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Haefner

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[54] **PHOTOGRAPHIC DIFFUSION TRANSFER PRODUCT AND PROCESS**

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[52] **U.S. Cl.** .... **117/68,** 96/76 R, 117/73, 117/76 P
[51] **Int. Cl.** **B05c 9/04**
[58] **Field of Search** .... 96/76 R, 29, 87 A, 96/87 R, 85; 117/68, 73, 76 F, 76 P, 34

[56] **References Cited**

UNITED STATES PATENTS

2,584,030	1/1952	Land	96/110 X
2,789,054	4/1957	Land	96/29
3,421,893	1/1969	Taylor	96/29
3,419,389	12/1968	Haas et al.	96/3
3,682,639	8/1972	Barbehenn et al.	96/85
3,265,505	8/1966	Yudelson	96/76

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[57] **ABSTRACT**

A receiving sheet for use in a diffusion transfer process comprises a polyolefin surface such as polyethylene over which is coated a cellulose ester layer such as cellulose triacetate, an acid layer such as polyacrylic acid, a timing layer and an image receiving layer. The image receiving layer can be a nucleated layer for use in black-and-white diffusion transfer or a mordanted layer for use in color diffusion transfer.

6 Claims, 2 Drawing Figures

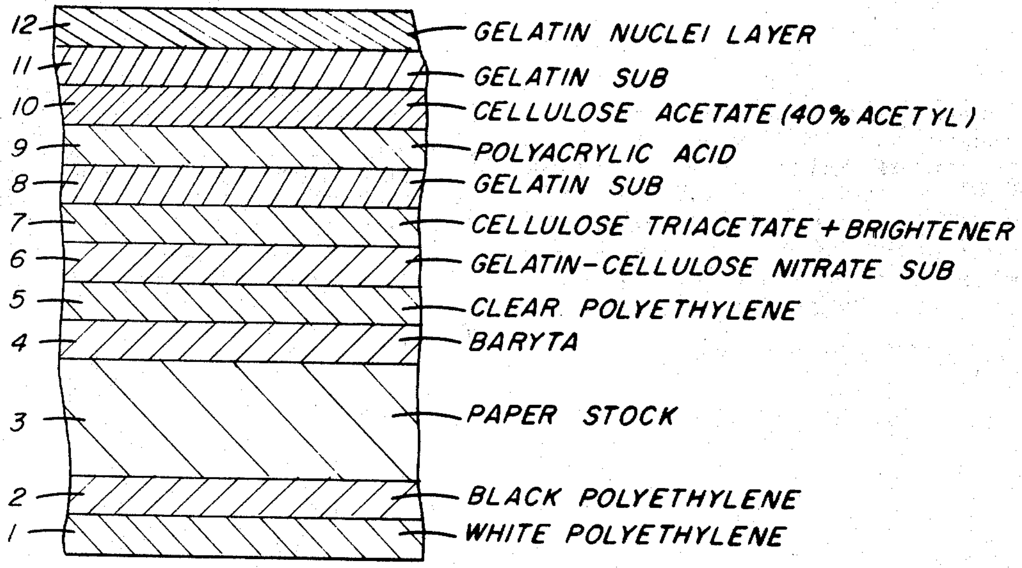


FIG. 1

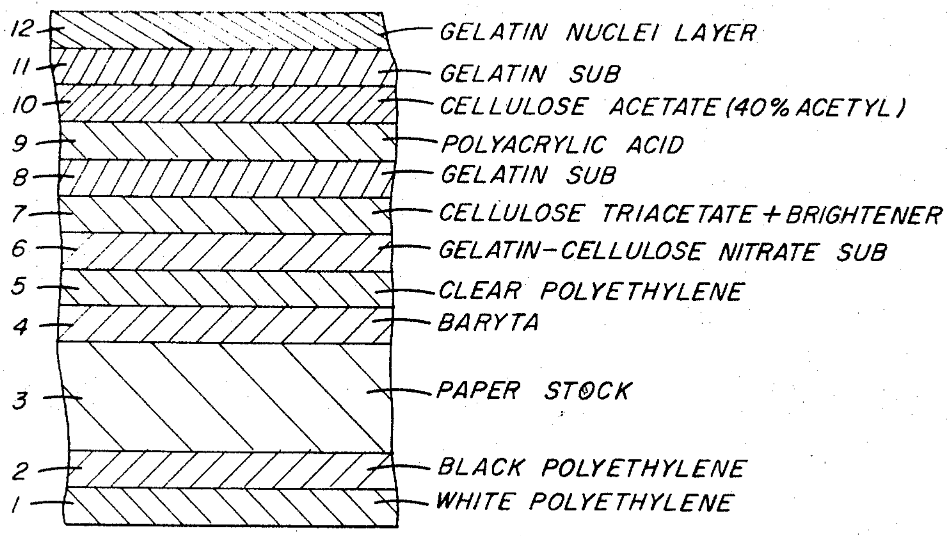
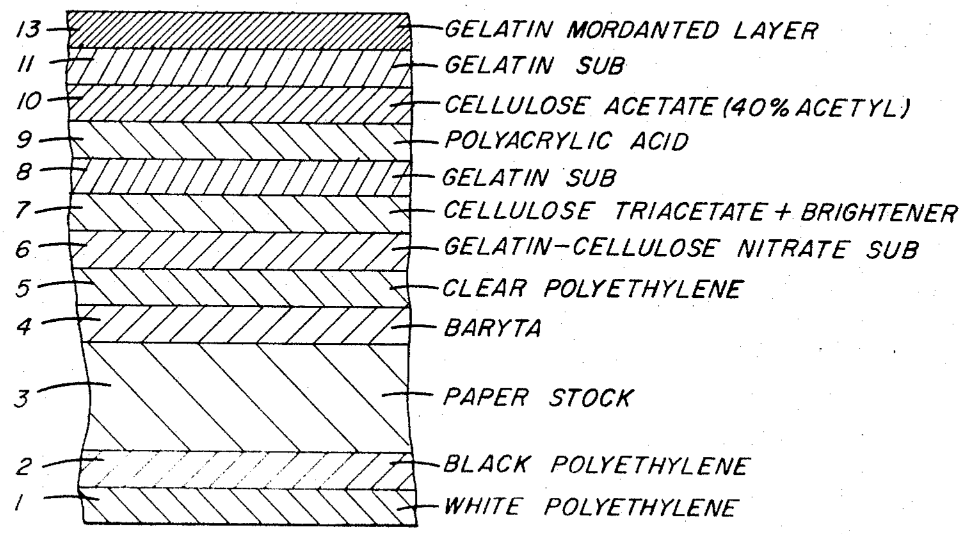


FIG. 2



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PHOTOGRAPHIC DIFFUSION TRANSFER PRODUCT AND PROCESS

BACKGROUND OF THE INVENTION

This invention concerns receiving sheets for use in a diffusion transfer process. More particularly, it concerns receiving sheets having improved abrasion resistance and improved stability, particularly to hydrogen sulfide.

Diffusion transfer processes are well known. For example, Rott U.S. Pat. No. 2,352,014 describes such a process wherein undeveloped silver halide of an exposed photographic emulsion layer is transferred as a silver complex imagewise by imbibition to a silver precipitating or nucleating layer, generally to form a positive image therein. A silver precipitating or nucleating layers generally comprises a binder containing nuclei such as nickel sulfide, colloidal metal or the like.

In a conventional black-and-white diffusion transfer process, a processing solution containing a silver halide developer, a silver halide solvent and a viscous film-forming agent hving a relatively high pH is employed. An element is processed by squeezing the viscous processing material between the exposed silver halide emulsion and the receiving sheet. The receiving sheet is then separated from the silver halide emulsion layer and the receiving sheet contains the desired print.

Photographic color diffusion transfer processes utilizing dye image receiving elements are also well known as is illustrated by Beavers et al U.S. Pat. No. 3,445,228 issued May 20, 1969, Bush U.S. Pat. No. 3,271,147 issued Sept. 6, 1966, Whitmore U.S. Pat. No. 3,227,552 and Whitmore et al. U.S. Pat. No. **3,227,550** issued Jan. 4, 1966.

In photographic color diffusion transfer processes, image reproduction is effected by developing an exposed silver halide emulsion layer having associated therewith a non-diffusible color-forming coupler that forms a diffusible dye when reacted with an oxidized color developing agent, reacting oxidized aromatic primary amino color developing agent with such coupler, and allowing the resulting dye to diffuse to a reception layer for such dyes. A color diffusion transfer system typically employs a photosensitive element comprising three differentially spectrally sensitized silver halide emulsion layers, each of which layers having associated therewith a non-diffusible coupler compound capable of yielding the appropriate diffusible complementary color dye upon development with oxidized aromatic primary amino color developing agent.

The reception layer is typically a mordanted layer on a suitable support. The transfer of the color dye images to the reception layer is accompanied by small amounts of development reaction products and unused color developing agent. Such materials transferred with the dye image to the reception element are objectionable because of the tendency of these transfer materials to form stain, particularly in the highlight or D_{min} areas. In a similar manner, prints obtained by the black-and-white diffusion transfer process have been subjected to various problems including the problem of stability with respect to the presence of processing chemicals retained in the element.

A desired photographic receiving element should have the qualities which are essential for an excellent receiving sheet: opacity, dimensional stability, moisture vapor proofness, adhesion of layers, low temperature flexibility, resistance to crazing on aging, heat and light stability; high reflectiveness, fluorescence, surface smoothness, gloss and particularly image abrasion resistance together with image resistance to fading.

Efforts for stabilizing a silver image in a chemical transfer system include the use of solutions consisting of vinyl pyridine polymer, hydantoin-formaldehyde polymer, weak acid or zinc acetate and other heavy metal salts combined in a swab coating, for example, U.S. Pat. Nos. 2,692,675; 2,719,791; 2,830,900; 2,866,705; 2,874,045; and 2,979,477.

U.S. Pat. No. 2,584,030 issued Jan. 29, 1952 describes the use of a polymeric acid, such as cellulose acetate hydrogen phthalate, to obtain pH reduction of the alkaline activator after formation of a silver salt diffusion transfer image; the polymeric acid is located adjacent to the inner surface of the print receiving layer, or beneath the inner surface of the print receiving element, said acid being overlayed with a layer of solid material slowly permeable to the processing liquid. The slowly permeable layer may itself be an acid or acid ester. In color diffusion transfer systems, a timer or spacer is disclosed as customarily used under the image receiving layer. For example, U.S. Pat. No. 3,362,819 discloses a spacer layer of polyvinyl alcohol or a partial acetal of polyvinyl alcohol; a coating of polymeric acid and cellulose ester is overcoated with a spacer layer of partially hydrolyzed polyvinyl acetate.

U.S. Pat. No. 3,419,389 discloses a spacer layer of cyano-ethylated polyvinyl alcohol; U.S. Pat. No. 3,421,893, a spacer layer of polyvinyl amide; and U.S. Pat. No. 3,433,633, a spacer layer of hydroxy propyl cellulose. In a typical timing or spacing layer, the penetration and the neutralization of the alkaline processing solution occurs within about 60 seconds of the time of image formation.

It has been desirable to employ a paper support having a polymeric coating thereon such as a polyolefin coating, in particular polyethylene, which reduces the penetration of development reaction products and the like into the paper support, thereby reducing stain and improving the stability of the dye image. However, the use of polyethylene coated paper has resulted in problems such as poor adhesion, low abrasion resistance, and the like. Electron bombardment of polyethylene surfaces or similar treatments have been conventionally used in order to improve the adhesion of coatings thereon, but the use of electron bombardment or similar treatments by themselves have not resulted in satisfactory adhesion or resistance to abrasion.

In a copending application entitled "Photographic Diffusion Transfer Product and Process" filed concurrently herewith in the name of Timothy F. Parsons Ser. No. 91,042 is described a method of improving the abrasion resistance of receiving sheets by coating on a polyolefin surface a cellulose ester layer over which can be coated a suitable image receiving layer.

One of the most serious problems with the keeping of transfer images is the problem of image degradation by hydrogen sulfide present in the atmosphere. In this form pf degradation the black silver image becomes yellow, most likely becoming silver sulfide. It appears desirable that the alkalinity of the positive image be lowered, neutralized or slightly acidified to prevent image degradation by hydrogen sulfide. It is also desirable that the development and transfer of the image is complete before pH reduction takes place.

Moreover, residues from processing chemicals in the photographic element cause stain and/or stability problems so that it is desirable to find some means of counteracting the effect of the processing chemical residue.

Accordingly, it has been desirable to provide a receiving sheet which would be useful in diffusion transfer both for black and white and for color processes which would have good abrasion resistance and which would provide stability for an image in an image receiving layer.

SUMMARY OF THE INVENTION

It has now been found that the aforementioned problems are overcome with receiving elements for use in the black-and-white or color diffusion transfer process which elements comprise a polyolefin surface such as polyethylene having thereon a cellulose ester such as cellulose triacetate over said ester layer an acid layer, and over said acid layer a timing layer. Over the timing layer is located an image receiving layer. It will be appreciated that other layers may be interposed between the cellulose ester layer and the receiving layer or that subbing layers may be employed in order to still further improve adhesion of these layers.

The combination of a polyolefin surface having thereon a cellulose ester layer, a polymeric acid layer and a spacer or timing layer with an image receiving layer over the timing layer results in a synergistic combination having improved image stability and improved abrasion resistance over that obtained by any of the layers taken individually.

In a preferred embodiment for use in a silver diffusion transfer process, a polyethylene surface is electron bombarded to improve adhesion. A layer of cellulose triacetate containing a brightener is then coated over the polyethylene and on this layer of cellulose triacetate is coated a gelatin-cellulose nitrate subbing, a polyacrylic acid layer, a cellulose acetate timing layer, a gelatin sub, and a gelatin layer containing silver precipitating nuclei such as palladium metal. In a preferred embodiment for use in color diffusion transfer, and employing a similar structure, a gelatin mordanted receiving layer is used instead of a silver precipitating layer.

A receiving element is described above is used advantageously to provide a photographic print having an image in a receiving layer on a support by the photographic silver salt diffusion transfer process or color diffusion transfer process.

DESCRIPTION OF PREFERRED EMBODIMENTS

If the polyolefin surface is carried on a separate support, a paper support is preferred. The paper can be any conventional cellulosic paper support including those prepared from cotton, linen, and wood (sulfate and sulfite pulped) and which supports are typically about 5–60 pounds per 1,000 square foot papers.

The polyolefin material which forms the surface for the receiving sheet of this invention can be coated over any support, typically in a thickness of about 0.3 to 5 mils. For instance, particularly useful polyolefin materials include the olefin homo- or copolymers prepared from alpha-olefins having 2–10 carbon atoms. Blends of polyolefins can also be employed in forming a suitable surface. The coatings may be applied by extrusion or hot melt coating techniques, as latexes, as solvent coatings, etc. If the polyolefin is self-supporting, it can be of any convenient thickness.

In some instances it is desirable to incorporate in the polyolefin at least one pigment or dye, especially where a white background is required, but this is not required. In a particularly useful embodiment, titanium dioxide is incorporated as a pigment in an amount of up to 25 percent, preferably 10–15 percent by weight of the resin. Other pigments or dyes which may be useful include those commonly known as pigments or dyes for polymeric materials.

The polyolefin surface can be given an additional treatment when the polyolefin material such as polyethylene is extruded but this is not necessary to this invention. Shortly after extrusion, the polymeric material is contacted against a chilled roll which may be glossy, preferably, or matte depending upon the desired finish. In another embodiment, the coating is placed on the support as a latex or solvent coating and then contacted against a hot glossy roll in order to provide a glossy or matte finish. This is particularly suitable when a latex coating has been applied or when the polymeric surface has been softened on the surface by contacting with a semisolvent solution which softens the surface of the coating. In still another embodiment a latex coating may be applied to a support after which the coated support is subjected to heat such as by hot air impinging on the surface or from infrared lamps directed to the surface.

The polymeric surface is then given a treatment to improve the hydrophilic character of the surface to improve adhesion. Typical treatments which are particularly suitable for use with hydrophobic polyolefin polymers, such as polyethylene, include electron bombardment, radiation by ultraviolet light, etc.

Electron bombardment of polymeric surfaces is conveniently carried out by means of a corona discharge. The level of electron bombardment or similar surface treatment of the polymeric surface can be measured by the contact angle obtained when a drop of distilled water is placed on a level sample of the polymeric coating. By projecting the image of the drop and sample on a suitable screen, and measuring the angle of a line tangent to the drop image at the point of the drop touches the polymeric sample, a contact angle is obtained which can be measured and utilized to determine the degree of hydrophilicity. Generally untreated polyethylene coated paper gives a contact angle of about 90°. A contact angle of preferably from about 40° to about 75° improves the adhesion of hydrophilic coatings and is highly desirable for coatings such as cellulose ester coatings, subbing coatings or the like. With polypropylene, the preferred contact angle is preferably less than 54° for subsequent coatings.

Typical methods of treating polyethylene by electron bombardment are disclosed in Traver U.S. Pat. No. 3,018,189 directed to methods for treating the surface of polyethylene with electrostatic discharges to change the surface properties of the polyethylene with respect to adhesion of materials coated thereon. British Pat. Spec. No. 715,915 issued to the Visking Corp., published Sept. 22, 1954 also discloses a method and apparatus for treating plastic structures with a corona discharge.

Another method of improving the adhesion of a cellulose ester to a polyolefin coated surface is illustrated by Alsup U.S. Pat. No. 3,161,519 issued Dec. 15, 1964 in which colloidal silica is employed in a coating over the polyolefin surface. In the particular disclosure therein, a coating mixture containing colloidal silica is coated on untreated polyethylene coated paper and dried with hot air at about 150°F. A particularly useful coating composition is disclosed in Example 6 in which an acrylic resin is employed in the coating composition. In any event, the use of the coating of cellulose ester over the polyolefin coated surface improves the abrasion resistance regardless of whether the polyolefin has received an additional treatment to improve its adhesion.

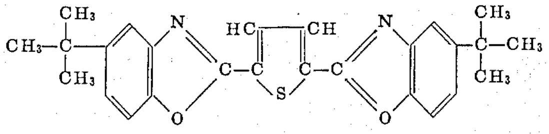
It will be appreciated that various layers of polymer may be coated on a support such as paper. For instance, in order to obtain opacity, a layer of polyethylene pigmented black can be coated on the back of the paper covered by a layer of polyethylene pigmented white. On the face side of the paper, it is sometimes desirable to coat a layer of baryta plus a dye or brightener over which can be coated a layer of clear polyethylene plus a pigment such as titanium dioxide. However, in order to obtain the advantages of the invention, a layer of cellulose ester is coated over the polyolefin either with or without a subbing applied between the polyolefin surface and the cellulose ester layer. Over the cellulose ester layer can be coated a receiving layer with or without a subbing layer. If a subbing layer is used, it can be of the type described herein as useful between the polyolefin layer and the cellulose ester layer.

Cellulose esters which can be coated over the polyolefin layer include those which are obtained from organic acids having 2–4 carbon atoms including mixed esters such as cellulose acetate butyrate, cellulose acetate propionate and the like. Particularly useful esters are those of lower aliphatic, preferably monocarboxylic acids, such as cellulose acetate, cellulose triacetate, cellulose butyrate and the like. Typical cellulose ester formulations are described in Fordyce et al. U.S. Pat. Nos. 2,492,977 and 2,492,978 issued Jan. 3, 1950, Fordyce et al. U.S. Pat. No. 2,739,070 issued Mar. 20, 1965 and Fordyce et al. U.S. Pat. No. 2,607,704 issued Aug. 19, 1952.

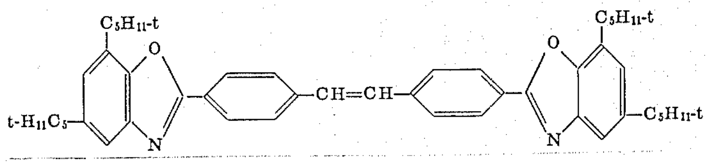
For some purposes, a subbing can be used such as a gelatin-cellulose nitrate subbing. The gelatin nitrate sub is particularly useful when coating a gelatin coating on the surface of a plastic overcoat such as cellulose ester. Typical coatings are disclosed in the Nadeau et al. U.S. Pat. No. 2,614,932 issued Oct. 21, 1952, Nadeau U.S. Pat. No. 2,133,110 issued Oct. 11, 1938. Of course, the nature of the subbing coated on the cellulose ester layer depends upon the nature of the binder used in the mordanted or nucleated layer coated over the subbing. In a preferred embodiment employing gelatin in the receiving layer, it is particularly useful to use the gelatin-cellulose nitrate subbing such as is disclosed in the above Nadeau et al patent.

The cellulose ester can be applied as a solvent coating so that it provides a cellulose ester layer having a thickness of about 0.1 to 0.4 mils or a coverage of 0.3 g/m² to 10 g/m². The cellulose ester can contain addenda such as a pigment or a brightener, dyes, plasticizers, etc.

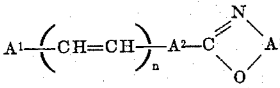
The brighteners which can be incorporated in the cellulose ester coating in any suitable concentrations, particularly good results being obtained at concentrations at about 0.01 to about 1.0 percent by weight of a whitening or brightening agent. For example, 4-4'bis(benzoxazol-2yl)stilbene compounds are especially useful. Other compounds which are useful include those having the following structure and described in Belgian Pat. No. 612,775:



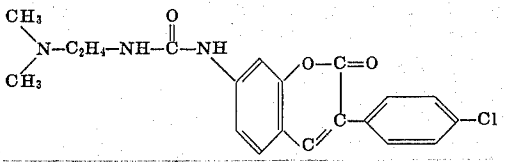
and 4,4'-bis(5,7-di-t-amylbenzoxazol-2-yl)stilbene



Other whiteners include coumarins of the type described in British Pat. No. 786,234 and fluorescent compounds of the formula:



in which A^1 is substituted or unsubstituted phenyl radical, A^2 is a substituted or unsubstituted p-phenylene radical, A_3 is a substituted or unsubstituted arylene radical, e.g., an o-phenylene radical or a 1,2-naphthylene radical, in which two vicinal carbon atoms are bonded to the oxygen and nitrogen atoms respectively of the oxazole ring and *n* is an integer from 1 to 2, as described in Saunders Canadian Pat. No. 700,147 issued Dec. 15, 1964. Another useful brightener is 3-(p-chlorophenyl)-7-(2[dimethylaminoethyl]ureido coumarin, Tinopal SFG (Geigy), having the formula:



The plasticizing agents can be omitted, but if desired, any of those typically used in cellulose esters can be employed.

The acid layer can be any acid reacting layer which contains non-diffusible acid groups, e.g., acid radicals attached to a polymer so as to be non-diffusible. The acid reacting layer can also contain a water-insoluble polymer, preferably a cellulose ester which acts to control or modulate the rate at which the alkali salt of the polymeric acid is formed.

Examples of polymeric acids wich may be used include polyacrylic acid, copoly(butylacrylate-acrylic acid 60:40 mole percent), cellulose acetate hydrogen phthalate, ethylmethacrylatemethacrylic acid copolymer, methylmethacrylate-methacrylic acid copolymer. Acid groups which are particularly useful are carboxylic acid and sulfonic acid groups which are capable of forming salts with alkali metals, such as sodium, pottasium, etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide or potentially acid yielding groups, such as anhydrides or lactones or other groups which are capable of reacting with bases to capture and retain them. The acid reacting group is non-diffusible from the acid polymer layer.

In the preferred embodiments the acid polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxylic groups prior to imbibition. While many available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used.

Examples of specific polymeric acids which can be used ad dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives of cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo-substituted aldehydes, e.g., o-, m- or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methylvinyl ether/maleic anhydride copolymers such as the butyl half-ester of medium viscosity poly(methylvinyl ether/maleic anhydride); etc.; other acids such as zeolites (hydrated alkali aluminum silicate) $Na_2O{\cdot}2Al_2O_3 \cdot 5(SiO)_x{\cdot}(H_2O)_y$, organic acids such as phthalic acid, acid salts such as zinc acetate, etc.

Preferably the acid layer is hardened, e.g., polyacrylic acid containing a bisepoxy ether as described in Houck et al. U.S. Pat. No. 3,062,674 or in Hurwitz U.S. Pat. No. 2,954,358. The acid layer preferably contains at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 13 to 14 to a pH of at least 11 or lower at the end of the imbition period, e.g., about 20–60 seconds and preferably to a pH of about 5–8 within a short time after imbibition of the processing solution. As previously noted, the pH of the processing composition frequently is of the order of at least 13 to 14. The coating thickness of the acid layer is about 0.1 to 0.4 mils or a coverage of 0.3 g/m² to 10 g/m² preferably 1–7 g/m².

The timing layer or spacer layer is an alkali permeable layer coated over the acid layer in order to retard penetration of chemicals and the like from the image receiving layer to the acid layer. In a preferred embodiment, the timing layer is a cellulose acetate layer which cellulose acetate has about 40 percent acetyl and becomes hydrolyzed by the action of the processing chemicals so that this layer is slowly penetrated, e.g., about 12–24 hours after image formation, by the developer solution so that the pH reduction of the alkaline developer by the acid layer is affected only after image transfer is complete; this pH reduction stabilizes the silver image without the need for treatment of the print after processing. The layer thickness depends upon the nature of the timing layer and is generally from about 0.2 g/m² to about 1.5 g/m², preferably about 0.6 to 1.0 g/m².

Various other materials may be used for the timing layer, for example, a polymer such as polyvinyl alcohol or a partial acetal of polyvinyl alcohol such as a partial polyvinyl butyral. Other materials such as gelatin which are inert to alkali but through which the alkali may diffuse to the acid layer may be used. The inert timing layer acts to time control the pH reduction by the acid layer. This timing is a function of the rate at which the alkali diffuses through this inert timing layer. The pH does not drop until the alkali has passed through this timing layer, i.e., the pH is not reduced to any significant extent by the mere diffusion to the timing layer, but the pH drops quite rapidly once the alkali diffuses through the layer into the acid layer.

A polymeric material which is particularly useful, for example, is a solution dyable polymer such as N-methoxymethyl polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers, cellulose acetate with fillers as, for example, one-half cellulose acetate and one-half oleic acid; alkali-impermeable cellulose ester, e.g., cellulose diacetate which can be made permeable to alkalis by alkaline hydrolysis; gelatin; and other materials of similar nature. Typical timing or spacer layers are disclosed in U.S. Pat. No. 3,419,389 issued Dec. 31, 1968. For use in a color product as an image receiving layer, the timing or spacing layer may also be the mordanted layer and the layer may contain a dye mordant such as poly-4-vinylpyridine.

Another example of a suitable timing layer is hydroxy propyl cellulose. Still another example of a timing layer is cyano-ethylated polyvinyl alcohol.

Additional examples are hydroxy propyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyloxazolidione, hydroxypropyl methyl cellulose, partial acetals of polyvinyl alcohol such as partial polyvinyl butyral, partial polyvinyl formal, partial polyvinyl acetal, partial polyvinyl propional, and the like, and including a mixture of the polymers as, for example, a mixture of hydroxy propyl methyl cellulose and partial polyvinyl butyral.

In one embodiment for the color diffusion transfer element, a mordant is used in a gelatin layer as the receiving layer in the photographic element described herein. Any satisfactory mordant may be used. However, particularly useful mordants are those disclosed in Bush U.S. Pat. No. 3,271,147.

Mordanting and thus immobilizing, soluble dyes in hydrophilic polymeric colloids such as gelatin which are commonly employed as the film-forming colloids of photographic materials is commonly accomplished by causing the dyes to enter into a salt-forming reaction with

1. ionic groups in the principal film-forming colloid,
2. ionic groups in a compatible polymer admixed in minor proportion with the colloid, or

3 ionic groups in non-polymeric compounds admixed with a colloid.

A wide variety of protective colloids can be used as vehicles for the mordanting compounds. Suitable protective colloids such as hydrophilic polymers as gelatin and its water soluble derivatives; other proteinaceous materials which are water permeable, such as polyvinyl alcohol and its water soluble derivatives including copolymers thereof; water soluble vinyl polymers such as polyacrylamide, imidized polyacrylamide, etc.; colloidal albumin; water soluble cellulose derivatives cellulose acetate; and related water soluble film-forming hydrophilic polymers that form water permeable coatings. If the organic acidic mordanting composition is a hydrophilic organic colloid, an excess of this material over that utilized to form a salt with the dyes can be used as a protective colloid for the dispersed salt. Mixtures of two or more colloids can be utilized. Gelatin is a preferred colloid.

In one embodiment a mordant salt is uniformly dispersed in a hydrophilic polymer as finely divided particles that are generally less than about 30 microns in diameter and preferably less than about 10 microns in diameter.

In another embodiment, the mordanting compound is dispersed in a suitable solvent. Typical low boiling or water soluble organic solvents that can be utilized in preparing a mordant dispersion include:

1. substantially water insoluble low boiling solvents such as ethyl and butyl acetates, ethyl propionate, butyl alcohol, ethyl formate, nitroethane, chloroform, etc.

2. water soluble solvents such as methyl isobutyl ketone, β-ethoxy ethyl acetate, β-butoxy-β-ethoxy ethyl acetate, tetrahydrofurfuryl adipate, diethylene glycol monoacetate, β-methoxymethyl acetate, acetonyl acetone, diacetone alcohol, diethylene glycol monomethyl ether, ethylene glycol, dipropylene glycol, acetone, ethanol, acetonitrile, dimethylformamide, dioxane, etc.

The low-boiling or water-soluble solvent can be removed from the dispersion, for example, by air drying a chilled, noodled dispersion, or by continuous water washing.

Likewise, high-boiling, water-immiscible, organic liquids having a boiling point above about 175°C. can be utilized in the mordant dispersion system. Any of the high-boiling, water-immiscible solvents described on page 2, column 2, and page 3, column 1, of U.S. Pat. No. 2,322,027 issued June 15, 1943 can be used. Particularly useful solvents are organic carboxylic acid esters and organic phosphate esters. Typical solvents include di-n-butyl-phthalate, benzyl phthalate, ethyl benzyl malonate, tetrahydrofurfuryl succinate, triphenyl phosphate, tri-o-cresyl phosphate, diphenyl mono-p-tert-butylphenyl phosphate, monophenyl di-o-chlorophenyl phosphate, tri-p-tert-butylphenyl phosphate, 2,4-di-n-amylphenol, and the like.

Precipitating agents which are particularly useful for use in the receiving sheet for use in a black and white diffusion tranfer process include nuclei which are useful as precipitating agents with a silver halide complex, including all of those which are commonly useful in the diffusion tranfer process. The particular nuclei employed include silver precipitating agents known in the art such as sulfides, selenides, polysulfides, polyselenides, heavy metals, thiourea, stannous halides, heavy metal salts, fogged silver halide, Carey Lea silver, and complex salts of heavy metals with a compound such as thioacetamide, dithiooxamide and dithiobiuret. As examples of suitable silver precipitating agents and of image-receiving elements containing such silver precipitating agents, reference may be made to U.S. Pat. Nos. 2,698,237, 2,698,238 and 2,698,245 issued to Edwin H. Land on Dec. 28, 1954, U.S. Pat. No. 2,774,667 issued to Edwin H. Land and Meroe M. Morse on Dec. 18, 1956, U.S. Pat. No. 2,823,122 issued to Edwin H. Land on Feb. 11, 1958, U.S. Pat. No. 3,396,018 issued to Beavers et al. Aug. 6, 1968 and also U.S. Pat. No. 3,369,901 issued to Fogg et al. Feb. 20, 1968. The noble metals, silver, gold, platinum, palladium, etc., in the colloidal form are particularly useful.

Noble metal nuclei are particularly active and useful when formed by reducing a noble metal salt using a borohydride or hypophosphite in the presence of a colloid as described in Rasch U.S. Pat. No. 3,647,440, issued Mar. 7, 1972. The metal nuclei are prepared in the presence of a proteinaceous colloid such as gelatin and coated on the receiving sheet. The same or a different colloid may be added if desired. It will be appreciated that the coating composition generally contains not only nuclei, but also reaction products which are obtained from reducing the metal salt. Accordingly, it is within the scope of our invention to include in the receiving layer the reaction by-products which are obtained during the reducing operation.

The amount of colloid used in preparing the above active noble metal nuclei can be varied depending upon the particular colloid, reducing agent, ratio of proportions, etc. Typically about 0.5 percent to about 20 percent by weight based on the total reaction mixture of colloid is used, preferably from about 1 percent to about 10 percent.

In a particularly useful embodiment, 30 to 80 micrograms per square foot of active palladium nuclei in 80 mg. of colloid (solids basis) is coated per square foot of support. Suitable concentrations on the receiving sheets of active noble metal nuclei as disclosed above can be about 1 to about 500 micrograms per square foot. Other silver precipitants can be coated in a concentration of up to 5 mg/ft^2.

Various colloids can be used as dispersing agents or as binders for the precipitating agents in the receiving layer. Any suitable colloids can be used. Particularly useful colloids are hydrophilic colloids which are used for binders in silver halide emulsions. Advantageously, they are coated in a range of about 5–5000 mg/ft^2. Included among suitable colloids are gelatin, preferably coated at a level in the range of about 7–100 mg/ft^2, polymeric latices such as copoly(2-chloroethylmethacrylate-acrylic acid) preferably coated in the range of 15–350 mg/ft^2 in a polymeric vehicle containing two components (1) polyvinyl alcohol, and (2) interpolymer of n-butylacrylate, 3-acryloyloxypropane-1-sulfonic acid, sodium salt and 2-aceto-acetoxyethyl methacrylate, in a preferred range of about 10–300 mg/ft^2.

It will also be appreciated that the precipitating agents can be formed in situ or can be applied by precipitating or evaporating a suitable precipitating agent on the surface.

Toning agents are generally present during the diffusion transfer step. For example, various toning agents can be in the processing solution or even, in some instances, contained in the silver halide emulsion. Toning agents which can be included for improving the tone of the image to make the tone blacker or more blue-black include sulfur compounds such as 2-mercaptothiazoline, 2-amino-5-mercapto-1,3,4-thiadiazole, 2-thionoimidazolidene, 2-mercapto-5-methyloxazoline and 2-thiono-imidazoline. It will be appreciated that these toners can be used either alone or in conjunction with other toning agents. They are particularly useful in a range of 0.01 to 3.0 mg/ft^2 either in the receiving layer or coated in a layer on top of the image layer. Other toning agents which may be used include seleno tetrazoles, the 5-mercaptotetrazoles of Abbott et al, U.S. Pat. No. 3,295,971 and Weyde, U.S. Pat. No. 2,699,393. Still other toning agents are disclosed in Tregillus et al. U.S. Pat. No. 3,017,270.

The receiving layers of our invention may also have therein particles such as silica, bentonite, diatomaceous earth such as kieselguhr, powdered glass and fuller's earth. In addition, colloids and colloidal particles of metal oxides such as titanium dioxide, colloidal alumina, coarse aluminum oxide, zirconium oxide and the like may be used with the nuclei in the receiving layers.

In carrying out the diffusion transfer process, conventionally a silver halide emulsion is exposed to a light image after which it is contacted with a silver halide developing agent containing a silver halide complexing agent. The exposed emulsion is developed in the light struck areas and the unexposed silver halide is complexed with the silver halide complexing agent after which the emulsion is contacted against a receiving sheet and the complex silver halide diffuses imagewise to the receiving sheet containing a silver precipitant.

Silver halide developing agents used for initiating development of the exposed sensitive element can be conventional types used for developing films or papers with the exception that a silver halide solvent or complexing agent such as sodium thiosulfate, sodium thiocyanate, ammonia or the like is present in the quantity required to form a soluble silver complex which diffuses imagewise to the receiving support. Usually, the concentration of developing agent and/or developing agent precursor employed is about 3 to about 320 mg/ft^2 of support.

Developing agents and/or developing agent precursors can be employed in a viscous processing composition containing a thickener such as carboxymethyl cellulose or hydroxyethyl cellulose. A typical developer composition is disclosed in U.S. Pat. No. 3,120,795 of Land et al. issued Feb. 11, 1964.

Developing agents and/or developing agent precursors can be employed alone or in combination with each other, as well as with auxiliary developing agents. Suitable silver halide developing agents and developing agent precursors which can be employed include, for example, polyhydroxybenzenes, alkyl substituted hydroquinones, as exemplified by t-butyl hydroquinone, methyl hydroquinone and 2,5-dimethylhydroquinone, catechol and pyrogallol; chloro substituted hydroquinones such as chlorohydroquinone or dichlorohydroquinone; alkoxy substituted hydroquinones such as methoxy hydroquinone or ethoxy hydroquinone; aminophenol developing agents such as 2,4-diaminophenols and methylaminophenols. These include, for example, 2,4-diaminophenol developing agents which contain a group in the 6 position, and related amino developing agents, e.g.:

6-methyl-2,4-diaminophenol
6-methoxy-2,4-diaminophenol
6-ethyl-2,4-diaminophenol
6-phenyl-2,4-diaminophenol
6-para tolyl-2,4-diaminophenol
6-chloro-2,4-diaminophenol
6-morpholinomethyl-2,4-diaminophenol
6-piperidino-2,4-diaminophenol 3,6-dimethyl-2,4-diaminophenol
6-phenoxy-2,4-diaminophenol
2-methoxy-4-amino-5-methyl phenol
4-aminocatechol
4-aminoresorcinol
2,4-diaminoresorcinol
methyl-3,4-diaminophenol
methoxy-3,4-diaminophenol
methyl-2,5-diaminophenol
methoxy-2,5-diaminophenol
methyl-1,2,4-triamino benzene
methoxy-1,2,4-triamino benzene
p-hydroxyphenyl hydrazine
p-hydroxyphenyl hydroxylamine

The aminophenol developing agents can be employed as an acid salt, such as a hydrochloride or sulfate salt.

Other silver halide developing agents include ascorbic acid, ascorbic acid derivatives, ascorbic acid ketals, such as those described in U.S. Pat. No. 3,337,342 of Green issued Aug. 22, 1967; hydroxylamines such as N,N-di(2-ethoxyethyl)-hydroxylamine; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone, including those described in Kodak British Pat. No. 930,572 published July 3, 1963; and acyl derivatives of p-aminophenol such as described in Kodak British Pat. No. 1,045,303 published Oct. 12, 1966; pyrimidine developing agents, such as 4-amino-5,6-dihydroxy-2-methyl pyrimidine; and aminomethyl hydroquinone silver halide developing agents, such as 2-methyl-5-pyrrolidinomethyl hydroquinone, 2-methyl-5-morpholinomethyl hydroquinone, and 2-methyl-5-piperidinomethyl hydroquinone. The aminomethyl hydroquinone silver halide developing agents are especially suitable incorporated in the negative photographic element.

Another suitable silver halide developing agent which can be used in the practice of the invention is a reductone silver halide developing agent, especially an anhydro dihydro amino hexose reductone silver halide developing agent, such as

anhydro dihydro piperidino hexose reductone,
anhydro dihydro pyrrolidino hexose reductone, and/or
anhydro dihydro morpholino hexose reductone.

The described reductone silver halide developing agents can be prepared as described in U.S. Pat. No. 2,936,308 of Hodge, issued May 10, 1960 and in an article by F. Weygand et al., *Tetrahedron*, Volume 6, pages 123—138 (1959). Typically the described anhydro dihydro amino hexose reductone compounds are prepared from the corresponding anhydro amino hexose reductones by hydrogenation in the presence of a suitable hydrogenation catalyst, such as Raney nickel catalyst. The reductone silver halide developing agent can be employed in various locations in the diffusion transfer system, but is especially suitable in the processing composition. These can be used alone or in combinations of developing agents. These developing agents provide little or no stain and improved stability.

Lactone derivative silver halide developing agents which have the property of forming a lactone silver halide developing agent precursor under neutral and acid conditions are particularly useful. Typical lactone derivatives are described in Oftendahl U.S. Pats., No. 3,615,521, issued Oct. 26, 1971 and U.S. Pat. No. 3,615,439, issued Oct. 26, 1971. The particularly suitable lactone derivatives provide desired developing activity and reduction of stain without adversely affecting desired maximum density, minimum density, photographic speed and other desired sensitometric properties. Suitable lactone derivative developing agents include those which under neutral, slightly alkaline or acid conditions, i.e., when the pH is lowered to a level of about 9 or lower, i.e., about 2 to about 9, do not have significant developing activity, if any, due to formation of a developing agent precursor.

Silver halide emulsions employed with receiving layers and elements of this invention can contain incorporated addenda, including chemical sensitizing and spectral sensitizing agents, coating agents, antifoggants and the like. They can also contain processing agents such as silver halide developing agents and/or developing agent precursors. Of course, the processing agents can be incorporated in a layer adjacent to the silver halide emulsion if desired.

The photographic emulsions employed can also be x-ray or other non-spectrally sensitized emulsions or they can contain spectral sensitizing dyes such as described in U.S. Pat. No. 2,526,632 of Brooker et al. issued Oct. 24, 1950 and U.S. Pat. No. 2,503,776 of Sprague issued Apr. 11, 1950. Spectral sensitizers which can be used include cyanines, merocyanines, styryls and hemicyanines.

The photographic emulsions can contain various photographic addenda, particularly those known to be beneficial in photographic compositions. Various addenda and concentrations to be employed can be determined by those skilled in the art. Suitable photographic addenda include hardeners, e.g., those set forth in British Pat. No. 974,317; buffers which maintain the desired developing activity and/or pH level; coating aids; plasticizers, speed increasing addenda, such as amines, quaternary ammonium salts, sulfonium salts and alkylene oxide polymers; and various stabilizing agents, such as sodium sulfite. The photographic silver salt emulsions can be chemically sensitized with compounds of the sulfur group such as sulfur, selenium and tellurium sensitizers, noble metal salts such as gold, or reduction sensitized with reducing agents or combinations of such materials.

Various photographic silver salts can be used in the practice of the invention. These include photographic silver halides such as silver iodide, silver bromide, silver chloride, as well as mixed halides such as silver bromoiodide, silver chloroiodide, silver chlorobromide and silver bromochloroiodide. Photographic silver salts which are not silver halides can also be employed such as silver salts of certain organic acids silver-dye salts or complexes, etc.

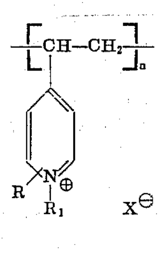
The photographic silver salts are typically contained in an emulsion layer comprising any binding materials suitable for photographic purposes. These include natural and synthetic binding materials generally employed for this purpose, for example gelatin, colloidal albumin, water-soluble vinyl polymers, mono and polysaccharides, cellulose derivatives, proteins, water-soluble polyacrylamides, polyvinyl pyrrolidone and the like, as well as mixtures of such binding agents. The elements can also contain releasing layers and/or antistatic layers (i.e., conducting layers).

Stripping agents can be used either on the surface of the silver halide emulsion layer, on the receiving layer containing the nuclei, or can be contained in the developing or processing solutions. When added to the processing solution in concentrations of about 3 to about 10 percent by weight, the stripping agents prevent the processing solution from sticking to the receiver. Suitable stripping agents normally are used which have a composition different from the binder used in the silver halide emulsion. Typical stripping agents include alkali permeable polysaccharides such as, for example, carboxymethyl cellulose or hydroxyethyl cellulose, 4,4'-dihydroxybiphenol, glucose, sucrose, sorbitol (hexahydric alcohol $C_6H_8(OH)_6$), inositol (hexahydroxycyclohexane $C_6H_6(OH)_6 \cdot 2H_2O$), resorcinol, phytic acid sodium salt, thixcin (a castor bean product), zinc oxide, and finely divided polyethylene. These coatings are relatively thin having a preferred coverage of about 6.0 mg/ft^2. However, a useful range may be from 1.0 mg. to 1.0 g/ft^2.

Release agents can be used either on the surface of the silver halide emulsion layer, on the receiving layer containing the nuclei, or can be contained in the developing or processing solutions. In a typical integral element, a silver halide emulsion is coated over the receiving layer. Particularly useful emulsions are described in Yackel et al. U.S. Pat. No. 3,020,155. The exposed photographic element is processed using a silver halide developing solution containing a silver halide solvent such as sodium thiosulfate. The undeveloped silver halide, complexed with thiosulfate, diffuses to the nucleated underlayer where an image is formed in the nucleated layer. The unhardened silver halide emulsion is then removed by washing with warm water. In other integral elements, the image may be viewed through the base without removing the emulsion layer.

In the event that a proteinaceous binder is employed with a silver precipitating agent, gelatin is preferred, but other proteins such as casein, zein, albumin, etc., may be used. However, any suitable colloid or colloids may be used, including both water-soluble polymers and water-insoluble polymers. A latex or hydrosol may advantageously be employed if the polymer is insoluble in water. Polymers which are particularly useful are water soluble polyvinyl quaternary salts, as described in VanHoff et al. U.S. Pat. No. 3,174,858 issued Mar. 23, 1965. These water soluble basic polymeric quaternary salts have a polyvinyl chain having 2 to 10,000 monomeric units, each monomeric unit of which is linked directly to a five or six membered heterocyclic nucleus containing as heteroatoms only nitrogen atoms, one of which hetero-nitrogen atoms being a quaternary nitrogen atom.

In one embodiment, the polymer has the following structure:



in which n is an integer from 2 to 10,000 and X is any suitable anion such as $CH_3SO_4^{\ominus}$, para toluene sulfonate $\ominus$, iodide, etc. R represents H, an alkyl group having one to 10 carbon atoms such as, for example, methyl, ethyl, propyl, butyl, etc., halogen, NO_2, NH_2, aralkyl, aryl, etc. R_1 is selected from the same group as R, but can be a different group than R. It will be appreciated, of course, that the heterocyclic nucleus can contain additional nitrogen atoms and that the ring may be substituted with other groups. The substituents can be the same or different.

Typical polymeric materials include poly(1,2-dimethyl-5-vinylpyridinium methylsulfate), poly(1,4-vinylpyridinium methylsulfate), poly(1-methyl-2-vinylpyridinium iodide), poly(1-methyl-2-vinylpyridinium methylsulfate), poly(1-methyl-4-vinylpyridinium iodide), poly(1-methyl-4-vinylpyridinium methylsulfate), poly(1-vinyl-3-methyl imidazolium iodide) and poly(1-vinyl-3-methyl imidazolium methylsulfate).

In a particularly useful coating composition is employed from 0.1 to 80 mg/ft², preferably 0.2 to about 5 mg/ft². In a typical embodiment, 30 mg. of the polyvinyl polymer are used for 1 g. of gel in the receiving layer.

An alkali or alkali metal iodide such as, e.g., ammonium, sodium, potassium, lithium iodide, etc., can be present in the receiver in an amount of about 0.1 to about 20 mg/ft², preferably 0.5 to about 10 mg/ft². An improvement in cold tone in certain receiving layers which is obtained as a result of iodide is particularly unexpected, since potassium iodide contained in the processing solution in an amount of about 1.6 g. of potassium iodide per liter and which is coated at a coverage of about 3.5 ml/ft² fails to give a satisfactory tone. Also, iodide present in the negative in an amount of about 10 mg/ft², also fails to have an effect on the tone.

The addition of a silver salt or complex such as, e.g., silver nitrate, to certain receiving sheets further improves the tone as does the addition of diffusion transfer toners. Any silver salt or complex can be used, including both organic and inorganic silver compounds. A typical organic silver complex is, for example, silver dipyridyl nitrate. Other silver salts and complexes which are included are described in Gilman et al., U.S. Pat. No. 3,446,619. Still other silver salts of mercaptotetrazoles and mercaptotriazoles and related heterocyclic mercapto compounds are described in U.S. Pat. No. 2,432,864. However, silver nitrate is preferred. The silver compound can be used in an amount of about 0.01 to about 10 mg/ft², preferably 0.05 to about 5 mg/ft².

Various toners can be used by incorporating the toner in the receiver sheet. Particularly useful toners are those disclosed for use with certain quaternary salts in Tregillus and Rasch U.S. Pat. No. 3,017,270 issued Jan. 16, 1962.

In a preferred embodiment, the toner used is a seleno tetrazole, including seleno tetrazoles substituted by aliphatic residues, as for example, 1-allyl-5-seleno-1,2,3,4-tetrazole, seleno tetrazoles substituted by aromatic or heterocyclic residues having 1–12 carbon atoms, as for example, 1-phenyl-5-seleno-1,2,3,4-tetrazole, etc. The toners can be used in the amount of about 0.005 to about 5.0 mg/ft², preferably 0.01 to about 1 mg/ft². These toners may be contained in a developer or activator solution. A particularly useful combination employs phenyl mercaptotetrazole and potassium iodide in a developer or activator solution.

Coating solutions which contain addenda other than a silver precipitant are also useful in preparing receiving layers. In addition to various components contained in the coating composition according to this invention, toners, surfactants, coating aids, developing agents, silver halide solvents, etc., may be added to improve the image quality in the receiving sheet.

Particularly useful surfactants and spreading agents in receiver coatings include saponin, lauryl alcohol sulfate, p-tert octyl phenoxy ethoxy ethyl sodium sulfonate, etc.

Developers, which can be used in a solvent transfer system such as described in U.S. Pat. No. 2,543,181 of Land issued Feb. 27, 1951, can contain release agents. When added to the developer in concentrations of about 3 to about 10 percent by weight, the release agents aid in preventing the developer from sticking to the receiver. Suitable release agents include, for example:

4,4′-dihydroxybiphenyl
glucose
sucrose
sorbitol (hexahydric alcohol $C_6H_8(OH)_6$)
inositol (hexahydroxy-cyclohexane $C_6H_6(OH)_6 \cdot 2H_2O$)
resorcinol
phytic acid sodium salt
thixcin (a castor bean product)
zinc oxide, and
finely divided polyethylene.

It will also be appreciated that a lithographic printing plate can be prepared using the photographic element of this invention. After the image is formed in the receiving layer, it can be treated by methods known in the art such as by treatment with a thiol or similar sulfur containing compound in order to improve the ink-water differential between the image areas and the non-image areas of the receiving layer. Subsequently, the element can be used as a printing plate by wetting and inking in the typical lithographic process.

In the attached drawing is given a structural configuration of the layers employed in a preferred structure for the receiving sheet of this invention.

FIG. **1** illustrates a black-and-white receiving sheet in which paper stock **3** has coatings **2** and **1** of black polyethylene **2** and white polyethylene **1** respectively on the back side of the paper **3**. On the face side of paper stock **3** are coated a baryta layer **4** and over the baryta layer a layer of clear polyethylene **5**. The clear polyethylene **5** is subbed with a gelatin-cellulose nitrate subbing **6** over which is coated a layer **7** of cellulose triacetate plus a brightener. On this layer **7** is solvent coated a gelatin subbing **8**.

Over the gelatin subbing layer **8** is coated a polyacrylic acid layer **9** and a cellulose acetate layer **10**, a gelatin subbing **11** and a gelatin nuclei layer **12**.

In FIG. **2**, the structure is the same as FIG. **1** except that a gelatin mordant layer **13** is coated as the top layer instead of gelatin nuclei layer **12**.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

Receiving elements are prepared having a nucleated layer comprising a gelatin binder containing finely divided palladium nuclei. In each instance, white polyethylene coated papers are employed in which the polyethylene surface has been electron bombarded to a contact angle below 70° measured with water to improve the adhesion. Over the polyethylene surfaces are coated in order, a gelatin cellulose nitrate subbing, a cellulose triacetate layer containing a brightener and a gelatin sub. A control receiving sheet A has the nucleated layer coated directly on the gelatin sub. Receiving sheet B has a polyacrylic acid layer coated over the gelatin sub and has a gelatin nuclei layer coated directly on a polyacrylic acid layer. The remaining receiving sheets C–H are prepared with various concentrations of polyacrylic acid coated over the gelatin sub and have a cellulose acetate layer coated over the polyacrylic acid, a gelatin sub coated over the cellulose acetate layer and finally a gelatin nucleated layer. The concentrations of polyacrylic acid and cellulose acetate are listed in the table below.

All the receiving sheets are tested by placing them in contact with an imagewise exposed silver bromoiodide emulsion coated on a paper base with an image obtained by means of rupture of a pod containing a viscous developer solution having the following formulation:

Potassium sulfite	50.0 g
Sodium thiosulfate pentahydrate	40.0 g
Potassium iodide	1.6 g
Potassium hydroxide	16.7 g
Sodium hydroxide	17.5 g
Anhydro dihydro piperidino hexose reductone	5.0 g
Hydroxy ethyl cellulose (Natrosol 250H, a trade name for hydroxy ethyl cellulose sold by the Hercules Powder Co., U.S.A.)	30.0 g
Water	to 1 liter

After 30 seconds contact, the receiving sheet and negative are separated. The resulting receiving sheets containing the transferred image are then cut in half lengthwise with one half kept as the control and the other half subjected to air containing 10 parts per million of H_2S at 80 percent RH for four hours with the following results.

	Poly-acrylic acid (mg./ft. ²)	Cell-ulose acetate (mg./ft. ²)	Control			H_2S test		
			$D_{max.}$	$D_{min.}$	Tone	$D_{max.}$	$D_{min.}$	Tone
A			1.36	0	Black	0.74	.03	Yellow-brown.
B	300		(*)			(*)		
C	75	60	1.37	0	Black	1.37	0	Black.
D	150	120	1.44	0	do	1.37	0	Do.
E	150	60	1.37	0	do	1.38	0	Do.
F	150	30	1.44	0	do	1.40	.03	Do.
G	300	120	1.12	0	do	1.35	0	Do.
H	300	60	1.40	0	do	1.40	0	Do.

*No image.

These results show the degradation of the image by H_2S without a polymeric acid layer present in the receiving sheet, and the stabilization of the images when a polymeric acid layer is present. However, as shown by the D_{max} and D_{min} values for the H_2S test, the alkali-permeable timing layer must also be present for the production of good images.

EXAMPLE 2

Receiving sheets with and without a polyacrylic acid layer and timing layer are prepared according to the procedure and layer configuration of Example 1. The tests in the following table are made on the receiving sheets after they have been placed in contact with an imagewise exposed silver bromoiodide emulsion coated on a paper base. The transferred images are obtained by means of rupture of a pod containing a viscous developer solution having the approximate formulation of that in Example 1 above.

Poly-acrylic Acid (mg/ft²)	Cellulose Acetate Timing Layer (mg/ft²)	Scratch Print Resistance[1]	Stain[2]	Print Stability	
				Density Loss[3]	H_2S[4]
None	None	310	+1.7	-0.20	poor (yellow brown image tone)
300	80	420	-3.3	-0.05	very good (black image)

[1] Scratch resistance of the nucleated surface is measured on processed samples using a Taber Scratch Tester Model 503. This instrument applies an adjustable load to a 15-mil. radius sapphire stylus which is placed on the material to be tested. The material is moved beneath the loaded stylus at a constant speed and the load is adjusted until the stylus scratches through the nucleated coating to the substrate. This point is visually observed by noting when the white substrate is apparent in the scratched area. Testing is carried out within about 2 minutes after the receiver and negative are stripped apart after processing. Values given in the table are the weight in grams necessary to scratch the sample.

[2] Print stain is measured after keeping the processed print in roomlight for 1 day. The values recorded above determine the change in image tone. A positive value indicates a yellow stain in the minimum density area of the print, while a negative value indicates a more pleasing blue cast to the print.

[3] Print stability is determined after keeping the processed print in the dark for 7 days at 100°F/94% R.H. The density loss on keeping is expressed as a log E shift at 0.6 density above fog.

[4] Print stability to sulfide is evaluated after subjecting the samples to air containing 1 part per million of hydrogen sulfide at 75–80 percent relative humidity for 4 hours.

EXAMPLE 3

Receiving elements are prepared having a nucleating layer containing finely divided palladium nuclei. In each instance, white polyethylene coated papers are employed in which the polyethylene surface has been electron bombarded to a contact angle below 70° measured with water to improve the adhesion. Following the electron bombarment of the polyethylene face coat, the following acid layers are employed in an amount of about 7 g/m².

ACID LAYER

1. Blend of approximately equal amounts of polyvinyl alcohol and polyacrylic acid,
2. Copolymer of ethylmethacrylate and methacrylic acid,
3. Copolymer of methylmethacrylate and methacrylic acid,
4. Methyl vinyl ether maleic anhydride,
5. Styrene maleic anhydride.

A thin layer of cellulose acetate having a thickness of about 0.7 g/m² followed by a gelatin-cellulose nitrate sub in an amount of about 0.3 g/m² is then coated. A gelatin nucleation layer is applied over the gelatin-cellulose nitrate sub. The products are tested as in Example 1 and show good results with both the H_2S test and abrasion test.

EXAMPLE 4

A receiving sheet for use in obtaining an image by the dye diffusion transfer process is prepared as in Example 1 except that a dispersion containing a dye mordanting composition comprising octadecyl tri-n-butyl ammonium bromide as described in Example 1 of U.S. Pat. No. 3,271,147 is coated in place of the nuclei layer. The receiving sheet used in the image transfer color process as is described in Example 6 of U.S. Pat. No. 3,271,147. Subsequent testing for abrasion indicates that the abrasion values are at least 500 when tested as described in Example 2. Stain levels are satisfactory as measured in the D_{min} areas following incubation and light exposure.

The use of other mordant compounds as described in the above patent also result in satisfactory receiving sheets.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A receiving element for use in a diffusion transfer process comprising a polyolefin surface having thereon a cellulose ester layer, over said ester layer a polyacrylic acid layer and next a timing layer comprising a cellulose ester of a monocarboxylic acid, and over said timing layer an image receiving layer comprising silver precipitating nuclei.

2. An element of claim 1 in which said image receiving layer comprises gelatin.

3. An element of claim 1 in which said image receiving layer comprises polyvinyl alcohol.

4. An element of claim 1 in which said image receiving layer contains palladium nuclei.

5. An element of claim 1 in which said polyolefin is coated on a paper support having on a back side of said support a layer of black polyethylene and superimposed over the black polyethylene a layer of white polyethylene.

6. An element of claim 1 in which said acid layer comprises at least sufficient acid groups to effect a reduction in the pH of said image layer from a pH of 13 to a pH of at least 11 at the end of an imbibition period of about 60 seconds.

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