United States Patent [19]

Waxman et al.

[11] **3,728,116**

[45] **Apr. 17, 1973**

[54] **INSTANT ACCESS ONE-LAYER COLOR PHOTOGRAPHY**

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[73] Assignee: **GAF Corporation,** New York, N.Y.

[22] Filed: **June 15, 1971**

[21] Appl. No.: **153,186**

[52] **U.S. Cl.**.....**96/29 D,** 96/3, 96/25, 96/77, 96/100, 96/118

[51] **Int. Cl.**.....**G03c 1/40,** G03c 5/54, G03c 7/08

[58] **Field of Search**.....96/118, 25, 80, 29 D, 96/3

[56] **References Cited**

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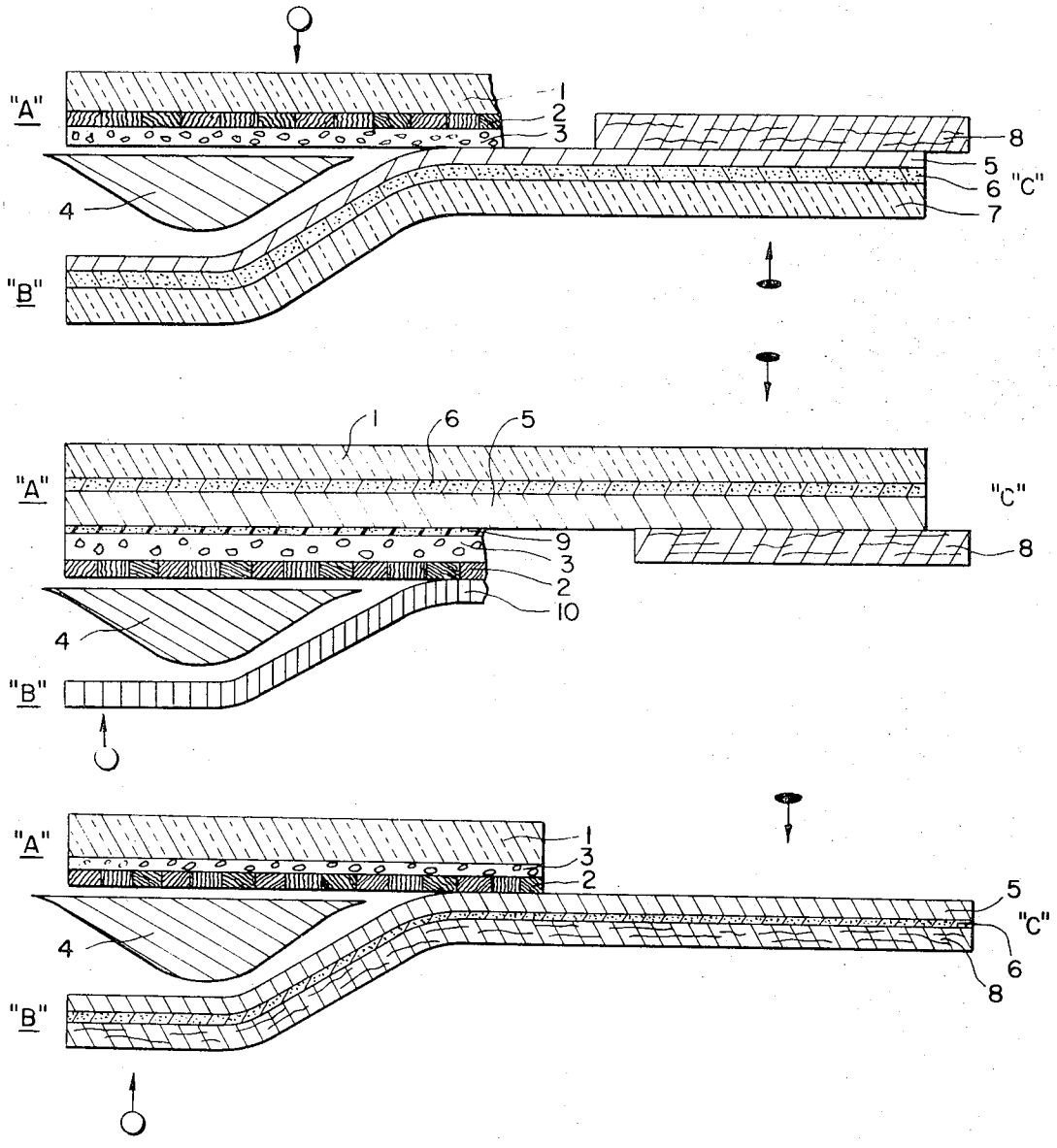
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[57] **ABSTRACT**

An improved instant access diffusion transfer process for photographic materials in which multicolor dye images are produced in a transfer sheet by exposing a panchromatically sensitized silver halide emulsion through a single multicolor screening layer and subsequently developing the emulsion at a high pH and transferring it to an unsensitized receiving sheet.

11 Claims, 14 Drawing Figures



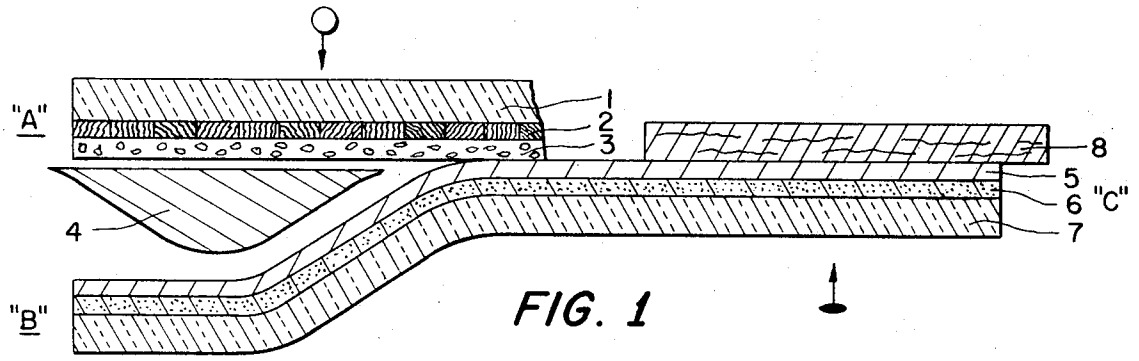


FIG. 1

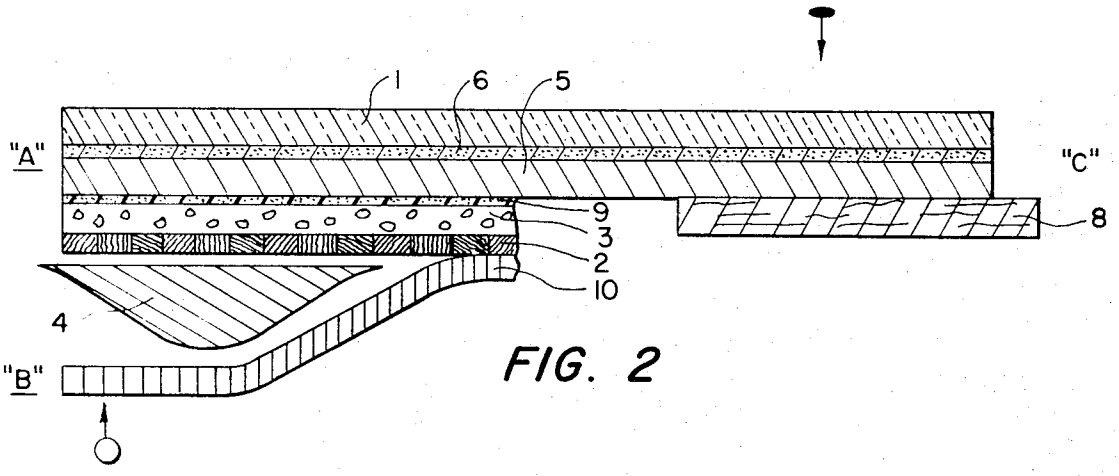


FIG. 2

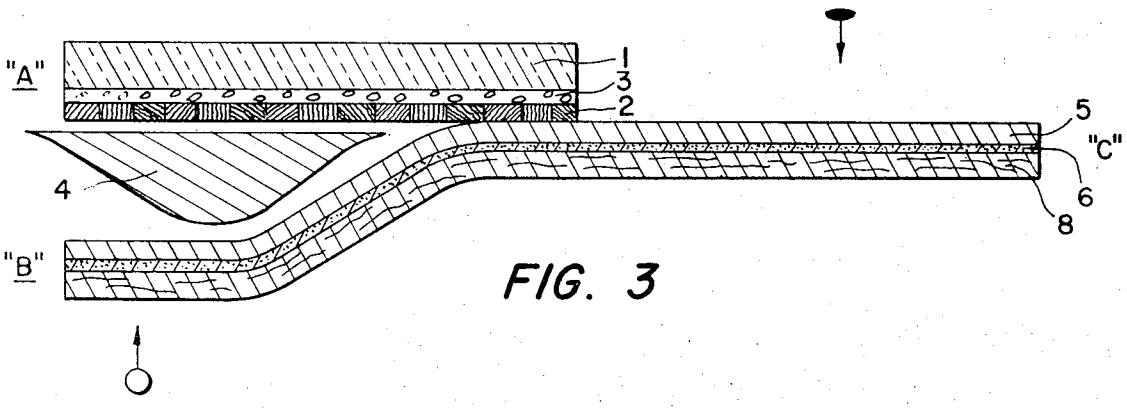


FIG. 3

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FIG. 4a

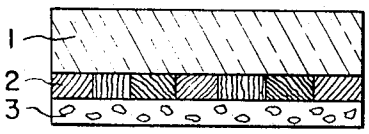


FIG. 4b

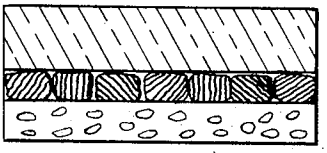


FIG. 4c

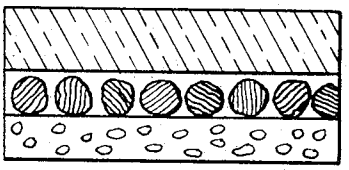


FIG. 5a

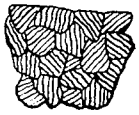


FIG. 5b



FIG. 5c



FIG. 6

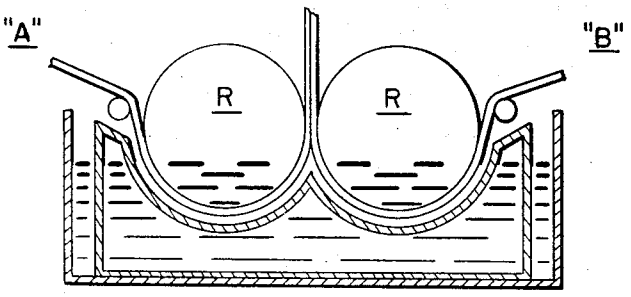


FIG. 7

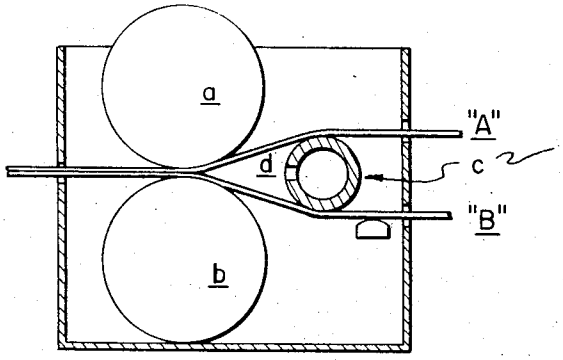
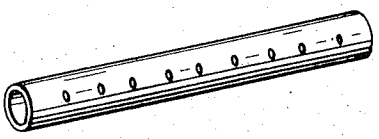


FIG. 8

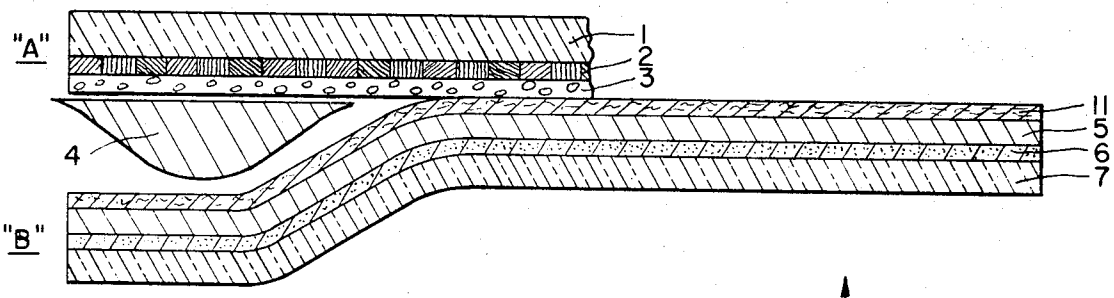


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FIG. 9



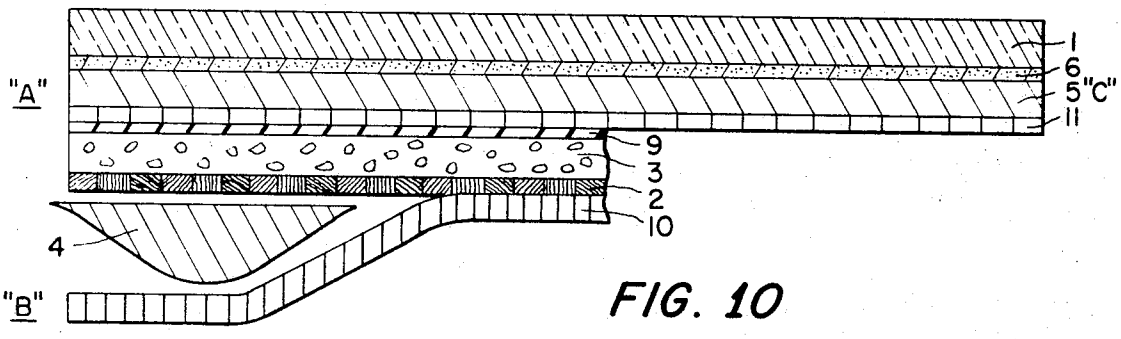


FIG. 10

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INSTANT ACCESS ONE-LAYER COLOR PHOTOGRAPHY

The present invention relates to color photography, and especially to a color diffusion transfer process by which unreacted color former(s) in the unexposed or partially exposed areas of a color negative are diffused imagewise, after color developing the negative, to a transfer sheet in which the color former(s) are reacted with oxidized color developer to produce positive dye images.

The use of the diffusion transfer process, described in U.S. Pat. No. 2,352,014, has been found to be very effective in black and white photography. This is particularly true in the system of E. H. Land of the Polaroid Corporation which employs pods of the processing chemicals between the light sensitive element and the transfer sheet.

Systems are known using mono- or multilayer coatings containing differently sensitized silver halide emulsions and corresponding color formers capable of yielding dyes complementary in color to the light rays to which each emulsion is sensitized, a color former being incorporated and dispersed in resinous or oily packets throughout the emulsion with the silver halide grains either incorporated in the colloidal carrier (gelatin or gelatin substitute) of the emulsion, or in the resinous packets, or in both. The technique based on this process is generally referred to as "packet" or "-mixed grain emulsion" technique. Such technique is described, for example, in British Patent Specification 864,060, in British Patent Specification 718,404, French Patent Specification 1,080,967 and U. S. Pat. Nos. 2,490,749; 2,544,640; 2,698,794; 2,698,795; 2,698,797; 2,798,544 and 2,322,027. These patent specifications indicate the steps to be followed and the oils to be used in preparing the "packet" or "mixed grain emulsions."

Other methods are known wherein a single color print may be reproduced by exposing a negative through a light filter and pressing the development negative into contact with a transfer sheet containing a color former. In this instance, excess developer migrates to the transfer sheet where it couples with the stationary color formers upon air oxidation of the developer. This system requires several layers each with a separate dye to produce a multicolor print.

In order to produce instant access color prints, the prior art employs either several layers exposed through several light filters, or by differently sensitized silver halide emulsions, or both.

We have now found that with the use of a single unique screening layer, it is possible to produce multicolor positive prints by the diffusion transfer process. This screening layer acts as a multicolor light filter system capable of screening specific light waves in accordance with the requirements of this invention. The screening layer and a panchromatically sensitized silver halide emulsion layer constitute the photosensitive element, or negative material.

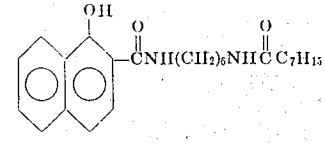
In conjunction and coordination with the photosensitive element are special color formers which reside therein that become diffusible upon development at high pH in accordance with requirement of the diffusion transfer process herein disclosed.

A diffusion transfer process which produces multicolor dye images in a transfer sheet by exposing a

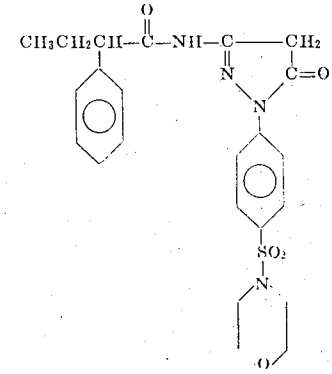
panchromatically sensitized silver halide emulsion through a screening layer, and development at high pH constitutes the object of this invention.

In commercial color photography, the color formers which are employed in the screening layer are either of the hydrophilic type, e.g., those solubilized by alkalies or of the hydrophobic or lipophilic type, e.g., those dissolved in oils of the type described in for instance U. S. Pat. No. 2,322,027, and are of such high molecular weight that they resist diffusion from the emulsions even at a high pH. The color former(s) which we employ and which have been characterized above as of a special type, partake in part of the characteristics of the lipophilic color formers of the prior art, but are of a much lesser molecular weight so that at high pH, i.e., 12.5–13, they are diffusible in an aqueous medium. Specifically, the color formers which we use must possess the following attributes: 1) medium molecular weight, 2) freedom from water solubilizing groups, such as carboxy or sulfonic acid groups, 3) sufficiently oil soluble to be incorporated in resinous or oily packets, 4) contain such groups which only at high pH (12.5–13) are able to form an alkali metal salt which renders the color former molecule diffusible in aqueous medium, e.g., groups such as phenolic hydroxyl and enolic hydroxyl, and 5) produce non-diffusible dyes with conventional primary aromatic amino color developing agents, such as N-diethyl-p-phenylenediamine; N-ethyl-N-β-hydroxyethyl-p-phenylenediamine and N-diethyl-3-methyl-p-phenylenediamine and the like.

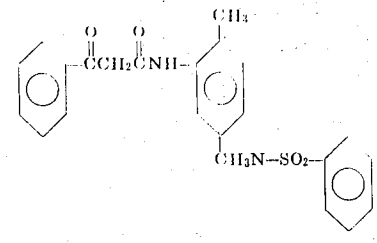
Examples of couplers contemplated for use according to the present invention and which meet the above attributes include the following:



I



II



III

The compounds I, II, and III are the preferred color formers, but other color formers can be selected by a simple test. Thus, couplers which are free from solubilizing groups, but are sufficiently soluble in an oil and which diffuse only at the high pH specified would be adequate for use, such as those listed in U. S. Pat. No. 3,301,772.

No diffusion of these couplers results during preparation of the sensitized element or negative color development usually effected at a pH of 10.0–11.5, a condition which excludes the use of hydrophilic color formers which are soluble in solutions of low alkalinity. Hydrophilic color formers which are thus excluded are, for example, of the type described in U. S. Pat. No. 2,186,849. On the other hand, diffusion of our couplers ensues as soon as the pH of the environment reaches or exceeds 12.5. This excludes the lipophilic type color formers of high molecular weight presently used in commercial color products which are not diffusible regardless of the pH. Accordingly, in our procedure the color formers which are not reacted during color development of the negative image are caused to diffuse by raising the pH from about 10–11.5 to about 12.5–13. The diffusion of the unused couplers is, therefore, controlled, not by structural modifications of the color former molecule, but by the pH of the surrounding medium. The diffused color formers will form a positive dye image on a contacting unsensitized transfer sheet in the presence of an oxidizing agent and unused color developer.

Generally speaking, the quantity of color former used per unit of silver halide is selected in such a way that maximum density in the high light regions of a subject, or the transparent portions of a pattern, is achieved on exposure of the color negative material to the subject, or to the pattern and color developing such areas to maximum density. Thus, in the areas of exposure yielding maximum density on color development, all of the color former will be used up and none can transfer. In other areas, the unused coupler will diffuse and be imagewise received in the transfer sheet. Consequently, where maximum density is achieved in the negative materials, no dye image will form in the transfer sheet. Dye images will only form in the transfer sheet to the extent that the coupler remains unreacted after color development of the negative material. Specifically, it is recommended that with a screen coating of from 0.4 to 0.8 micron in thickness, about 0.4–0.8 g. of color former/m^2 be used. This requires in practice about 0.7–1.5 g. AgX/m^2 in the emulsion coating. Using emulsions with Ag^o/gelatin ratio of 0.70 this would require an emulsion coating of thickness of 2.0–4.0 microns.

Preferred forms of this invention will be more fully understood by reference to the accompanying drawings in which:

FIGS. **1**, **2**, **3**, **9** and **10** disclose cross sectional views of the instant access photographic element showing several alternative ways of obtaining lateral reversal of the image and the individual layer arrangement for carrying each out, and which constitutes several physical embodiments of the invention.

The screening layer can be coated on a film base, as in FIGS. **1** and **9**, or the panchromatic emulsion layer as in FIGS. **2**, **3** and **10**.

In the assembly represented in FIGS. **1** and **2**, the positive receiving material is then pressed film base up in contact with a white cardboard material which becomes reflective base for the print. In the case described in FIG. **3**, the stripped positive receiving sheet is the new print which could be mounted later to a more rigid cardboard base.

FIGS. **9** and **10** described systems similar to the ones in FIGS. **1** and **2** except that the white opaque reflectance is created not by paper base added later, but is obtained by incorporating white pigment, such as TiO_2 in a layer through which the color former has to diffuse before forming a positive transfer image. Processing as in FIG. **2** incorporates a positive receiving sheet underneath the negative element.

FIG. **4** pictorially shows what is happening during the development process to the flattened out and lightly packed oil droplets within the gelatin membrane of the oil screen, pointing out that in the dry state maximum filtration is obtained whereas during processing the supply of color former for diffusion is contracted because of gelatin swelling characteristics. This helps to reduce side-wise diffusion during exposure and during the diffusion step.

FIG. **5** pictorially describes and defines the various layers referring to FIGS. **1**, **2**, **3**, **9** and **10**.

FIGS. **6**, **7** and **8** are schematic representations of equipment, a pod, used in evaluating coatings, and for the mechanical pressure and developer contacting apparatus for evaluating and processing the coatings in the transfer system, and could be used inside or outside of the camera, and a camera reproduction work.

FIG. **7** shows a mechanical pod device wherein a) or b) are soft rollers, and c) is a stainless steel tube of ¼ inch diameter and closed at one end and perforations in one row facing the rubber rollers. FIG. **8** is a perspective view of stainless steel tube c shown in FIG. **7**. The open end is connected to a repeater syringe filled with viscous developer and adjusted to measure out enough viscous developer to be spread evenly between inserted negative photosensitive element "A" and contacting material "B." The latter sheets are of such width as to snugly fit between the two nylon roller end plates which keep the developer confined in volume *d*).

A discussion of the photographic layers which are used in the several alternative arrangements according to the invention, such as depicted in FIGS. **1**, **2**, **3**, **9** and **10**, is provided so that the physical behavior of the chemicals and apparatus may be better understood.

Layer **1**. is a transparent film base, such as polyester, cellulose acetate, cellulose acetate butyrate, and the like, with a thickness of 2 ½ – 9 mils.

Layer **2**. is the oil droplet screen layer containing screening dyes and color couplers. Coating the screen to 4–8 microns thick coated about 0.4 – 0.8 g. coupler/m^2, with oil droplet sizes are from 5–15 microns.

Layer **3**. is the panchromatically sensitized emulsion layer. The emulsions intended for use herein are:

Panchromatically sensitized bromo iodide emulsion of average crystal size 0.4 – 1.0 micron, containing 4–12 mole percent iodide, gold and sulfur sensitized.

Panchromatically sensitized bromo chloride emulsion of average crystal size 0.2 – 0.5 micron containing 70–90 mole percent bromide.

Panchromatically sensitized bromo chloride emulsion of average crystal size of 0.2 – 0.5 micron and containing 10–40 mole percent bromide.

With the layer thickness and concentration levels of

the coupler in layer 2, the requirement in practice of the emulsions are about 0.7–1.5 g. of Ag/m² emulsion coating. Using emulsions with Ag°/gelatin ration of about 0.7, would require a dry emulsion coating thickness f 2–4 microns.

Layer 4. Pod

Layer 5. is an image receiving layer, and may be of the conventional type such as baryta paper, and the like, 8–16 microns thick.

Layer 6. is the encapsulated oxidizer and neutralizer layer, of conventional materials 2–4 microns thick.

Layer 7. is a transparent base or overlay which becomes the protective layer or covering on the positive print after separation.

Layer 8. is a paper base. The materials contemplated relating to FIGS. 1 and 2 would be white cardboard for mounting the stripped print for lateral reversal. In FIG. 3, it would be flexible single or double weight paper base support.

Layer 9 is an alkali stripping layer 2–4 microns in thickness.

Layer 10 is a contact stripping sheet and may be any flexible composition or film base which has one side treated so as to cause good adhesion to screen layer 2 when developer is spread between said layers. This allows after the required diffusion time to physically strip off layers 2 and 3 as a new integral packet of 10 + 2 + 3 which is then discarded.

Layer 11 is a white opaque pigment layer containing TiO_2, or the like.

The screening layer 2 consists of numerous minute oil droplets (5–15 microns in size) held in place and closely packed within a gelatin membrane (see FIG. 4 and Examples I and II). Upon drying the oil droplets flatten out and form a mosaic pattern with gelatin membrane between the colored oil droplets. The screen could be coated on a film base as in FIG. 1, or over the panchromatic emulsion layer as in FIGS. 2 and 3.

Within each separate oil droplet is a dye which colors it (such as blue, red and green dyes) and a complementary color coupler (based upon a subtractive color system). The combination of numerous colored oil droplets constitutes a screening device acting as a single layer multilight filter through which the AgX emulsion is exposed.

The screening layer is placed between the AgX emulsion and the object to be exposed, thus the light reaching the AgX emulsion must first pass through the screening layer. Since the droplets are colored, only that light of a specific spectrum of wavelength corresponding to that color are allowed to be transmitted through each oil droplet screen to the underlying AgX emulsion layer. The red dyed droplet transmits only red light, the green droplets transmit green, and the blue blue. The silver halide receiving this actinic colored light is activated according to that of the light reaching it.

If the red oil droplet transmits red light to the silver halide emulsion layer, the cyan color former within it, upon development, diffuses and is coupled by developer oxidized by the AgX activated by that red light transmitted. Thus, the color former of said oil droplet is immobilized, and developed cyan colored (in the negative), and not allowed to reach the transfer sheet. However, the positive will thus develop minus the cyan dye which will appear red when all its color combination densities are transferred to the transfer positive, according to the subtractive dye system. The same logic applies to the other colored droplets and their complementary color couplers therein.

Upon development of the photographic element, the couplers filter and diffuse out of the oil droplets and into the silver halide emulsion layer. The silver halide is non-diffusible imagewise or non-imagewise, and some of the color formers are imagewise intercepted by developer oxidized by the reduced AgX, and become immobilized in place in layer 3 instead of reaching the image receiving layer. The non-immobilized excess of color former which has not been imaged out by color coupling with AgX and developer is thus allowed to diffuse imagewise to the transfer sheet where it reacts with oxidized developer forming positive dyes.

The dyes contemplated for use in this invention within the colored oil droplets are as follows:

Blue

Sudan Blue CSP

Methyl Violet Base

Sudan Blue BA

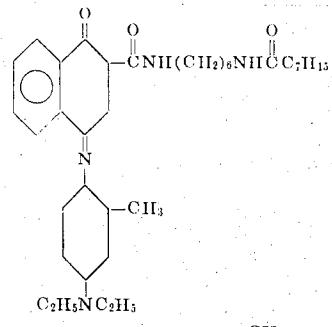
Red

Sudan Red GGA

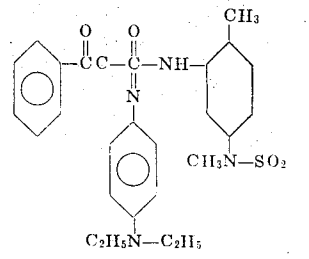
Sudan Red BBA

Green

IV + V



IV



V

Note that these filter dyes are non-diffusing at all times, and that the subtractive dyes formed from color formers by the coupling process are non-diffusing under all processing conditions.

The color formers must be non-diffusing under prevailing conditions making screen dispersions, coating the same and for overcoating with other layers. Color formers must be diffusing and alkali soluble in aqueous phase under processing conditions requiring reduction of AgX by paraphenylene diamine type developer, and coupling the latter with color formers.

The process hereof may be carried out by alternative techniques. In one method, it is envisaged that the negative material, after exposure, is contacted by developer of high pH (12.5–13) and developed to maximum density, and then is brought into contact with the

transfer sheet containing an oxidizing agent such as potassium ferricyanide, hydrogen peroxide, potassium dichromate, or the like. The alkalinity of the developer is transferred to the environment of the color formers, causes their diffusion into the AgX emulsion layer, where some is coupled with oxidized developer, and the remainder are received in the transfer sheet.

Another procedure involves initiating developer oxidation, after exposure, by placing the negative material in a color developer solution for 1–3 minutes having a pH of 10.5–11.5, and completing the development by contacting the negative material with a developer solution having a pH of 12.5–13.

For this purpose use may be made of a transfer sheet containing a 2 percent solution of sodium hydroxide, potassium hydroxide, or the like. The transfer sheet is then used to pick up the diffused color former and to provide a medium in which it is converted into a dye image in the presence of an oxidizing agent and unused color former.

Yet another, and the preferred procedure involves color development to be carried out by passing the exposed negative material "A" (see FIG. 1) and the contacting material "B" through a roller assembly (see FIG. 6) whereby they have a presoak in the developer solution of 3–5 seconds at pH of 12.5–13, before they are pressed into physical contact under moderate roller pressure. After 1 minute (30 seconds - 2 minutes contact, which varies for optimum results on developer temperature), the sheets are pulled apart, this high pH developer having caused diffusion of the couplers into the AgX emulsion layer, and to the transfer sheet where it images out in a positive print. As in FIG. 1 and 2, the positive receiving material is then pressed film base up in contact with a white cardboard material which becomes reflective base for the print. In this case described in FIG. 3, the stripped positive receiving sheet is the new print which could be mounted later on a more rigid cardboard base.

It is thus evident that three different techniques may be resorted to in order to obtain correct transfer color images. The first method is intended to completely immobilize the color former corresponding to the exposed silver halide and then to transfer along with excess developer the imagewise diffusible non-immobilized color former to form the final image.

The second method is intended to oxidize the developer corresponding to the exposed silver halide in the negative in low pH developer, and then completing the processing by introducing the high pH developer rendering the color formers diffusible and where some are immediately immobilized in the silver halide emulsion, and the remainder diffused, along with excess developer to the transfer sheet.

The third and preferred method does not require imagewise color developer diffusion, and wherein the negative material and the contacting material are simultaneously contacted, after exposure, by a high pH presoak developer solution which renders the couplers diffusible into the AgX layer and to the transfer sheet where the non-immobilized couplers form a dye image with developer oxidized by an oxidizing agent encapsulated within the contacting material.

The following examples will further explain the present invention, although it is to be understood that this invention is not restricted to such examples.

EXAMPLE I

The oil droplets for use in the screening component of the aforesaid invention which are to be used in the instant access mono layer color photography are prepared as follows:

A. Blue screen component is made as follows:

0.5 g. of yellow color former (III) and
0.15 g. of Sudan Blue CSP and
0.25 g. of Methyl violet base are
dissolved in
1.0 cc of dibutylphthalate and
2.0 cc of Santicizer 160 (Butyl Benzyl Phthalate) (Monsanto Co.)
by heating on a hot plate. When dissolved, the oil phase is dispersed under slow stirring speed (mechanical) for 100 seconds in
45 cc of 8 percent gelatin solution and
6.0 cc of Alkanol B dispersing agent (Sodium Alkyl Naphthalene Sulfonate) (E.I. duPont deNemours and Co.).
Droplet size 5 – 15 microns.

B. Red screen component is made as follows:

0.7 g. of cyan color former (I) and
0.25 g. of Sudan Red GGA and
0.25 g. Sudan Red BBA are
dissolved in
1.0 cc of dibutylphthalate and
2.0 cc of Santicizer 160
by heating on a hot plate. When dissolved, the oil phase is dispersed under slow stirring (mechanical) for 100 seconds in
45 cc of 8 percent gelatin solution and
2.2 cc of Alkanol B dispersing agent.
Droplet size 5 – 15 microns.

C. Green screen component is made by dissolving:

0.7 g. of magenta color former (II) and
0.25 g. of cyan dye (IV) and
0.10 g. of yellow dye (V) in
1.0 cc of dibutylphthalate and
2.0 cc of Santicizer 160
by heating on a hot plate. When dissolved, the oil is then dispersed under slow stirring (mechanical) for 100 seconds in
45 cc of 8 percent gelatin solution and
4.5 cc of Alkanol B dispersing agent.
Droplet size 5 – 15 microns.

EXAMPLE II

The mixed screen layer 2 (see FIG. 1) for use in the instant access mono layer color photography are prepared by mixing:

30 cc of blue screen dispersion A
30 cc of red screen dispersion B
30 cc of green screen dispersion C
under very gentle hand stirring. The combined screen dispersion is then coated to form 4–8 micron thick - dry layer in gelatin. In the drying step, the oil droplets flatten out and form a mosaic pattern with a gelatin membrane between the colored oil patterns. The screen can be coated on a film base, as in FIG. 1, or over the panchromatic emulsion layer as in FIGS. 2 and 3. Coating the screen to 4–8 microns thick creates about 0.4–0.8 g. of color former/m^2.

EXAMPLE III

A photosensitive layer "A" of Example I is exposed to a subject image, and developed to maximum density for 2 minutes at 20°C. by spreading the following viscous developer solution onto layer A:

sodium sulfite	8 g.
sodium hexametaphosphate	1 g.
N-ethyl-N-β-hydroxyethyl-p-phenylene-diamine	5 g.
sodium carbonate, monohydrate	10 g.
sodium bromide	1 g.
sodium hydroxide	17.5 g.
water to make	1000 cc

The developer has a pH of 13.

The color formers thus migrate into the silver halide emulsion layer and developer develops the negative latent image; where development occurs, color formers are coupled with oxidized developer to form an immobile dye. The negative material "A" is then pressed into contact with the image carrying layer "B," and the unreacted color couplers and developer migrate to the image carrying layer presoaked in a potassium ferricyanide. The developer once oxidized by the oxidizing agent couples with the color formers to form a visible positive image with values corresponding to the original.

EXAMPLE IV

A photographic element of the type depicted in FIGS. **1** and **10** was prepared utilizing the screen layer prepared in Example II, with layers **2** and **3** comprising the negative photosensitive element "A."

Element "A" is exposed in a step wedge sensitometer and developed to maximum density for 2 minutes at 20°C. in the following developer:

sodium sulfite	8 g.
sodium hexametaphosphate	1 g.
N-ethyl-N-β-hydroxyethyl--p-phenylene-diamine	5 g.
sodium carbonate, monohydrate	10 g.
sodium bromide	1 g.
water to make	1000 cc

the developer has a pH of 10.7.

The developed strip, without working, is pressed into contact for three minutes with a transfer sheet of baryta coated paper "B," presoaked for 5 minutes in a 2 percent aqueous solution of sodium hydroxide. This provides a pH in the environment of the photosensitive element of 12.5–13, i.e., sufficiently high pH to cause the color former to migrate through the emulsion layer, and those which are not immobilized in the emulsion layer diffuse to transfer sheet.

The transfer sheet is then separated from the negative coating and placed for 1 minute in a 1 percent solution of potassium ferricyanide which oxidizes the developer present in the transfer sheet. Reaction between oxidized developer and diffused color formers produce visible positive image with tone values corresponding to the original.

EXAMPLE V

A photographic element of the type depicted in FIG. **1** was prepared by utilizing the screen layer prepared in Example **2**, with layers **2**, and **3** comprising the negative photosensitive element "A," and layers **5**, **6**, and **7** comprising the contacting material "B." Color development is carried out, after exposure of the photosensitive element to a subject image, by passing the exposed negative material "A" and contacting material "B" through a roller assembly (see FIG. **6**), whereby they have a 3–5 second presoak in the following highly alkaline viscous developer solution:

sodium sulfite	8 g.
sodium hexametaphosphate	1 g.
N-ethyl-N-β-hydroxyethyl-p-phenylene-diamine	5 g.
sodium carbonate, monohydrate	10 g.
sodium bromide	1 g.
sodium hydroxide	17.5 g.
water to make	1000 cc

before they are pressed into physical contact under moderate roller pressure. The developer has a pH of at least 12.5. After 1 minute contact time, at 20°C., the sheets are pulled apart.

Referring to FIG. **1**, when developer **4** is spread between "A" and "B": and the negative element and the contacting material are "squeezed" together, color developer and alkali start diffusing into the swelling emulsion layer **3** and into the image receiving layer **5**. By the time exposed silver halide crystals start developing and thereby producing oxidized color developer, alkali has reached color former filter layer **2**, mobilizing color former from oil droplets and letting it diffuse out into the emulsion layer where it will couple with oxidized developer, where present, to form immobile dye. Where no exposure had taken place, color former moves on through the emulsion layer into the image receiving layer **5** and the layer containing encapsulated oxidizer **6**. In the latter layer, slow release of oxidizer takes place creating a low concentration of oxidized developer which couples with the color former forming immobile positive dye image.

The removal of color former in the receiving layer helps to establish concentration gradient which helps to gain high maximum density in the receiving layer. At the end of development time (1 minute) color former concentration in the original screen layer has dropped to very low level since it was being used up as fast as it diffused out, forming negative dye image in the negative element and a positive dye image in the receiving layer. Side-wise diffusion is kept at the minimum for several reasons:

1. Alkalinity front moves in from emulsion side exposing a large area of the oil droplet to high alkalinity and will start diffusion to front side only.
2. As alkalinity penetrates between the droplets, gelatin swells and causes physically bigger distance between the droplets which at this stage return to their spherical shape (see FIG. **4**).

It will be evident that the process contemplated herein may be effected in a camera or in a copying device. The only requirements are the ability to expose the sensitized material, develop the same and to contact the developed material at a high pH with a transfer sheet in the presence of an oxidizing agent.

In most of the Examples, the emulsions employed use gelatin for the colloidal matrix. It is understood, however, that gelatin substitutes, such as polyvinyl alcohol,

methyl cellulose, casein and other gelatin substitutes, may be employed.

It may be added that the color formers which are employed are those which are capable of forming non-diffusing quinoneimine or azomethine dye images upon color development with a primary aromatic amino developer. Such color formers are pyrazolones, phenols or straight chain ketomethylene compounds. They must not only possess such structural features, but must also meet the attributes previously specified.

We claim:

1. An instant access multicolor reproduction process utilizing a photographic element comprising on a transparent filmbase a single panchromatically sensitized light sensitive silver halide emulsion layer in contiguous contact with a single red, green and blue screen layer, said process comprising the steps of (1) imagewise exposing to actinic light said panchromatically sensitized silver halide emulsion layer through the multicolor screening layer made of red, green and blue colored oil droplets, each droplet containing a single non-diffusing dye having one of the primary colors and a colorless color former diffusible only at a pH of 12.5 and higher and capable of forming a dye complementary in color to the screen droplet upon coupling with the oxidation product of a paraphenylenediamine color developer, and (2) bringing into intimate contact the exposed negative photosensitive element with a receiving sheet in the contiguous presence of a paraphenylenediamine color developer solution having a pH of at least 12.5 and thereby causing the diffusion of said color formers from said screening to said silver halide emulsion layer, thereby causing imagewise immobilization by coupler coupling in the exposed areas and diffusion of the unused portions of said color formers from the unexposed areas to the receiving sheet, (3) converting the imagewise transferred color formers to a multicolor dye image in the unsensitized receiving sheet by coupling said color formers with said paraphenylenediamine color developer in the contiguous presence of an oxidizing agent.

2. An instant access multicolor reproduction process utilizing a photographic element carrying on a suitable transparent base in the following order a single red, green and blue screen layer in contiguous contact with a panchromatic silver halide emulsion layer, said process comprising (1) imagewise exposing to actinic light the panchromatically sensitized silver halide emulsion layer through the red, green, blue multi-colored screen layer, said screen layer being made up of three separate oil droplet dispersions, each containing a non-diffusible filter dye having one of the primary colors red, green or blue and containing in addition a color former which becomes diffusible at a pH of at least 12.5 and which is capable of reacting with the oxidation products of a paraphenylenediamine color developer to form a non-diffusible dye complementary in color to the primary color of the dye in the oil droplet, said color formers being free from water solubilizing groups but sufficiently oil soluble to be incorporated in an oily packet but containing a group which at a pH of at least 12.5 is capable of rendering the color former soluble in the developer solution, the imagewise exposure being sufficient to ensure maximum density in the silver halide emulsion upon color development in those areas of the emulsion receiving maximum exposure (2) color developing the emulsion in a paraphenylenediamine developer solution of a pH of at least 12.5 to produce maximum image density with complete conversion of the non-diffusing color formers to non-diffusible dye images in the areas of maximum density by pressing the negative photosensitive element into contact with a receiving sheet in the contiguous presence of said alkaline color developer solution, the high alkalinity causing diffusion of the color formers from the oil droplets into the emulsion layer, thereby imagewise immobilizing the color formers in the exposed areas by coupling action with oxidized developer, permitting the diffusion of the residual non-coupled color former and developer solution into an unsensitized image receiving layer which contains an encapsulated oxidizer thus permitting oxidation of developer and coupler to form a positive dye image in the layer.

3. The process of claim 1 wherein the exposed element and the receiving sheet are presoaked for a short time in said developer solution before being pressed into physical contact.

4. The process of claim 2 wherein the exposed element and the receiving sheet are presoaked for a short time in said developer solution before being pressed into intimate physical contact.

5. The process of claim 3 wherein said developer solution has a pH of 12.5 – 13.

6. The process of claim 3 wherein said developer solution has a pH of 12.5 – 13.

7. The process of claim 3 wherein the presoak time is 3–5 seconds.

8. The process of claim 4 wherein the presoak time is 3–5 seconds.

9. The process of claim 1 wherein developer contact time is 1 minute.

10. The process of claim 2 wherein developer contact time is 1 minute.

11. A light sensitive photographic material carrying on a transparent film base in the following order a colloidal layer having dispersed therein an encapsulated oxidizing agent, followed by a second colloidal layer to serve as a receiving layer, said receiving layer being overcoated by a peelable polymer layer of polyvinyl alcohol capable of delaminating from the receiving layer at the end of processing, said peelable layer being overcoated by a panchromatically sensitized silver halide emulsion layer which is in contiguous contact with a multicolor screening layer made of red, green and blue colored oil droplets, each droplet containing a non-diffusing dye having one of the primary colors in addition to a color former which becomes diffusing at a pH of at least 12.5 and is capable of forming upon coupling with the oxidation products of a paraphenylenediamine color developer a non-diffusing dye complementary in color to the dye of the oil droplet in which said color former was contained.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,728,116 Dated April 17, 1973

Inventor(s) Burton Harvey Waxman, Robert Thomas Shannahan and Felix Viro

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

Abstract, Line 1, delete "improved"
Line 4, after "multicolor" insert --,--
Line 5, before "screening" insert --color former containing--
Line 5, delete "and"
Line 7, change "it" to --the color formers from the screening layer--

Column 1, line 5, change "in" to --corresponding to--
Column 1, line 18, change "Systems" to-Multicolor systems--
Column 1, line 27, delete ", or in both"
Column 1, line 27, before "technique" insert -- latter --
Column 1, line 39, change "color" to -- multicolor --
Column 1, line 40, change "a negative" to -- three negatives --
Column 1, line 41, change "a light filter" to -- three light filters --

Column 1, line 43, delete "In this instance excess developer"
Column 1, delete lines 44 and 45
Column 1, line 46, delete "developer"
Column 1, lines 46 and 47, change "several layers each with a separate dye to produce a multicolor print" to -- at least three separate steps and is obviously not a one-step instant access process --
Column 1, line 49, delete "either"

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,728,116 Dated April 17, 1973

Inventor(s) Burton Harvey Waxman, Robert Thomas Shannahan and Felix Viro

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

Page 2

Column 1, lines 49 and 50, change "exposed through several ligl filters, or by" to -- of --
Column 1, line 51, change "," after "emulsions" to -- . -- and cancel rest of line
Column 1, line 52, delete "single"
Column 1, line 53, after "unique" insert -- dual action --
Column 1, line 55, before "screening" insert -- dual action --
Column 1, line 55, after "as" insert -- both --
Column 1, line 56, after "waves" insert -- and as a provider of color formers yielding complementary dyes --
Column 1, line 63, change "therein that" to -- in the screen and --; same line, change "development" to -- treatment with
Column 1, line 64, after "pH' insert -- solution --
Column 1, line 64, change "requirement" to -- the requirements
Column 1, line 65, after "disclosed." insert the following sentence: -- The color formers incorporated within the scree are positioned in a point to point relationship with the dyes to which they form complementary colors when reacted with oxidized color developer. --
Column 2, line 2, change "a" before "screening" to -- the aforesaid --
Column 2, line 5, delete "which are employed in the screening layer"
Column 3, line 10, change "usually" to -- if initially --
Column 3, line 11, delete "hydrophilic"
Column 3, line 13, change "Hydrophilic" to -- Such --
Column 3, line 23, change "caused" to -- free --
Column 3, line 24, change "by raising" to -- to the receiving sheet when --

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,728,116 Dated April 17, 1973

Inventor(s) Burton Harvey Waxman, Robert Thomas Shannahan and Felix Viro

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

Page 3

Column 3, line 24, change "from about 10-11.5 to about" to -- is at --
Column 3, line 26, change "controlled" to -- caused --
Column 3, line 29, after "image" insert -- modulated by imagewise oxidative coupling and immobilization in the emulsion layer --
Column 3, line 40, after "up" insert -- while diffusing through the emulsion layer --; same line, change "can" to -- is left over for --
Column 3, line 48, change "after" to -- while diffusing during the --; same line, change "of" to -- through --
Column 3, line 47, change "material" to -- silver halide element --
Column 4, line 56, delete "are"
Column 5, line 3, change "ration" to -- ratios --
Column 5, line 5, change "thickness f" to -- thickness of --

Column 5, line 54, change "are" to -- is --

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

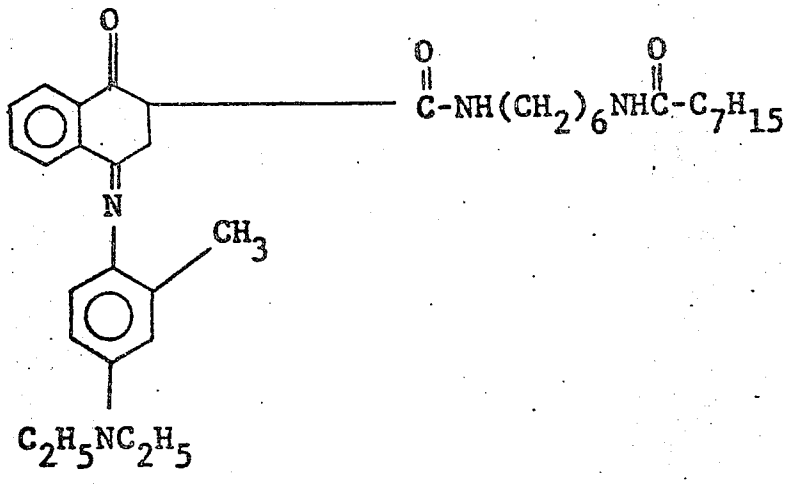
Patent No. 3,728,116 Dated April 17, 1973

Inventor(s) Burton Harvey Waxman, Robert Thomas Shannahan and Felix Viro

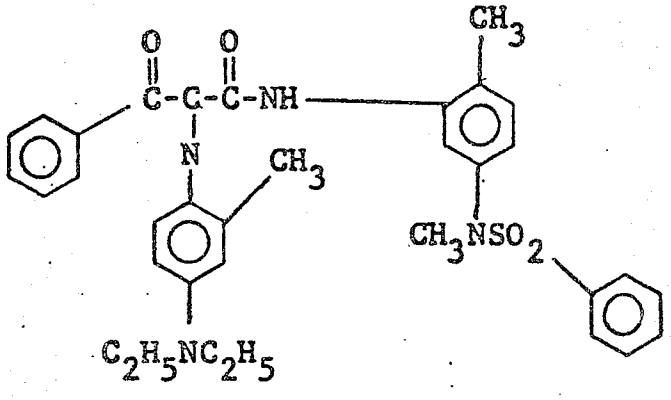
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Page 4

Column 6, Formula IV should be



Column 6, Formula V should be:



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(5/69)

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CERTIFICATE OF CORRECTION

Patent No. 3,728,116 Dated April 17, 1973

Inventor(s) Burton Harvey Waxman, Robert Thomas Shannahan and Felix Viro

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

Page 5

Column 6, line 68, delete "then"
Column 6, line 68, insert -- simultaneously -- after "is"
Column 7, line 6, change "is" to -- are --
Column 8, line 54, change "are" to -- is --
Column 9, line 21, change "then" to -- simultaneously --
Column 9, line 24, delete "a"
Column 12, line 6, change "of at least" to -- below --
Column 12, line 8, delete "non-diffusing"
Column 12, line 10, change "by" to -- ; --
Column 12, line 12, change "said" to -- an --
Column 12, line 12, after "solution" insert -- of pH of at least 12.5 --
Column 12, line 13, change "high" to -- higher --
Column 12, line 17, after "," insert -- and --

Signed and sealed this 31st day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents