ammonium salt to form improved images. The images formed generally have improved heat and light stability, improved spectrophotometric characteristics of the image dyes, reduced staining propensity of the developing agent and reduced emulsion desensitization by the color developing agent when it is in association with the silver halide before imagewise exposure.

In addition, the 'onium indophenoxides appear to overcome some of the problems occurring with prior-art image dyes in photographic elements, especially where the element is washed or remains wet for extended periods, the 'onium indophenoxides formed with pholymeric 'onium compounds do not appear to wash out or migrate as readily as other dyes, for example, as an indophenol dye mordanted on a polyvinyl pyridine.

When the oxidized p-aminophenols react with the color-forming couplers, an indophenol compound is formed. It is understood, of course, that "indophenol" refers to those reaction products of the oxidized p-aminophenol and the coupler represented by the generic formula:

$$(COUP)=N-Ar-OH$$

wherein Ar is an arylene group containing six to 20 carbon atoms including substituted and unsubstituted arylene groups, fused-ring substituents and the like, and is preferably a phenylene group which preferably is substituted with halogen atoms or groups containing halogen atoms in the ortho or meta positions of the ring; and COUP is a color-forming coupler linked through a carbon atoms such as a phenolic coupler, a pyrazolone coupler, couplers having open-chain active methylene groups and the like, and preferably soluble couplers which have solubilizing groups attached thereto to provide a diffusible coupler, and the like. Upon treatment with a positively charged coupound, such as an 'onium compound, the above indophenol compounds form 'onium indophenoxides which are represented by the formula:

$$(COUP)=N-Ar-O^{-}\quad {}^{+}M$$

wherein M is an 'onium compound and is preferably a quaternary ammonium compound. These latter compounds are referred to herein as 'onium indophenoxides.

The accompanying FIGURE is an absorption curve of three day according to the invention compared with three dyes of the prior art. The curves are normalized curves, i.e., the curves are recorded by taking the spectrophotometric readings, not at the maximum density of the dye images, but rather at a selected density of 1.00 in each of three samples.

In one embodiment, the dyes of this invention can be formed in image transfer elements. A mobile color coupler can be incorporated in each of the spectrally sensitized emulsions of a transfer element, such as described in U.S. Pat. No. 2,661,293 issued Dec. 1, 1953. The exposed photographic element is then developed in the presence of an alkaline composition wherein the silver halide developer is predominantly a p-aminophenol. In the areas where the silver halide emulsion has been imagewise-exposed, the p-aminophenol will reduce the silver halide to silver, become oxidized and then react with the color coupler to form a relatively immobile product. Meanwhile, the unreacted coupler and unoxidized p-aminophenol can migrate to an image-receiving layer where they can react with an oxidizing agent or by aerial oxidation followed by coupling. Coupling can occur in the presence of an 'onium compound such as a quaternary mordant, or the 'onium compound can be placed in a layer in association with the image-receiving layer such as an adjacent layer whereby it will contact the coupled product to form the image dye. The mobile color couplers can generally be pyrazolone couplers, phenolic couplers, open-chain ketomethylene couplers, and the like as disclosed in the art. Typical examples are the alkali-soluble and diffusible couplers disclosed in U.S. Pat. Nos. 2,407,210 by Weissberger et al. issued Sept. 3, 1946; 2,298,443 by Weissberger issued Oct. 13, 1942; 2,875,057 by McCrossen et al. issued Feb. 24, 1959; 3,265,506 by Weissberger et al. issued Aug. 9, 1966; 3,408,194 by Loria issued Oct. 29, 1968; 3,447,928 by Loria issued June 3, 1969; 2,369,489 by Porter et al. issued Feb. 13, 1945; 2,600,788 by Loria et al. issued June 17, 1952; 2,908,573 by Bush et al. issued Oct. 13, 1959; 3,062,653 by Weissberger et al. issued Nov. 6, 1962; 3,419,391 by Young issued Dec. 31, 1968; 3,519,429 by Lestina issued July 7, 1970; 3,152,896 by Tuite issued Oct. 13, 1964; 2,423,730 by Salminen et al. issued July 8, 1947; 2,474,293 By Weissberger et al. issued June 28, 1949; 3,476,563 by Loria issued Nov. 4, 1969;

2,772,162 by Salminen et al. issued Nov. 27, 1956; and 3,002,836 by Vittum et al. issued Oct. 3, 1961; which are all incorported herein by reference.

In highly preferred embodiments of this invention, immobile couplers are incoprorated in an image transfer system and development occurs in a developing composition wherein the developing agent is predominantly a p-aminophenol compound. Typical image transfer formats where the present invention can be utilized are disclosed in U.S. Pat. No. 3,227,550 and 3,227,552 and U.S. Ser. Nos. 115,459 and 115,552, both filed Feb. 16, 1971, now abandoned.

Typical useful nondiffusible couplers employed in this invention include those having the formula:

$$\text{BALL-LINK-(COUP-SOL)}_n$$

wherein:

1. LINK is a connecting radical such as an azo radical, a mercuri radical, an oxy radical, n alkylidene radical, a thio radical, a dithio radical, an azoxy radical, an aminoalkyl radical as disclosed in Cressman et al., U.S. Pat. No. 3,419,390, a sulfonyloxy radical as disclosed in Porter, U.S. Pat. No. 3,415,652, an acyloxy radical as disclosed in Loria, U.S. Pat. No. 3,311,476, and an imido radical as disclosed in Loria, U.S. Pat. No. 3,458,315.
2. COUP is a coupler radical such as a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, COUP being substituted in the coupling position with LINK;
3. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render such coupler nondiffusible during development in an alkaline processing composition;
4. SOL is a hydrogen atom or an acidic solubilizing group when the color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when the color developing agent is free of an acidic solubilizing group; and
5. n is an integer of 1 to 2 when LINK is an alkylidene radical, and n is 1 when LINK is an azo radical, a mercuri radical, an azoxy radical, an aminoalkyl radical, a sulfonyloxy radical, an acyloxy radical or an imido radical, a thio radical, a dithio radical or an azoxy radical.

The acidic solubilizing radicals attached to the diffusible dye-producing couplers described above can be solubilizing radicals which, when attached to the coupler or developer moieties of the dyes, render the dyes diffusible in alkaline processing compositions. Typical of such radicals are carboxylic, sulfonic, ionizable sulfonamide and hydroxy-substituted groups that lend to dyes negative charges.

The nature of the ballast groups in the diffusible dye-producing coupler compounds described above (BALL-) is not critical as long as they confer nondiffusibility to the coupler compounds. Typical ballast groups include long-chain alkyl radicals linked directly or indirectly to the coupler molecules, as well as aromatic radicals of the benzene and naphthalene series, etc., linked directly or indirectly to the coupler nolecules by a splittable linkage, or by a removable or irremovable but otherwise nonfunctional linkage depending upon the nature of the coupler compound. Generally, useful ballast groups have at least eight carbon atoms.

With regard to the above-described coupler radicals (COUP—), the "coupling position" is well-known to those skilled in the photographic art. The 5-pyrazolone coupler radicals couple at the carbon atom in the 4-position, the phenolic coupler radicals, including α-naphthols, couple at the carbon atom in the 4-position, and the open-chain ketomethylene coupler radicals couple to the carbon atom forming the methylene moiety (e.g.,

$$-\overset{\overset{\large O}{\|}}{C}-\underset{*}{C}H_2-\overset{\overset{\large O}{\|}}{C}-$$

*denoting the coupling position). Pyrazolotriazole couplers and their coupling position are described, for example, in U.S. Pat No. 3,061,432 and U.S. Ser. No. 778,329 of Bailey et al. filed Nov. 22, 1968, now abandoned.

The term "nondiffusing" used herein as applied to the couplers has the meaning commonly applied to the term in color photography and denotes materials which for all practical purposes do not migrate or wander through organic colloid layers, such as gelatin, comprising the sensitive elements of the invention. The same meaning is to be attached to the term "immobile."

The term "diffusible" as applied to the dyes formed from the "nondiffusing" couplers in this invention has the converse meaning and denotes materials having the property of diffusing effectively through the colloid layers of the sensitive elements in the presence of the "nondiffusing" materials from which they are derived. "Mobile" has the same meaning.

When couplers having the formula $\text{BALL-LINK-(coup-SOL)}_n$ as described above are reacted with an oxidized color developing agent, the connecting radical (LINK) as split and a diffusible dye is formed with the color developing agent oxidation product and the coupling portion (COUP) of the coupler which diffuses imagewise to a reception layer. Diffusibility can be imparted to the dye by an acidic solubilizing group attached to a non-coupling position of the coupling portion (COUP) of the coupler or to the color developing agent. The ballasted portion of the coupler remains immobile. In this type of coupler, the color of the diffusible dye is determined by the color of the 'onium indophenoxide formed during processing.

In using the couplers in the invention, the production of diffusible indophenols or 'onium indophenoxides is a function of the reduction of developable silver halide images which may involve direct or reversal development of the silver halide emulsions with a p-aminophenol developing agent. If the silver halide emulsion employed is a direct-positive silver halide emulsion, such as an internal-image emulsion or a solarizing emulsion, which is developable in unexposed areas, a positive image can be obtained in the receiver portion of the film unit. In this embodiment, the nondiffusible coupler can be located in the silver halide emulsion itself. After exposure of the film unit, the alkaline processing composition permeates the various layers to initiate development of the exposed layers of photosensitive silver halide emulsion. The p-aminophenol color developing agent present in the film unit develops each of the silver halide emulsion layers in the unexposed areas (since the silver halide emulsions are direct-positive ones), thus causing the developing agent to become oxidized imagewise corresponding to the unexposed area of the direct-positive silver halide emulsion layers. The oxidized developing agent then reacts with the nondiffusible coupler present in each silver halide emulsion layer to form imagewise distributions of indophenols as a function of the imagewise exposure of each of the silver halide emulsion layers. At least a portion of the imagewise distribution of diffusible indophenols diffuses to the image-receiving layer wherein it can be contacted with an onium compound to produce the respective image dyes. After being contacted by the alkaline processing compositions, a pH-lowering layer in the film unit, if one is present, lowers the pH of the film unit to stabilize it. Specific examples of such nondiffusing couplers and other details concerning this type of photographic chemistry are found in U.S. Pat. Nos. 3,227,550 and 3,227,552 which are incorporated herein by reference.

Another embodiment of the invention employing the non-diffusible couplers described above to produce a diffusible indophenol is to employ them in combination with development inhibitor-releasing couplers as described in U.S. pat. No. 3,227,551. In such an embodiment, the photosensitive portion of the photosensitive element would comprise at least two color-forming units in layers sensitive to different regions of the visible spectrum, separated by a barrier layer comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans, each of the color-forming units comprising:

1. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by a p-aminophenol color developing agent to substantial density without exposure to light, the metal salt having contiguous thereto the nondifusible coupler capable of reacting with an oxidized p-aminophenol color developing agent to form a diffusible indophenol; and
2. a photosensitive silver halide emulsion layer, the silver halide of which has contiguous thereto a non-diffusible development inhibitor-releasing coupler which is capable of reacting with an oxidized p-aminophenol color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to the adjacent developable emulsion layer to inhibit development therein.

The developing agent is predominantly a p-aminophenol and preferably consists essentially of a p-aminophenol developing agent and is generally present in the alkaline processing composition, and the developable emulsion is preferably an emulsion of a hydrophilic colloid, silver thiocyanate and physical development nuclei that can be developed to substantial density without exposure to light. The developable emulsion can also be made from a metal salt which is made spontaneously developable by incorporating in the emulsion a wide variety of well-known physical development nuclei as disclosed in the above-mentioned U.S. Pat. No. 3,227,551, column 6, lines 63–75, and column 7, lines 1-10. Another method that can be utilized to make the water-insoluble salts spontaneously developable is by prefogging the emulsion with light or with chemical reducing agents such as alkali metal borohydrides and the like in accordance with well known photographic fogging techniques.

In another embodiment of the invention, the nondiffusible couplers described above are used in combination with physical development nuclei in a nuclei layer associated with each photosensitive silver halide emulsion layer to produce a diffusible dye image-providing material. The film unit contains a silver halide solvent, preferably in a rupturable container with the alkaline processing composition, and each photosensitive silver halide emulsion layer contains an immobilizing coupler, e.g., a coupler with a ballast group, which is capable of reacting with an oxidized p-aminophenol color developing agent to form an immobile product. Each photosensitive silver halide emulsion layer and its associated nuclei layer are separated from the other silver halide emulsions and their associated nuclei layers in the film by means of an alkaline solution-permeable barrier layer for retaining silver complexes. After exposure of the film unit, the alkaline processing composition permeates the various layers to initiate development of the latent image contained in each photosensitive silver halide emulsion layer. The p-aminophenol color developing agent present in the film unit develops each of the exposed silver halide emulsion layers, thus causing the p-aminophenol color developing agent to become oxidized imagewise. The oxidized developing agent then reacts with the immobilizing coupler present in each said photosensitive silver halide emulsion layer to form an immobile product. The remaining silver halide in each silver halide emulsion layer corresponding to unexposed and thus undeveloped areas forms a soluble silver ion complex with the silver halide solvent present in or activated by the processing composition and migrates to each associated nuclei layer. The transferred silver complex is reduced or physically developed in the nuclei layer, thus causing the developing agent to become oxidized. The oxidized developing agent then reacts with the non-diffusible coupler present in each nuclei layer to form imagewise distributions, respectively, of diffusible cyan-forming indophenol, magneta-forming indophenol and yellow-forming indophenol as a function of the imagewise exposure of each said silver halide emulsion layer. At least a portion of said imagewise distributions of diffusible indophenols then diffuses to the image-receiving layer which, when contacted with an 'onium compound, provides positive 'onium indophenoxide dye images. After being contacted by the alkaline processing composition, a pH-lowing layer in the film unit, if one is present, lowers the pH of the film unit to stabilize it.

In the above-described embodiment, the physical development nuclei can be any of those well-known to those in the art such as colloidal metals, e.g., colloidal silver, gold, platinum, palladium, colloidal metal sulfides, e.g., colloidal silver sulfide, zinc sulfide, etc. Materials which form physical development nuclei may also be used, such as reducing agents and labile sulfur compounds. The nuclei layer can also be split into two layers, one on each side of the photosensitive silver halide emulsion layer, if desired. The silver halide solvent employed can be any of those well-known to those skilled in the art, such as alkali metal and ammonium thiosulfates and thiocyanates, e.g., sodium thiosulfate, ammonium thiosulfate, ammonium thiocyanate, potassium thiocyanate, etc., and may be incorporated in a separate layer, if desired. Spacer layers comprising gelatin are preferably employed between the nuclei layers and the photosensitive silver halide emulsion layers to prevent undesirable mixing of the two layers upon coating. The spacer layers may also contain nuclei and a nondiffusible coupler capable of reacting with oxidized color developing agent to form an immobile product in order to increase its efficiency. Other details concerning this type of photographic chemistry are found in British Patent 904,364, page 19, lines 1–41.

In the above-described embodiments employing nondiffusible couplers, interlayers are generally employed between the various photosensitive color-forming units to scavenge the oxidized developing agent and prevent it from forming an unwanted dye in another color-forming unit. Such interlayers would generally comprise a hydrophilic polymer such as gelatin and an immobilizing coupler, as described above, which is capable of reacting with an oxidized p-aminophenol color developing agent to form an immobile product. Such interlayers may also scavenge other materials such as soluble silver ion complexes or mercaptans in the described systems to prevent such materials from contaminating other color-forming units. A developer scavenging interlayer may also be employed in the above-described embodiments adjacent to the light-reflective layer to prevent excess color developing agent from staining the image-receiving layer. Such a layer can comprise, for example, a nondiffusible coupler capable of reacting with an oxidized color developing agent to form an immobile product and a silver halide emulsion, preferably one which is developable without exposure.

As previously mentioned, the p-aminophenol color developing agent employed in the above-described embodiments is preferably present in the alkaline processing composition in the rupturable pod. The p-aminophenol color developing agent can also be incorporated into the negative portion of the film unit as a separate layer or in the same layer as the silver halide emulsion. Such incorporated developing will be activated by the alkaline processing composition. While the incorporated developing agent can be positioned in any layer of the photosensitive element from which it can be readily made available for development upon activation with alkaline processing composition, it is generally either incorporated in the light-sensitive silver halide emulsion layers or in layers contiguous thereto.

The p-aminophenols which can be reacted in the oxidized form to provide the dye intermediates of this invention are generally any substituted or unsubstituted p-aminophenol which has a primary amine on the ring and a para hydroxy group. In those instances where high solubility of the developer or the formed dye intermediate is desired, such as to form diffusible dye intermediates, water-solubilizing groups such as halogen groups or halogen-containing groups are preferably substituted in the ortho and/or meta positions of the ring. Generally useful p-aminophenols include those compounds represented by the formula:

$$H_2N—Ar—OH$$

wherein Ar is an arylene group containing from 6 to 20 carbon atoms, including substituted arylene, unsubstituted arylene, fused-ring arylene and the like, and is preferably a phenylene group containing six carbon atoms and is unsubstituted or can have substituents in the ortho and/or meta positions which are preferably halogen atoms or groups containing halogen atoms.

The developing compositions used in this invention contain color developing agents which are predominantly p-aminophenols as described above, and preferably the color developer of the developing composition consists essentially of p-aminophenols. The term "color developer" is understood to refer to that closs of compounds known in the art as color developers which generally refers to silver halide developers which in their oxidized form will couple with a color-forming coupler to form a dye. Generally, those compounds are aryl compounds having one $—NH_2$ group substituted thereon.

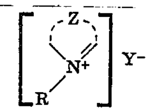
In accordance with this invention, indophenol compounds are formed in the presence of or with subsequent treatment with 'onium compounds to form 'onium indophenoxides. The 'onium compounds can either be soluble compounds which can be added by contacting the indophenol with a solution of the 'onium compound or be high-molecular-weight compounds which are relatively insoluble in water and can be placed in at least one layer of the photographic element, such as in the mordant layer where the indophenol produces the 'onium indophenoxide image dye.

'Onium compounds have been used in the photographic art for quite some time. For example, U.S. Pat. No. 2,648,604 discloses the use of non-surface-active quaternary compounds as development accelerators, and U.S. Pat. Nos. 2,271,623, 2,271,622 and 2,275,727 disclose the use of quaternary ammonium quaternary phosphonium and tertiary sulfonium compounds as sensitizers for silver halide emulsions. Moreover, U.S. Pat. Nos. 3,146,102 and 3,212,893 disclose the use of 'onium compounds in combination with dye developers in image transfer systems. Nevertheless, there does not appear to be any recognition in the art of the highly useful 'onium indophenoxide dyes as set forth in this invention.

In one embodiment, especially useful dye images have been obtained through the combination of indophenols and quaternary ammonium compounds. As is known, quaternary ammonium compounds are organic compounds containing a pentavalent nitrogen atom. Generally, they can be considered as derivatures of ammonium compounds wherein the foud valances usually occupied by the hydrogen atoms are occupied by organic radicals. Generally, the organic radicals are joined directly to the pentavalent nitrogen through a single or double carbon-to-nitrogen bond. The term "quaternary ammonium," as used herein, is intended to cover compounds wherein the pentavalent nitrogen is one of the nuclear atoms in a heterocyclic ring, as well as those wherein each of the four vacancies is attached to separate organic radicals, e.g., tetraalkyl quaternary ammonium compounds. As illustrations of quaternary ammonium compounds, mention may be made of those represented by the following formulae:

(1)

$$\left[R-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{N^+}}}}-R \right] Y^-$$

(2)


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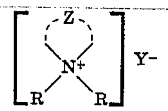


wherein each R is an organic radical, Y is an anion, e.g., hydroxy, bromide, chloride, toluenesulfonate, etc., and Z represents the atoms necessary to complete a heterocyclic ring. As examples of compounds within Formulae 1, 2 and 3, mention may be made of tetraethylammonium bromide, N-ethylpyridinium bromide, N,N-diethylpiperidinium bromide, ethylene-bis-pyridinium bromide, 1-ethylpyridinium bromide, 1-phenethyl-3-picolinium bromide, tetraalkylammonium salts, cetyltrimethylammonium bromide, polyalkylene oxide bis-quaternary ammonium salts such as polyethylene oxide bis-pyridinium perchlorate, the heterocyclic quaternary ammonium salts mentioned which form the methylene bases including 3-methyl-2-ethylisoquinolinium bromide, 3-methylisoquinolinium methyl-p-toluenesulfonate, 1-ethyl-2-methyl-3-phenethylbenzimidazolium bromide, 5,6-dichloro-1-ethyl-2-methyl-3-(3-sulfobutyl)benzimidazolium betaine and the pyridinium salts below.

The tertiary sulfonium and quaternary phosphonium compounds may be represented by the formulae:

$$(R)_3S^+X^- \quad (4) \text{ and}$$

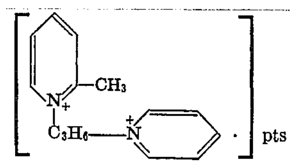
$$(R)_4P^+X^- \quad (5)$$

wherein each R is an organic radical, e.g., alkyl, aralkyl, aryl, etc., groups, and X is an anion, e.g., hydroxy, bromide, chloride, toluenesulfonate, etc. As examples of tertiary sulfonium and quaternary phosphonium compounds, mention may be made of lauryldimethylsulfonium p-toluenesulfonate, nonyldimethylsulfonium p-toluenesulfonate and octyldimethylsulfonium p-toluene-sulfonate, butyldimethylsulfonium bromide, triethylsulfonium bromide, tetraethylphosphonium bromide, dimethylsulfonium p-toluenesulfonate, dodecyldimethylsulfonium p-toluenesulfonate, decyldimethylsulfonium p-toluenesulfonate and ethylene-bis-oxymethyltriethylphosphonium bromide.

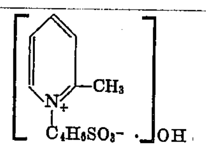
The 'onium compounds may be used as the hydroxide or as the salt. When the 'onium compounds are used as the salt, the anion may be a derivative of any acid. However, it should be noted that when the anion is iodide, such iodide may have deleterious effects on the emulsion and suitable precautions should be taken if it is to be in contact with the emulsion before development is complete. Especially good results are obtained when the 'onium compounds employed are bromides.

Useful heterocyclic quaternary ammonium compounds which form the methylene bases diffusible in alkaline solution have the general formula:

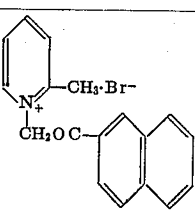
1-γ-phenylpropyl-2-picolinium bromide
2,4-dimethyl-1-phenethylpyridinium bromide
2,6-dimethyl-1-phenethylpyrdinium bromide
5-ethyl-2-methyl-1-phenethylpyridinium bromide
2-ethyl-1-phenethylpyridinium bromide
1-[3-(N-pyridinium bromide)propyl]-2-picolinium p-toluenesulfonate



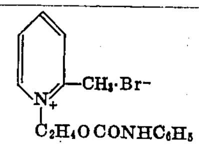
anhydro-1-(4-sulfobutyl)-2-picolinium hydroxide



α-picoline-β-naphthoylmethyl bromide



1-β-phenylcarbamoyloxyethyl-2-picolinium bromide



1-methyl-2-picolinium p-toluenesulfonate
1-phenethyl-2,4,6-trimethylpyridinium bromide
1-phenethyl-4-n-propylpyridinium bromide
4-γ-hydroxypropyl-1-phenethylpyridinium bromide and 1n-heptyl-2-picolinium bromide

In highly preferred embodiments of the invention, the image dye is mordanted in a polymeric material such as polymer with 'onium groups thereon. Typical useful mordants of this type are vinylpyridinium compounds of the type disclosed in U.S. Pat. No. 2,484,430 issued NOv. 10, 1949; polymers containing quaternary ammonium groups such as disclosed in U.S. Ser. Nos. 734,873 by Cohen et al. filed June 6, 1968, now U.S. Pat. No. 3,625,694 100,487 by Cohen et al. filed Dec.

21, 1970, 100,491 by Cohen et al. filed Dec. 21, 1970, now U.S. Pat. No. 3,709,690 and **709,793** by Cohen et al. filed Mar. 1, 1968, now U.S. Pat. No. 3,639,357 and U.S. Pat. Nos. 3,488,706 by Cohen et al. issued Jan. 6, 1970, and 3,557,006 by Cohen et al. issued Jan. 19, 1971; and the like.

In another preferred embodiment, the mordant is an 'onium coacervate mordant such as disclosed in Bush, U.S. Pat. No. 3,271,147 issued Sept 6, 1966.

The alkaline processing composition employed in this invention is the conventional aqueous solution of an alkaline material, e.g., sodium hydroxide, sodium carbonate or an amine such as diethylamine, preferably possessing a pH in excess of 12 and preferably containing a developing agent as described previously. The solution also preferably contains a viscosity-increasing compound such as a high-molecular-weight polymer, e.g., a water-soluble ether inert to alkaline solutions, such as hydroxyethyl cellulose or alkali metal salts of carboxymethyl cellulose such as sodium carboxymethyl cellulose. A concentration of visocity-increasing compound of about 1 to about 5 percent by weight of the processing solution is preferred which will impart thereto a viscosity of about 100 cps. to about 200,000 cps.

While the alkaline processing composition used in this invention can be employed in a rupturable container, as described previously, to facilitate conveniently the introduction of the processing composition into the film unit between the transparent sheet and the photosensitive element, other methods of inserting processing composition into the film unit could also be employed, e.g., interjecting processing solution with communicating members similar to hypodermic syringes which are attached either to a camera or camera cartridge.

The present invention of forming 'onium indophenoxides in image transfer systems can be utilized effectively with several image transfer formats.

The dye image-receiving layer in the above-described film unit can be located on a separate support adapted to be superposed on the photosensitive element after exposure thereof. Such image-receiving elements are generally disclosed, for example, in U.S. Pat. No. 3,362,819. A rupturable container is employed and is positioned in relation to the photosensitive element and the image-receiving element so that a compressive force applied to the container by pressure-applying members, such as would be found in a typical camera used for in-camera processing, will effect a discharge of the container's contents between the image-receiving element and the outermost layer of the photosensitive element. After processing, the dye image-receiving element is separated from the photosensitive element.

The dye image-receiving layer in the above-described film unit can also be located integral with the photosensitive element between the support and the lowermost photosensitive silver halide emulsion layer. A general format for integral receiver-negative photosensitive elements is disclosed in copending U.S. application Ser. No. 027,991 of Barr, Bush and Thomas filed Apr. 13, 1970, now abandoned. In such an embodiment, the support for the photosensitive element is transparent and is coated with an image-receiving layer, a substantially opaque light-reflective layer, e.g., TiO_2, and then the photosensitive layer or layers described above. After exposure of the photosensitive element, a rupturable container containing an alkaline processing composition and an opaque process sheet are brought into superposed position. Pressure-applying members in the camera rupture the container and spread processing composition over the photosensitive element as the film unit is withdrawn from the camera. The processing composition develops each exposed silver halide emulsion layer and dye images are formed as a function of development which diffuse to the image-receiving layer to provide a positive, right reading image which is viewed through the transparent support on the opaque reflecting layer background. For other details concerning the format of this particular integral film unit, reference is made to the above-mentioned Barr, Bush and Thomas U.S. application Ser. No. 027,991.

Another format for integral negative-receiver photosensitive elements in which the present invention can be employed is disclosed in Cole U.S. application Ser. No. 027,990 filed Apr. 13, 1970, now abandoned. In this embodiment, the support for the photosensitive element is transparent and is coated with the image-receiving layer, a substantially opaque, light-reflective layer, the photosensitive layer or layers described above, and a top transparent sheet. A rupturable container containing an alkaline processing composition and an opacifier is positioned adjacent to the top layer and sheet. The film unit is placed in a camera, exposed through the top transparent sheet and then passed through a pair of pressure-applying members in the camera as it is being removed therefrom. The pressure-applying members rupture the container and spread processing composition and opacifier over the negative portion of the film unit to render it light-sensitive. The processing composition develops each silver halide layer and dye images are formed as a result of development which diffuse to the image-receiving layer to provide a positive, right-reading image which is viewed through the transparent support on the opaque reflecting layer background. For further details concerning the format of this particular integral film unit, reference is made to the above-mentioned Cole U.S. Application Ser. No. 027,990.

Any material can be employed as the image-receiving layer in this invention as long as the desired function of mordanting or otherwise fixing the 'onium indophenoxide dye images will be obtained. The particular material chosen will, of course, depend upon the dye to be mordanted and preferably the mordant is an 'onium compound, as mentioned previously, which will react with the indophenol to form an 'onium indophenoxide. If acid dyes are to be mordanted, the image-receiving layer can contain basic polymer mordants such as polymers of amino guanidine derivatives of vinyl methyl ketone such as described in Minsk, U.S. Pat. No. 2,882,156 issued Apr. 14, 1959, and basic polymeric mordants such as described in copending U.S. Ser. No. 100,491 of Cohen et al. filed Dec. 21, 1970, now U.S. Pat. 5,709,690. Other mordants useful in our invention include poly-4-vinylpyridine and coumarins, like. Effective mordanting compositions are also described in U.S. Pat. Nos. 3,271,148 by Whitmore and 3,271,147 by Bush, both issued Sept. 6, 1966.

Furthermore, the image-receiving layer can be sufficient by itself to mordant the dye as in the case of use of an alkaline solution-permeable polymeric layer such as N-methoxymethyl polyhexylmethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate; gelatin; and other materials of a similar nature. Generally, good results are obtained when the image-receiving layer, preferably alkaline solution-permeable, is transparent and about 0.25 to about 0.40 mil in thickness. This thickness, of course, can be modified depending upon the result desired. The image-receiving layer can also contain ultra-violet absorbing materials to protect the mordanted dye images from fading due to ultraviolet light, brightening agents such as the stilbenes, coumarings, triazines, oxazoles, dye stabilizers such as the chromanols, alkylphenols, etc.

Use of a pH-lowering material in the dye image-receiving element of a film unit according to the invention will usually increase the stability of the transferred image. Generally, the pH-lowering material will effect a reduction in the pH of the image layer from about 13 to 14 to at least 11 and preferably 5–8 within a short time after imbibition. For example, polymeric acids as disclosed in U.S. Pat. No. 3,362,819 or solid acids or metalic salts, e.g., zinc acetate, zinc sulfate, magnesium acetate, etc., as disclosed in U.S. Pat. No. 2,584,030 may be employed with good results. Such pH-lowering materials reduce the pH of the film unit after development to terminate development and substantially reduce further dye transfer and thus stabilize the dye image.

An inert timing or spacer layer can be employed in the practice of our invention over the pH-lowering layer which "times" or controls the pH reduction as a function of the rate at which alkali diffuses through the inert spacer layer. Examples of such timing layers include gelatin, polyvinyl alcohol or any of those disclosed in U.S. Pat. No. 3,455,686. The timing layer is also effective in evening out the various reactions over a wide range of temperatures, e.g., premature pH reduction is prevented when imbibition is effected at temperatures above room temperature, for example, at 95° to 100° F. The timing layer is usually about 0.1 to about 0.7 mill in thickness. Especially good results are obtained when timing layer comprises a hydrolyzable polymer or a mixture of such polymers which are slowly hydrolyzed by the processing composition. Examples of such hydrolyzable polymers include polyvinyl acetate, polyamides, cellulose esters, etc.

The invention can be further illustrated by the following examples.

Example 1: (control)

A. a sample of a supported single-layer gelatinous silver halide emulsion coating, containing per square foot of coating 150 mg. silver, 500 mg. gelatin, 114 mg. α-p-ivalyl-α-(3-pentadecyl-4-nitrophenoxy)-4-sulfamylacetanilide (Coupler I) and 114 mg. diethyl lauramide, is exposed through a graduated-density test object and treated with a viscous developer solution, whose composition is given below, while in contact for 2 minutes with an image-receiving sheet consisting of a supported single-layer coating of gelatin containing the quaternary mordant compound copoly [styrene-N,N-dimethyl-N-benzyl-N-3-maleiimidopropyl)ammonium chloride]. Upon separation of the silver halide emulsion coating from the receiving sheet, the latter contains a well-defined negative yellow dye image of the test object.

COMPOSITION OF DEVELOPING SOLUTION

KOH	35.9 g.
4-amino-N-ethyl-N-γ-hydroxyethylaniline	40.0 g.
piperidinohexosereductone	0.2 g.
5-methylbenzotriazole	0.2 g.
hydroxyethyl cellulose	30 g.
water to 1 liter	

Curve Y in the figure represents the spectrophotometric profile of the transferred yellow image dye.

B. The procedure described in Section A) above is repeated with a sample of a silver halide emulsion coating wherein the yellow dye-forming Coupler I is replaced with the magenta dye-forming coupler 1-phenyl-3-(3,5-dicarboxyanilino)-octadecylcarbamylphenylthio)-5-pyrazolone (Coupler II) (88 mg./ft.^{2} in 44 mg./ft.^{2} N-n-butylacetanilide, coupler solvent).

Curve M in the figure represents the spectrophotometric profile of the transferred image dye.

C. The procedure described in Section A) above is repeated with a sample of a silver halide emulsion coating wherein the yellow dye-forming Coupler I is replaced with the cyan dye-forming coupler 1-hydroxy-4-[α-(3′-pentadecylphenoxy)-butyramido]phenoxy-N-ethyl-(2″,5″-dicarboxy)-2-naphthanilide (Coupler III) (101 mg./ft.^{2} in 101 mg./ft.^{2} coupler solvent diethyl lauramide.

Curve C in the figure represents the spectrophotometric profile of the transferred image dye.

EXAMPLE 2

The procedures described in Sections A), B) and C) of Example 1 are repeated with a p-aminophenol developer composition as follows:

$Na_2CO_3 \cdot H_2O$	22 g.
KBr	1.0 g.
Na_2SO_3	2.0 g.
2,6-dibromo-4-aminophenol	7.4 g.
pH adjusted to 12 with NaOH	
water to 1100 ml.	

The spectrophotometric profiles of the transferred image dyes are represented by Curves Y′, M′ and C′ in the figure.

A comparison of the two sets of curves in the figure shows that the spectrophotometric qualities of the image dyes produced by the method according to our invention are generally as good as the qualities of dyes produced by the conventional p-phenylenediamine method, and better in some specific respects, in particular the narrower band width and lower unwanted blue absorption of the magenta dye represented by Curve M′.

EXAMPLE 2-A

A. A supported two-layer light-sensitive element is made with a silver halide emulsion layer containing per square foot of coating 108 mg. silver, 400 mg. of gelatin and 152 mg. of Coupler III. A layer coated over the silver halide emulsion layer contains per square foot 100 mg. of gelatin, 25 mg. of din-butyl phthalate, and ballasted scavenging couplers for excess oxidized p-aminophenol at concentrations of 25 mg. of 1-hydroxy-2-[Δ-(2,4-di-tert-amylphenoxy)-n-butyl]naphthamide and 25 mg. of 5-[α-(2,4-di-tert-amylphenoxy)hexanamido]-2-heptafluorobutyramidophenol. The element is exposed and processed by sensitometrically exposing through a graduated-density test object, then contacting for 60 seconds at room temperature with a copoly[styrene-N,N-dimethyl-N-benzyl-N-3-maleiimidopropyl)ammonium chloride] mordanted receiving sheet in the presence of a viscous processing fluid of the following composition:

NaOH	10 g.
2-chloro-4-aminophenol	13.2 g.
hydroxyethyl cellulose	20 g.

water to 1 liter

Upon separation, the receiver contains a well-defined negative cyan-colored reproduction of the photographed test object. The receiver is finally washed for 3 minutes and dried. The maximum and minimum densities of the image (read through a Status M Red Filter) are recorded in Table 1 below.

B. The procedures described in Section A) above is duplicated with a processing fluid which contains the conventional p-phenylenediamine color developing agent 4-amino-N-ethyl-N-β-hydroxyethylaniline, instead of 2-chloro-4-aminophenol, at a concentration such that the level of 4-amino-N-ethyl-N-β-hydroxyethylaniline is equivalent to 90 mg./ft.^{2} of surface area between the contacted units. The resulting image densities are also recorded in Table 1.

Table 1

Process	Dmin	Dmax
A	0.16	1.69
B	0.26	1.57

The data in the above table indicate that the p-aminophenol color developing agent of our invention produces a transferred dye image of more desirable sensitometric properties than does the conventional p-phenylenediamine.

EXAMPLE 3

A. (control) A sample of a supported single-layer gelatinous silver halide emulsion coating, containing per square foot of coating 150 mg. silver, 500 mg. gelatin, 110 mg. of cyan-forming coupler N-ethyl-N-(3,5-disulfamoylphenyl)-1-hydroxy-4-{4-[2-(3-pentadecylphenoxy)butyramido]phenoxy}-2-naphthamide (Coupler IV) and 110 mg. coupler solvent diethyl lauramide, is exposed through a graduated-density test object and subsequently developed with the processing fluid whose composition is given below, while in contact for 5 minutes at room temperature with copoly[styrene-N,N-dimethyl-N-benzyl-N-3-maleiimidopropyl)ammonium chloride], a mordant receiver. Upon separation of the coating sample from the receiver, the latter contains a well-defined negative cyan-colored reproduction of the test sample. The H and D curves of the image are recorded.

PROCESSING FLUID

$Na_2CO_3 \cdot H_2O$	22 g.
ascorbic acid	0.385 g.
KBr	0.825 g.
NaOH	4 g.
4-amino-N-ethyl-N-β-hydroxyethylaniline	11 g.

A second sample of the coating is similarly exposed and processed, and then submitted for 24 hours to a xenon light fading test.

The loss of the dye density in this second sample in an image area having an initial density of about 1.0 is recorded in Table 2 below.

A third sample of the coating is similarly exposed and processed and then subjected for 1 week to an oven test (140° F./70 percent r.h.). The change of dye density resulting from this treatment is recorded in Table 3.

B. When the procedures described in Section A) are repeated with a processing fluid wherein the p-phenylenediamine color developing agent 4-amino-N-ethyl-N-β-hydroxyethylaniline has been replaced with a p-aminophenol, 2,6-dibromo-4-aminophenol, according to this invention, improved dye stability is observed. The results are also recorded in Tables 2 and 3.

EXAMPLES 4-A and -B

When the procedures described in Sections A) and B) of Example 3 are repeated with a coacervate mordant receiving sheet containing a coacervate of N-n-hexadecyl-N-morpholinium ethosulfate and methyl-tri-n-dodecylammonium p-toluenesulfonate, as described in U.S. Pat. No. 3,271,147 (Coacervate I), equally favorable results are obtained with a p-aminophenol color developing agent, 2,6-dibromo-4-aminophenol, according to this invention. The results are tabulated in Tables 2 and 3.

EXAMPLES 5-A and -B

When the procedures described in Sections A) and B) of Example 3 are repeated with samples of a silver halide emulsion coating wherein the image transfer coupler IV has been replaced with Coupler III, equally favorable results are obtained with the p-aminophenol color developing agent 2,6-dibromo-4-aminophenol according to this invention. The results are recorded in Tables 2 and 3.

EXAMPLES 6-A and -B

When the procedures described in Sections A) and B) of Example 3 are repeated with samples of a silver halide emulsion coating wherein the image transfer Coupler IV has been replaced with the yellow dye-forming image transfer Coupler I, equally favorable results with respect to heat stability are obtained in the presence of a p-aminophenol color developing agent, 2,6-dibromo-4-aminophenol, according to this invention. The results are recorded in Tables 2 and 3.

EXAMPLES 7-A and -B

Similarly favorable results with respect to heat stability are observed when the procedures described in Example 6 are repeated with a coacervate mordant receiving sheet containing Coacervate I. The results are recorded in Table 3.

EXAMPLES 8-A and -B

Similarly favorable results with respect to heat stability are observed when the procedures described in Example 6 are repeated with samples of a coating where Coupler I has been replaced with the yellow dye-forming diffusion transfer coupler α-[4-(N-methyl-N-octadecylsulfamyl)phenoxy]-α-pivalyl-4-sulfoacetanilide potassium salt (Coupler V). The results are recorded in Table 3.

EXAMPLES 9-A and -B

Similarly favorable results with respect to heat stability are obtained when the procedures described in Example 8 are repeated with a coacervate mordant receiving sheet containing Coacervate I. The results are recorded in Table 3.

TABLE 2

LIGHT FADE

Example	Coupler	Mordant Receiver	24-hr. xenon Color Dev. Agent I*	Color Dev. Agent II**
3	IV	quaternary mordant compound (a)	0.39	0.16
4	IV	quaternary mordant coacervate (b)	0.16	0.11
5	III	quaternary mordant compound (a)	0.22	0.12

TABLE 3

HEAT FADE

Example	Coupler	Mordant Receiver	Oven — 1 Week Color Dev. Agent I*	Color Dev. Agent II*
3	IV	quaternary mordant compound (a)	0.11	+0.07
4	IV	quaternary mordant coacervate (b)	0.09	0.02
5	III	quaternary mordant compound (a)	0.01	+0.04
6	I	quaternary mordant compound (a)	0.51	+0.05
7	II	quaternary mordant coacervate (b)	0.30	0.11
8	V	quaternary mordant compound (a)	0.24	+0.06
9	V	quaternary mordant coacervate (b)	0.18	0.08

(a) copoly]styrene-(N,N-dimethyl-N-benzyl-N-3-maleiimidopropyl)-ammonium chloride]
(b) Coacervate I - a coacervate of N-n-hexadecyl-N-morpholinium ethusulfate and methyl-tri-n-dodecylammonium p-toluenesulfonate
*4-amino-N-ethyl-N-β-hydroxyethylaniline
**2,6-dibromo-4-aminophenol

EXAMPLE 10

A. A supported two-layer light-sensitive element is prepared with a silver halide emulsion coating on a support containing per square foot 108 mg. silver, 500 mg. gelatin, 152 mg. Coupler III and 90 mg. of 2-chloro-4-aminophenol. HCl, and a second layer is coated thereon containing per square foot 100 mg. gelatin, 25 mg. di-n-butylphthalate, and ballasted scavenger couplers at concentrations of 25 mg. of 1-hydroxy-2-[Δ-(2,4-di-tert-amylphenoxy)-n-butyl]naphthamide and 76 mg. of 5-[α-(2,4-di-tert-amylphenoxy)hexanamido]-2-heptafluorobutyramidophenol.

A first sample of the above illustrated element is sensitometrically exposed through a graduated-density test object, then contacted for 60 seconds at room temperature with the mordanted receiver copoly[styrene(N,N-dimethyl-N-benzyl-N-3-maleiimidopropyl)ammonium chloride] in the presence of a viscous processing fluid of the following composition:

NaOH	10 g.
hydroxyethyl cellulose	20 g.
water to 1 liter	

A second sample of the element is similarly exposed, then contacted for 90 seconds with another sample of the receiver under otherwise identical processing conditions.

Upon separation, each of the two receiving elements contains a well-defined cyan-colored reproduction of the photographed test object. The receivers are finally washed for 3 minutes and dried. The minimum and maximum densities of the image are recorded in Table 4 below.

B) When the procedures described in Section A) above are repeated with a light-sensitive element which contains 90 mg./ft.^{2} of the conventional p-phenylenediamine developing agent 4-amino-N-ethyl-N-β-hydroxyethylaniline, the two receivers record respectively an over-all dye density of 0.25 and 0.42 with no image discrimination. The densities are also recorded in Table 4 below.

TABLE 4

		Dmin	Dmax
2,6-dibromo-4-aminophenol	10''	0.06	0.80
	90''	0.08	1.04
4-amino-N-ethyl-N-β-hydroxyethylaniline	60''	0.25	0.25
	90''	0.42	0.42

The data in the above table illustrates an advantage offered by incorporating a p-aminophenol color developing agent in the light-sensitive element Vs. the incorporation of a conventional p-phenylenediamine.

EXAMPLE 11

This example demonstrates the usefulness of employing a p-aminophenol color developing agent in a color diffusion transfer system which features the combination of colorless and colored image transfer couplers in the photoelement.

An eight-layer multicolor reversal silver halide emulsion image transfer element of structure and composition as illustrated in Section A) below is exposed, processed and evaluated by the procedures described in Section B) below.

A. The element has the following structure with the listed concentration of ingredients per square foot:

1. cellulose acetate support;
2. layer containing a red-sensitive silver halide emulsion described in U.S. Pat. No. 3,227,552, 220 mg. of gelatin and 125 mg. of Coupler III.
3. layer containing 100 mg. of a mixture of secondary-alkyl hydroquinones as disclosed in U.S. Ser. No. 17,330 filed Mar. 6, 1970, now U.S. Patent No. 3,700,453, and 150 mg. gelatin.
4. layer containing 80 mg. of 4- { 4- { α-[4-(8-acetamido-1-hydroxy-3,8-disulfo-2-naphthylazo)phenoxy]acetamido } phenoxy } -N-[4-(2,4-di-t-amylphenoxy)butyl]-1-hydroxy-2-naphthamide, disodium salt (Coupler VI) and 100 mg. of gelatin;
5. layer containing a green-sensitive reversal silver halide emulsion of U.S. Pat. No. 3,227,552 at 125 mg. silver and 93 mg. gelatin;
6. layer containing 15 mg. of Carey Lea silver, 100 mg. of a mixture of secondary-alkyl hydroquinones as disclosed in aforementioned U.S. Ser. No. 17,330 filed Mar. 6, 1970, and 150 mg. of gelatin;
7. layer containing 80 mg. of N-[4-(2,4-di-t-amylphenoxy)butyl]-4-[4- {α-[4- { 4-[N-ethyl-N-(2-sulfoethyl)amino]-2-tolyazo} phenoxy]acetamido} phenoxy]-1-hydroxy-2-naphthamide (Coupler VII) and 100 mg. gelatin;
8. layer containing a blue-sensitive reversal silver halide emulsion of U.S. Pat. No. 3,227,552 at 125 mg. silver and 93 mg. gelatin; and
9. layer containing 80 mg. gelatin.

B. The above-illustrated element is exposed through a multicolor graduated-density test object and treated with the viscous processing fluid described below, while in intimate contact for 6 minutes at room temperature with a coacervate mordant receiver which comprises a support with a layer thereon containing Coacervate I as described in Example 4.

PROCESSING FLUID

2,6-dibromo-4-aminophenol	25 g.
4-aminophenol-HCl	1 g.
NaOH	20 g.
piperidino hexose reductone	0.8 g.
hydroxyethyl cellulose	28 g.
water to 1 liter	

Upon separation of the element from the receiver, the latter is washed for 5 minutes in water and dried.

The quality of the positive multicolor image produced in the receiver is excellent. The image features high-density, well-balanced yellow, magenta and cyan separation images, as well as a well-balanced, low minimum density. The dyes are of good hue and color purity.

EXAMPLE 12

A photographic image transfer element is made according to Example 11 with the coacervate image-receiving layer and an opaque layer containing titanium dioxide and carbon coated on the support before coating the photosensitive emulsion layers thereon. After imagewise exposure, the alkaline processing solution is inserted between the photosensitive element and a transparent cover sheet containing thereon a layer of a polyacrylic acid and a barrier layer. The film unit remains laminated after processing with a good image record in the coacervate image-receiving layer.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A process of forming an 'onium indophenoxide transfer image comprising a) imagewise-exposing a photographic element comprising a support having thereon at least one layer comprising a silver halide composition having associated therewith a nondiffusible photographic color coupler capable of reacting with an oxidized aromatic primary amino color developing agent to produce a diffusible dye, b) treating said photographic element with an alkaline processing composition to effect development with a color developing agent which is predominantly a p-aminophenol, and c) forming an imagewise distribution of diffusible dye image-providing material as a function of said imagewise exposure of said silver halide composition and providing an 'onium compound in association with said diffusible dye image-providing material to provide an 'onium indophenoxide image dye, and at least a portion of said diffusible dye image-providing material diffusing to a dye image-receiving layer.

2. A process according to claim 1 wherein the color developing agent consists essentially of a p-aminophenol.

3. A process according to claim 1 wherein said nondiffusible color coupler is a pyrazolone coupler, a pyrazolothiazole coupler, a phenolic coupler or an open-chain ketomethylene coupler.

4. A process according to Claim 1 wherein said nondiffusible coupler has the formula:

$$\text{BALL—LINK—(COUP—SOL)}_n$$

wherein:

1. LINK is a connecting radical which is an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical, an azoxy radical, an aminoalkyl radical, a sulfonyloxy radical, an acyloxy radical or an imido radical;
2. COUP is a coupler radical which is a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;
3. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;
4. SOL is a hydrogen atom or an acidic solubilizing group when said color-developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color-developing agent is free of an acidic solubilizing group; and
5. *n* is an integer of 1 to 2 when said LINK is an alkylidene radical, and *n* is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical, an azoxy radical, an aminoalkyl radical, a sulfonyloxy radical, an acyloxy radical and an imido radical.

5. A process according to claim 1 wherein said onium compound is quaternary ammonium compound.

6. A process according to claim 1 wherein said onium compound is a polymeric quaternary ammonium compound and is located in said image-receiving layer.

7. A process according to claim 1 wherein said p-aminophenol developing agent is incorporated in at least one layer of said photographic element.

8. A process according to claim 1 wherein said treatment step b) is effected by:

a. superposing over the layer outermost from the support of said photographic element said dye image-receiving layer coated on a support;

b. positioning a rupturable container containing said alkaline processing composition between said exposed photosensitive element and said dye image-receiving layer; and

c. applying a compressive force to said container to effect a discharge of the container's contents between said outermost layer of said exposed photographic element and said dye image-receiving layer.

9. A process according to claim 1 wherein said 'onium compound is a tertiary or quaternary 'onium salt and said 'onium compound is present in a concentration sufficient to combine with substantially all of the diffusible image dye-providing material.

10. A process of forming an 'onium indophenoxide transfer image comprising a) imagewise-exposing a photographic element comprising a support having thereon a layer containing blue-sensitive silver halide emulsion having associated therewith a nondiffusible yellow coupler, a layer containing green-sensitive silver halide emulsion having associated therewith a nondiffusible magenta coupler, and red-sensitive silver halide emulsion having associated therewith a nondiffusible cyan coupler, wherein said yellow, magenta and cyan couplers are capable of reacting with an oxidized primary amino color developing agent to produce a diffusible dye, b) treating said photographic element with an alkaline processing composition to effect development with a color developing agent which is predominantly a p-aminophenol, and c) forming an imagewise distribution of diffusible dye image-providing material as a function of said imagewise exposure of said silver halide composition and providing an 'onium compound in association with said diffusible dye image-providing material to provide an 'onium indophenoxide image dye, and at least a portion of said diffusible dye image-providing material diffusing to a dye image-receiving layer.

11 A process according to claim **10** wherein said yellow, cyan and magenta couplers are all of the general formula:

$$BALL—LINK(COUP—SOL)_n$$

wherein:

1. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;
2. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;
3. BALL is a photographically inert ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;
4. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color-developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color-developing agent is free of an acidic solubilizing group; and
5. *n* is an integer of 1 to 2 [when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and a azoxy radical].

12. A process according to claim **10** wherein said 'onium compound is a quaternary ammonium compound.

13. A photographic image transfer film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:

a. a photographic element comprising a support having at least one layer thereon containing a silver halide composition having associated therewith a nondiffusible photographic color coupler capable of reacting with an oxidized aromatic primary amino color developing agent to produce a diffusible dye image-forming material;
b. a dye image-receiving layer;
c. a container means containing an alkaline processing composition which is adapted to be positioned during processing of said film unit so that a compressive force applied to said container by said pressure-applying members will effect a discharge of the contents of said container means into said film unit; and
d. a silver halide developing composition located in at least one layer of said film unit in association with said silver halide emulsion or located in said container means, said developing composition comprising a color developing agent which is predominantly a p-aminophenol.

14. A film unit according to claim **3** comprising an 'onium salt located in association with said image-receiving layer.

15. The film unit of claim **3** wherein said photosensitive element comprises a support having thereon a red-sensitive silver halide emulsion layer having associated therewith a cyan dye image-providing material comprising a nondiffusible coupler capable of reacting with an oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye, a green-sensitive silver halide emulsion layer having associated therewith a magenta dye image-providing material comprising a nondiffusible coupler capable of reacting with an oxidized aromatic primary amino color developing agent to produce a diffusible magneta dye, and a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye image-providing material comprising a nondiffusible coupler capable of reacting with an oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye.

16. The film unit of claim **15** wherein said dye image-receiving layer is located in said photosensitive element between said support and the lowermost photosensitive silver halide emulsion layer.

17. The film unit of claim **16** wherein said support is transparent, said film unit also includes a transparent sheet superposed over the layer outermost from said transparent support of said photosensitive element, and said container means also contains an opacifying agent and is positioned transverse a a leading edge of said photographic element so that a compressive force applied to said container will effect a discharge of the container's contents between said transparent sheet and the outermost layer of said photographic element.

18. The film unit of claim **16** wherein said support is transparent, said film unit also includes a process sheet adapted to be superposed over the layer outermost from the transparent support of said photographic element, and said container means is adapted to be positioned during processing of said film unit so that a compressive force applied to said container will effect a discharge of the container's contents between said process sheet and the outermost layer of said photographic element.

19. A film unit according to claim **13** which also contains a pH-lowering material.

20. In a photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:

I. A photographic element comprising a support having thereon the following layers in sequence:
   a. a direct-positive, red-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with an oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye;
   b. a direct-positive, green-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with an oxidized aro-

matic primary amino color developing agent to produce a diffusible magenta dye; and

c. a direct-positive, blue-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with an oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye;

II. a dye image-receiving element comprising a support having thereon a dye image-receiving layer, said element being adapted to be superposed over said blue-sensitive silver halide emulsion layer after exposure of said photographic element; and

III. a container means containing an alkaline processing composition and which is adapted to be positioned during processing of said film unit so that a compressive force applied to said container means by said pressure-applying members will effect a discharge of the container's contents between said dye image-receiving layer and said blue-sensitive silver halide emulsion layer of said photosensitive element;

said film unit containing a color developing agent which is predominantly a p-aminophenol developing agent and also containing an onium salt in association with said image-receiving layer.

21. A film unit according to claim **20** wherein said onium salt is a polymeric quaternary ammonium salt located in said image-receiving layer.

22. A film unit according to claim **20** wherein said color developing agent is located in at least one layer of said photographic element.

23. A film unit according to claim **20** wherein said color developing agent is located in said container means.

24. A film unit according to claim **20** wherein substantially all of said color developing agent in said film unit is a p-aminophenol.

25. In a process of forming a transfer image in a photographic film unit containing at least one layer of a silver halide emulsion associated with a color-forming coupler, the improvement comprising the combination of 1) treating said silver halide emulsion to effect development with a silver halide color developing agent which is predominantly a p-aminophenol and 2) providing an 'onium compound in association with said color-forming coupler.

26. A process according to claim **25** wherein said 'onium compound is a polymeric 'onium compound located in at least one layer of said film unit.

27. A process according to claim **25** wherein said color developing agent is located in at least one layer of said film unit and development is effected by treatment with an alkaline solution.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,765,886 Dated October 16, 1973

Inventor(s) Walter Monroe Bush and John Warburton Gates, Jr.

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

Column 1, line 55, "pholymeric" should read ---polymeric---. Column 2, line 6, "atoms" should read ---atom---; line 22, "day" should read --dyes--. Column 3, line 3, "incorported" should read --incorporated--; line 19, "n" should read --an--; line 45, after "mercuri radical, an", --oxy radical, a thio radical, a dithio radical, an-- should be inserted; lines 47-48, ", a thio radical, a dithio radical or an azoxy radical" should be deleted; lines 65-66, "nolecules" should read --molecules--. Column 4, line 38, that part of formula reading "coup" should read --COUP --. Column 5, lines 38-39, "nondifusible" should read --nondiffusible--. Column 6, line 43, "magneta-forming" should read --magenta-forming--; line 51, "pH-lowing" should read --pH-lowering. Column 7, line 40, after "developing", --agent-- should be inserted. Column 8, line 9, "closs" should read --class--; line 34, after "ammonium", --,-- should be inserted; line 46, after "compounds", "," should read --.--; line 50, "foud" should read --four--. Column 11, line 21, "visocity-increasing" should read --viscosity-increasing--. Column 12, line 59, "5,709,690" should read --3,709,690--; line 60, "coumarins," should read --the--. Column 13, lines 10-11, "coumarings" should read --coumarins--; line 22, "metalic" should read --metallic--; line 42, "mill" should read --mil--; line 43, after "when", --the-- should be inserted. Column 14, line 3, that part of formula reading "N-γ" should read -- N-β --; line 28, after "lauramide", --)-- should be inserted; line 61, "din-butyl" should read -- di-n-butyl --. Column 15, line 20, "procedures" should read --procedure--. Column 17, line 33, that part of formula reading "copoly]styrene" should read --copoly[styrene--; line 36, "ethusulfate" should read --ethosulfate. Column 18, line 22, "Vs." should read --vs.--; line 61, that part of formula reading "tolyazo" should read --tolylazo--. Column 19, line 11, that part of formula reading

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Patent No. 3,765,886 Dated October 16, 1973

Inventor(s) Walter Monroe Bush and John Warburton Gates, Jr.

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

"-HCl" should read ---·HCl--. Column 21, line 43, after "2", through line 47, "[when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and a azoxy radical]" should be deleted.

Column 22, line 23, "magneta" should read --magenta--.

Signed and sealed this 3rd day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents