July 17, 1973 T. F. PARSONS 3,746,564

PHOTOGRAPHIC DIFFUSION TRANSFER PRODUCT AND PROCESS

Filed Nov. 19, 1970

FIG. 1

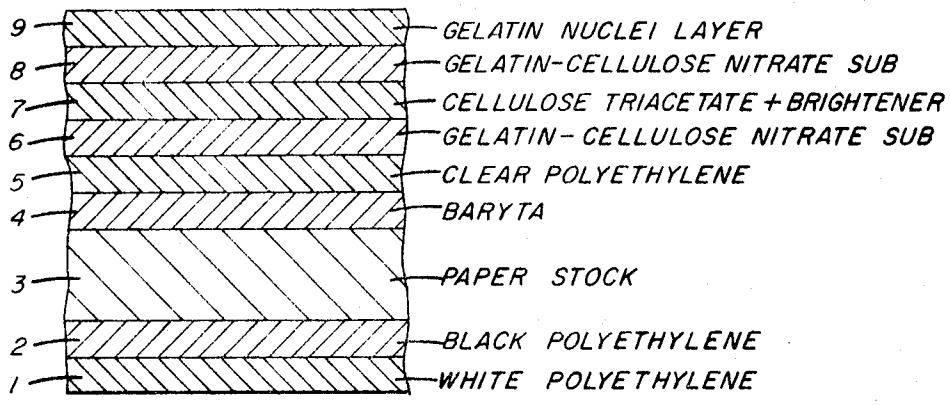
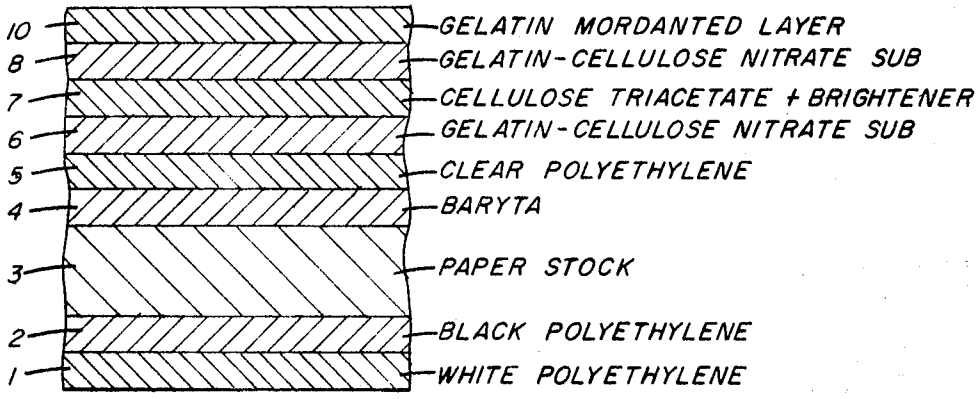


FIG. 2



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3,746,564

PHOTOGRAPHIC DIFFUSION TRANSFER PRODUCT AND PROCESS

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U.S. Cl. 117—68 7 Claims

ABSTRACT OF THE DISCLOSURE

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 and over which is then coated 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.

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 adhesion of image receiving layers.

Diffusion transfer processes are well known. For example, Rott U.S. Pat. 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 layer 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 as viscous film-forming agent having 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. Patent 3,445,228 issued May 20, 1969, Bush U.S. Patent 3,271,147 issued Sept. 6, 1966, Whitmore U.S. Patent 3,227,552 and Whitmore et al. U.S. Patent 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.

Therefore, 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 these 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 resistance to abrasion even though adhesion is good.

SUMMARY OF THE INVENTION

In accordance with this invention it has been found that a receiving element for use in a black and white or color diffusion transfer process comprises a polyolefin surface such as polyethylene having thereon a cellulose ester layer over which is coated 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.

In a preferred embodiment for use in a silver diffusion transfer process, a polyethylene surface is electron bombarded to improve adhesion and coated with a gelatin-cellulose nitrate subbing. 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 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 as 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 a support is employed, paper is preferred and can be any of the conventional cellulose supports including those prepared from cotton, linen, and wood (sulfate and sulfite pulped) and which supports are typically about 5–60 pounds per 1000 square foot papers.

The polymeric material which forms the surface for the receiving sheet of this invention can be coated over any support, typically in a thickness of about .3 to 5 mils. For instance, particularly useful materials include the polyolefins prepared from the alpa-olefins having 2–10 carbon atoms and blends of these polyolefins as well as copolymers. 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 thickness.

In some instances it is desirable to incorporate in the polymeric material 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%, preferably 10–15% by weight of the resin. Other pigments or dyes which may be useful include

those commonly known 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 treatments with a flame, use of an oxidizing agent such as nitric acid, sodium hypochlorate, chlorine, hydrogen peroxide, sulfuric acid and potassium chromate, etc., electron bombardment, radiation by ultraviolet light, etc.

Electron bombardment of polymeric surfaces is conveniently carried out by means of a corona discharge. Variations in electrical conditions may be used with respect to frequency, voltage, number of electrodes, spacing between the discharge gap, medium used in the discharge gap, such as an inert gas, ozone, etc. Apparatus disclosed in Rothacker patents, U.S. 2,864,755 and 2,864,-756, can be utilized. 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 where 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. 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 patent specification 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. 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 particular 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. Pats. 2,492,977 and 2,492,-978 issued Jan. 3, 1950, Fordyce et al. U.S. Pat. 2,739,-070 issued Mar. 20, 1965, and Fordyce et al. U.S. Pat. 2,607,704 issued Aug. 19, 1952.

For some purposes, a subbing can be used such as a gelatin-nitrate subbing. The gelatin nitrate sub is particularly useful when coating a gelatin coating on the surface of a plastic overcoat such as a cellulose ester. Typical coatings are disclosed in the Nadeau et al. U.S. Pat. 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.

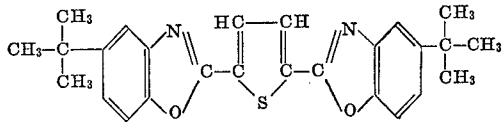
Subbing compositions which can be used on polyethylene to adhere to the cellulose ester coating do not require any gelatin but can include a wide variety of materials provided that one of the solid components is soluble in a solvent for the particular cellulose ester. Any of the subbing compositions mentioned above can be used either admixed with gelatin or by themselves. It will be appreciated that any subbing mixture can be used having good adhesion properties including those known for use in adhering silver halide emulsions to cellulose ester supports or those adhering silver halide emulsions to polyester supports, and the like. Typical coatings are described in Secrist U.S. Patents 3,212,897 issued Oct. 19, 1965 and 3,320,191 issued May 16, 1967. The subbing which can be employed to improve the adhesion of the cellulose ester layer to the polyolefin surface can perform an important function in the invention. It should be of sufficient strength and hardness and sufficiently adherent to the adjacent surfaces to bond the cellulose ester layer firmly to the polyethylene.

A sub of gelatin-cellulose nitrate mixture within relatively narrow limits can be used. The subbing layer, preferably contains between about 0.005 and 0.020 g. of solids per square foot, equivalent to 30 to 80 weight percent solids of gelatin and 70 to 20 weight percent solids of cellulose nitrate. The solvent used for applying the subbing layers should comprise a miscible mixture of solids for both components, preferably a mixture of acetone, methanol and water. In a particularly useful embodiment of this subbing, a solution containing 25 percent cellulose nitrate and 75 percent gelatin is coated at 0.012 g. per

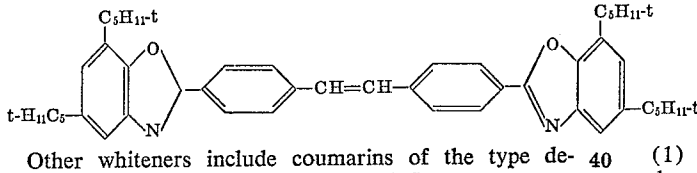
square foot using an acetone-methanol water solvent. The cellulose nitrate gelatin subbing can be prepared by blending cellulose nitrate resin with gelatin using water and one or more solvents such as methyl ethyl ketone, acetone, ethylene dichloride, ethyleneglycol monomethylether, etc. In another embodiment, a gelatin subbing can be employed by preparing the subbing with water and one or more solvents such as acetone, ethylene dichloride, ethyleneglycol monomethylether, etc. Still another subbing is made by blending a resin such as a polyacrylate, a carboxylated polyester, or a copolymer of 2-chloroethyl acrylate, vinylidene chloride and acrylic acid with gelatin and suitable solvents.

The cellulose ester can be applied as a solvent coating so that it provides a cellulose ester layer having a thickness of about .1 to .4 mil or a coverage of 2.5 g./m.^{2} to 10 g./m.^{2}. The cellulose ester can contain addenda such as a pigment or a brightener, dyes, plasticizers, etc.

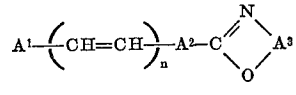
The brighteners which can be incorporated in the cellulose ester coating in any suitable concentrations, particularly good results being obtained at concentrations at about 0.01 to about 1.0 percent by weight of a whitening or brightening agent. For example, 4-4′-bis(benzoxazol-2-yl)stilbene compounds are especially useful. Other compounds which are useful include the following structure and described in Belgian Patent 612,775:



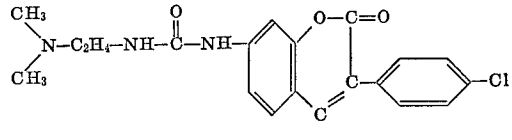
and 4,4′-bis(5,7-di-t-amylbenzoxazol-2-yl)stilbene



Other whiteners include coumarins of the type described in British Patent 786,234 and fluorescent compounds of the formula:



in which A^1 is a 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 U.S. application Ser. No. 229,162 filed Aug. 1, 1963, now abandoned. 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.

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. Patent No. 3,271,147, and Cohen et al. Belgian Patent No. 729,202.

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 such as ethanolamine and 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. Patent 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-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 transfer 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 transfer 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. 2,698,237, 2,698,238 and 2,698,245 issued to Edwin H. Land on Dec. 28, 1954, U.S. Pat. 2,774,667 issued to Edwin H. Land and Meroe M. Morse on Dec. 18, 1956, U.S. Pat. 2,823,122 issued to Edwin H. Land on Feb. 11, 1958, U.S. Pat. 3,396,018 issued to Beavers et al. Aug. 6, 1968, and also U.S. Pat. 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. patent application Ser. No. 796,552, filed Feb. 4, 1969, now Patent No. 3,647,440, patented 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% to about 20% by weight based on the total reaction mixture of colloid is used, preferably from about 1% to about 10%.

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-chloroethyl-methacrylate-acrylic acid) preferably coated in the range of 15–350 mg./ft.^{2}, a polymeric vehicle containing two components (1) polyvinyl alcohol, and (2) interpolymer of n-butylacrylate, 2-acryloyloxypropane-1-sulfonic acid, sodium salt and 2-acetoacetoxyethyl 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-thiononimidazolidene, 2-mercapto-5-methyloxazoline and 2-thionoimidazoline. 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. 3,295,971 and Weyde, U.S. Pat. 2,699,393. Still other toning agents are disclosed in Tregillus et al. U.S. Pat. 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.

In some instances it may be desirable to treat the receiving sheet in order to improve the stability of the sheet, particularly with regard to the silver image thereon. A simple stabilizing method merely involves washing the print in order to remove any processing chemicals which may remain thereon. However, the washing step does not protect the print from subsequent chemical reactions with oxygen, hydrogen sulfide, etc., in the atmosphere, which have an adverse effect on the stability of the silver image. For these reasons, it has been proposed to coat the print with a coating composition such as that disclosed in U.S. Patent 2,979,477 comprising a mixture of vinylpyridine polymer and a hydantoin-formaldehyde condensation polymer.

Suitable print coating compositions may also employ a polymeric material such as a methylmethacrylate-methacrylic acid copolymer or the combination of an acid group or sulfate group containing polymer such as copoly(methylmethacrylate-methacrylic acid) and a hydantoin-formaldehyde condensation polymer, such as that disclosed in French Patent 1,493,188. A heavy metal salt such as zinc acetate may also advantageously be incorporated in the print coating composition. Further improvement is obtained by incorporating in the coating composition an acid such as acetic acid, propionic acid or the like.

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. Patent 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 hy-

droquinones 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 cantain 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. Patent 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 Patent 930,572, published July 3, 1963; and acyl derivatives of p-aminophenol such as described in Kodak British Patent 1,045,303, published Oct. 12, 1966; pyrimidine developing agents, such as 4-amino-5,6-dihydroxy-2-methyl pyrimidine; and aminoethyl 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. Patent 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 copending U.S. applications Ser. Nos. 764,358 and 764,301, filed Oct. 1, 1968 now Pat. No. 3,615,521, patented Oct. 26, 1971, and Pat. No. 3,615,439, patented Oct. 26, 1971, respectively, both entitled, "Photographic Compositions and Processes," in the name of Oftedahl. The particular 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. Patents 2,526,632 of Brooker et al., issued Oct. 24, 1950, and 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 Patent 974,317; buffers which maintain the desired developing activtiy 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% 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 (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. 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 one embodiment a resinous mixed ester lactone release agent is employed as a binder for the silver precipitant in an amount of 1 mg./ft.^{2} to about 1 g./ft.^{2}. It will be appreciated that when smaller amounts are used, that the resinous material can be combined with a suitable colloid such as a proteinaceous material. For example, the resinous material might be coated at a range of 1 mg./ft.^{2} and be combined with gelatin in an amount of 13 mg./ft.^{2}. At the upper end of the range, the resinous material of 1 g./ft.^{2} can be used without incorporating any other colloidal material.

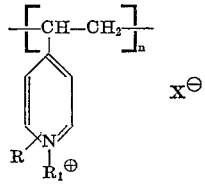
When used as an overcoat over a binder layer containing a silver precipitant, the materials may be used in a range of 1.0 to 20.0 mg./ft.^{2}, the preferred coverage being about 4.0 mg./ft.^{2} to about 8.0 mg./ft.^{2}.

Resinous lactones of the type described herein and the process of making these lactones are described in U.S. Patents 3,169,946; 3,007,901; 3,206,312; 3,260,706; 2,306,-071; and 3,102,028. Their use as release agents is described in Checkhak U.S. Patent application Ser. No. 2,965, filed Jan. 14, 1970, now abandoned.

In one embodiment a resinous lactone release agent is mixed with a silver precipitant, such as colloidal metal nuclei, a proteinaceous binder such as gelatin, a polyvinyl quaternary salt such as poly(1-methyl-4-vinylpyridinium methosulfate) and potassium iodide. The mixture is coated on a support of this invention and after drying can be used as a receiving sheet in a diffusion transfer process.

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 Van Hoff et al. U.S. Patent 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 hetero-atoms 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 1 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-vinylpyridiniummethylsulfate),
poly(1-methyl-2-vinylpyridinium iodide),
poly (1-methyl-2-vinylpyridinium methylsulfate),
poly(1-methyl-4-vinyl-pyridinium 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./ft.^{2}, preferably 0.2 to about 5 mg./ft.^{2}. 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./ft.^{2}, preferably 0.5 to about 10 mg./ft.^{2}. 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 spread at a coverage of about 3.5 ml./ft.^{2} fails to give a satisfactory tone. Also, iodide present in the negative in an amount of about 10 mg./ft.^{2}, 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. Patent No. 3,446,619. Still other silver salts of mercaptotetrazoles and mercaptotriazoles and related heterocyclic mercapto compounds are described in U.S. Patent 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./ft.^{2}, preferably 0.05 to about 5 mg./ft.^{2}.

Various toners can be used by incorporating the toner in the received sheet. Particularly useful toners are those disclosed for use with certain quaternary salts in Tregillus and Rasch U.S. Patent 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./ft.^{2}, preferably 0.01 to about 1 mg./ft.^{2}. 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. Patent 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% 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** and finally the gelatin nuclei layer **9**.

In FIG. 2 the structure is the same as FIG. 1 except that a gelatin mordant layer **10** is coated as the top layer instead of the gelatin nuclei layer **9**.

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 paper is employed in which the polyethylene surface has been electron bombarded to a contact angle below 70° measured with water to improve the adhesion. In Coating A the nucleated layer is coated directly on the polyethylene coated paper. In coatings B and C the nucleated layers are coated over a plastic layer of cellulose triacetate of about 10 grams per square meter which is located between the nucleated layer and the polyethylene surface.

In coating C, a thin subbing layer of a mixture of gelatin and cellulose nitrate of the following formula is applied to the polyethylene support before coating with cellulose triacetate. In coatings B and C a thin subbing layer of the same composition is coated over the triacetate layer before coating with the nucleated layer.

	Percent
Gelatin	1.25
Cellulose nitrate	0.6
Glacial acetic acid	1.0
Acetone	60.0
Water	3.0
Ethylene dichloride	5.0
Methanol	29.15

To this formula is added 1.5 percent of the weight of gelatin of hydrated chromium chloride as a hardener. Abrasion resistance measured as scratch resistance of the nucleated surface is measured on the 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 load 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 one hour after the receiver and negative are stripped apart after processing in a diffusion transfer system in which an exposed silver halide emulsion is developed in the presence of a silver halide solvent and in contact with the nucleated layer.

The following values are obtained in testing the above coatings.

Coating	Support description	Scratch value, grams
A	Polyethylene	5
B	Triacetate over unsubbed polyethylene	17
C	Triacetate over subbed polyethylene	500

EXAMPLE 2

Receiving elements are prepared as in coating B, Example 1. The following results are obtained by testing as in Example 1.

Polymer	Base	Scratch value, grams
Cellulose triacetate	Polyethylene coated paper	175
Cellulose acetate butyrate	do	115

Receiver stability with all coatings is good. Other polymer coatings employed over polyethylene in place of cellulose triacetate include polystyrene, polyvinyl butyral, and a styreneacrylonitrile copolymer. The triacetate has superior characteristics, such as adhesion, curl, toughness and flexibility.

EXAMPLE 3

Receiver elements are prepared as in Example 1 with subbings (a)–(e) between the electron bombarded polyethylene and the polymer overcoat to improve adhesion. Each of the following subbings coated at about 0.4 g./m.^{2} are found to be satisfactory.

(a) Poly(vinyl methyl ether) maleic anhydride in a water solution;

(b) Polyvinyl pyridine coated from methylene chloride solution;

(c) Polyvinyl pyridine coated from methanol solution;

(d) Carboxylated polyester coated from a methyl ethyl ketone solvent solution;

(e) Polyurethane resin coated from a 3 to 1 weight ratio of methyl ethyl ketone to dimethyl formamide.

EXAMPLE 4

Example 1 is repeated except that the polymer coat comprises a 1:1 weight ratio of carboxylated polyester and cellulose triacetate which is coated out of a solvent solution of methylene chloride and methyl alcohol in a weight ratio of 9:1. The polymer coating is applied to the electron bombarded polyethylene coated paper without a subbing but a cellulose nitrate sub as described in Example 1 is coated over the polymer coating prior to coating with the nucleated layer. Average scratch value is 300.

EXAMPLE 5

A receiving sheet for use in obtaining an image by the dye diffusion transfer process is prepared by using electron bombarded polyethylene coated paper as in Example 1. Over electron bombarded polyethylene is coated a sub as described in Example 1. Coatings are also made employing subs as described in Example 3. Over each of these subbed polyethylene coated paper supports are coated polymer layers including those described in Ex-

amples 1, 2 and 4. Over the polymer layer is coated a subbing over which is then coated a dispersion containing a dye mordanting composition comprising octadecyl tri-n-butyl ammonium bromide as described in Example 1 of U.S. Patent 3,271,147. The receiving sheets are used in the image transfer color processes as is described in Example 6 of U.S. Patent 3,271,147. Subsequent testing for abrasion indicates that the abrasion values are at least 500 when tested as described in Example 1. The use of other mordant compounds as described in the above patent also result in satisfactory abrasion resistant receiving sheets.

EXAMPLE 6

A receiving sheet for use in obtaining an image by diffusion transfer is prepared as in Example 1 except that a pigmented cellulose acetate butyrate is used as the support. The cellulose acetate butyrate support is subbed with a cellulose nitrate-gelatin sub as in Example 1 and nucleated as described in Example 1. Prints are obtained having very high gloss and high resistance to abrasion. The following results are obtained.

Support	$D_{max.}$	Scratch abrasion value, grams
Cellulose acetate butyrate, 8 mil	1.45	1,000
Cellulose acetate butyrate, 16 mil	1.45	300

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.

What is claimed is:

1. A receiving sheet comprising a polyolefin surface over which is coated a cellulose triacetate layer and over said cellulose triacetate layer is coated an image receiving layer containing palladium nuclei.

2. An element of claim **1** in which said polyolefin surface has a contact angle of about 40 to about 75° measured with water, prior to coating with the cellulose layer.

3. A receiving sheet of claim **1** in which said polyolefin is polyethylene.

4. An element of claim **1** in which said cellulose layer contains a brightener.

5. An element of claim **1** in which a gelatin-cellulose nitrate sub is employed over the said polyolefin surface.

6. An element of claim **1** comprising a paper support having a baryta layer on said paper and having said polyolefin over said baryta layer.

7. An element of claim **1** comprising a paper support having thereon said polyolefin.

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