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PHOTOGRAPHIC DIFFUSION TRANSFER PRODUCT AND PROCESS

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ABSTRACT OF THE DISCLOSURE

A receiving sheet for use in a diffusion transfer process comprises a support having an image receiving layer and having between the support and receiving layer, a layer comprising colloidal size inorganic particulate material such as silica, alumina, etc. The image receiving layer can be a nucleated layer for use in black and white 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 image stability.

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 a 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.

Various stability problems have been experienced with respect to the prints obtained by diffusion transfer processes. For instance, there has been a problem of fading of the image or change in color from that originally obtained to one which has a yellow or brown coloration, and I have found that a layer of inorganic particulate matter such as colloidal silica located between the support and the image receiving layer improves the stability of the print.

However, colloidal silica has been used in diffusion transfer receiving layers. For instance, U.S. Pat. 2,698,237 teaches that the rate of deposition of silver on the developing nuclei is accelerated by employing a silica matrix in which silver precipitating nuclei are supported. U.S. Pat. 3,257,206 teaches that colloidal silica added to a water-permeable covering layer of the image receiving layer initiates reduction of the diffusing silver complex so that a more rapid and more complete reduction of the silver complex in the image receiving material is obtained. However, the use of silica as a matrix for supporting the nuclei or the use of silica as an overcoat tends to result in a less glossy print than may be desired. In addition, a silica overcoat may be subject to fingerprinting.

It is also known to incorporate inorganic pigments in a reception layer according to British Pat. 878,064 or as an overcoat. However, the image must be viewed through the transparent support since pigment size particles tend to provide opacity.

It is one object of this invention to improve the stability of prints obtained by a black and white diffusion transfer process. Another object of this invention is to prevent fading of prints obtained by diffusion transfer. A further object is to retard or restrain the tendency of images obtained by diffusion transfer to become yellow or brown.

SUMMARY OF THE INVENTION

The above objects of this invention are obtained by incorporating a layer of colloidal inorganic particulate matter such as silica, alumina or the like, in a layer which is located in a receiving element for use in a diffusion transfer process between the support and the image receiving layer. The layer is preferably located directly underneath the receiving layer in an adjacent or contiguous position. However, it has been found that other layers such as a cellulose ester timing layer may be located directly under the receiving layer followed by a layer containing the colloidal size inorganic particulate matter and then by an acid layer or by the support itself.

In a preferred embodiment for use in a silver diffusion transfer process, a polyethylene surface such as polyethylene coated paper 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, an acid layer such as a polyacrylic acid layer, a cellulose acetate timing layer, a silica containing layer and a gelatin layer containing silver precipitating nuclei such as palladium metal.

Another embodiment comprises a polyethylene coated paper support having an acid layer of poly(styrene-maleic anhydride) and cellulose esters such as cellulose acetate, a silica containing layer next and then the receiving layer containing silver precipitating nuclei. In still another embodiment, a cellulose ester timing layer such as cellulose diacetate is located over the poly(styrene-maleic anhydride) and cellulose acetate layer and under the silica containing layer.

Receiving elements as described above are used advantageously to provide photographic prints having an image in a receiving layer on a support by the photographic silver salt diffusion transfer process.

DESCRIPTION OF PREFERRED EMBODIMENTS

The layer which is under the receiving layer preferably comprises colloidal silica although other inorganic particulate materials may be used. Colloidal size is used herein in its generally accepted sense and refers to particle sizes having average diameters in the range of about 3 to about 150 millimicrons. In the practice of this invention, a preferred average particle size range is about 5 to about 50. Colloidal silica is generally used as an aqueous dispersion containing about 30% by weight of the aqueous dispersion. It may be modified as described in Alexander et al. U.S. Pat. No. 2,892,707, issued June 30, 1959. The silica can be obtained as essentially pure silica sold as silica aerogel or colloidal silica obtained from natural sources such as diatomites variously known as diatomaceous earth, kieselguhr, and infusorial earth. Other inorganic colloidal materials which may be used include alumina, and the like. The surface coverage of the inorganic particulate material may vary widely but is generally from about 20 to about 450 milligrams per square foot. Surfactants can be incorporated with the particulate materials. Advantageously, nonionic surfactants such as disclosed in U.S. Pat. 3,514,293 are used.

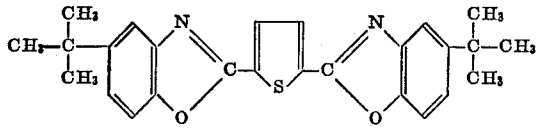
Paper is preferred as a support. Suitable paper supports include any of the conventional paper supports including those prepared from cotton, linen, and wood (sulfate and sulfite pulped). Such supports are typically about 5–60 pounds per 1000 square foot papers.

The support can have thereon a polymeric material, typically coated in a thickness of about .3 to 5 mils. Particularly useful polymeric materials include the polyolefins prepared from the alpha-olefins having 2–10 carbon atoms, blends of these polyolefins and copolymers of the alpha-olefins. The coatings may be applied by extrusion or hot melt coating techniques as latexes, as solvent coatings, etc.

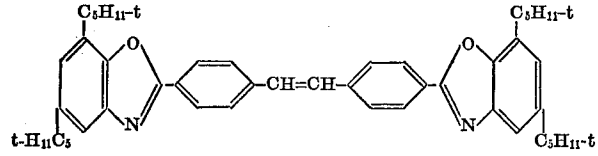
In some instances it is desirable to incorporate in the polymeric material at least one pigment or dye, especially where a white background is required but this is not required. In a particularly useful embodiment, titanium dioxide is incorporated as a pigment in an amount of up to 25%, preferably 10–15%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

It will be appreciated that, in practicing this invention, various layers may be coated on a suitable 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.

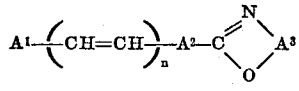
Brighteners can also be incorporated in one or more of the layers of the receiving sheet in any suitable concentrations, particularly good results being obtained at concentrations at about 0.01 to about 1.0 percent by weight of a whitening or brightening agent. For example, 4,4'-bis(benzoxazol-2-yl)stilbene compounds are especially useful. Other compounds which are useful include 2,5-bis(5-t-butyl-2-benzoxazolyl)thiophene



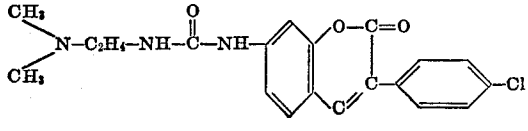
and 4,4'-bis(5,7-di-t-amyl-2-benzoxazol-2-yl)stilbene



Other whiteners include coumarins of the type described in British Pat. 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. Another useful brightener is 3-(p-chlorophenyl) - 7 - 2-[dimethylaminoethyl]ureido coumarin, sold by Geigy Co., New York, N.Y., under the trade name Tinopal SFG.



To improve the stability of the image formed in a receiving layer by diffusion transfer, it is desirable to incorporate an acid or acid reacting layer under the receiving layer between the receiving layer and the support. In this way, the processing solution which normally has a very high pH penetrates to the acid layer where it becomes neutralized and avoids detrimentally affecting the stability of the image in the image receiving layer. However, in order to permit the processing solution to carry out its function of providing an image in the image receiving layer, a timing layer is typically incorporated between the acid layer and the receiving layer. In another embodiment, the timing layer function is carried out by incorporating in the acid layer itself, a material which tends to retard or slow down the reaction of the acid material in the acid layer with the processing solution. For instance, cellulose derivatives can be mixed with a polymeric acid and coated over the support to form a cellulose derivative containing acid layer. Particularly useful cellulose derivatives are cellulose esters 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, gelatin-cellulose nitrate subbing can be used in the receiving sheets of this invention. The gelatin-cellulose nitrate sub is particularly useful when coating a gelatin coating on the surface of a plastic layer such as a cellulose ester layer. Typical coatings are disclosed in the Nadeau et al. U.S. Pat. 2,614,932 issued Oct. 21, 1952 and in Nadeau U.S. Pat. No. 2,133,110 issued Oct. 11, 1938. Of course, the nature of the subbing coated on a cellulose derivative containing layer depends upon the nature of the binder used in any layer, e.g., a receiving 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.

A cellulose derivative-acid layer can be applied as a solvent coating to provide a layer having a thickness of about .1 to about .4 mil of a coverage of .3 g./m.^{2} to 10 g./m.^{2}, preferably about 1–7 g./m.^{2}. Such a layer can contain addenda such as pigment or brightener, dye, plasticizer, etc. The cellulose derivative-acid layer can contain any polymeric acid which has non-diffusible acid groups, e.g. acid radicals attached to a polymer so as to be non-diffusible. The acid reacting layer can contain a water-insoluble cellulose derivative preferably a cellulose ester which acts to control or modulate the rate at which the alkali salt of the polymeric acid is formed. In a preferred embodiment, the acid reacting layer comprises copoly(styrene/maleic anhydride) and cellulose acetate. Water insoluble cellulose derivatives can be crosslinked with a suitable crosslinking agent, such as hexamethoxymethylmelamine which can be used as a crosslinking agent for a wide range of polymeric materials containing carboxyl, hydroxyl, or amide groups such as many epoxy resins, alkyd resins, certain types of acrylic and vinyl polymers, and cellulosics such as hydro cellulose, ethyl cellulose, hydroxyethyl cellulose and carboxylated cellulose derivatives. U.S. Pat. No. 2,906,724 issued Sept. 29, 1959, to Daniel discloses melamine type compositions and U.S. Pat. No. 2,453,608 issued Nov. 9, 1948, to West discloses crosslinking water-soluble cellulose ethers.

Examples of acidic copolymers which may be used include copoly(butylacrylate-acrylic acid 60:40 mole percent), cellulose acetate hydrogen phthalate, ethylmethacrylate-methacrylic 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, potassium, etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide. Also useful are 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 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, 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 derived from other classes of polymers may be used.

Specific polymeric acids which can be used are di-basic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups as exemplified by 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; copoly (styrene/maleic anhydride); interpolymers of an α,β-dicarboxylic acid anhydride with a vinyl organic acid ester such as maleic anhydride-vinyl acetal interpolymer, ethylene/maleic anhydride copolymers and their partial esters; methylvinyl ether/maleic anhydride copolymers and their partial esters such as the butyl half-ester of medium viscosity poly(methylvinyl ether/maleic anhydride). Additional acid materials which may be used include Zeolites (hydrated alkali aluminum silicate)

$$Na_2O \cdot Al_2O_3 \cdot (SiO)_x \cdot (H_2O)_y$$

organic acids such as phthalic acid, acid salts such as zinc acetate, etc.

Acid such as polmeric acids may be encapsulated and coated in the acid layer. In a particularly useful embodiment, the capsules are in an alkali impermeable polymer which hydrolyzes in alkali to form an alkali-permeable polymer, such as polyvinyl acetate. When the acid used is encapsulated, the timing layer over the acid layer may be omitted. By the use of encapsulation, many types of acids may be used without regard to their diffusibility, since the acid cannot diffuse to other layers. Particularly useful types of acids include Zeolites, organic acids such as phthalic acid, polymeric acids such as polyacrylic acid and acid salts such as zinc acetate.

The acid layer may be hardened, e.g., a polyacrylic acid containing layer can be hardened with a bisepoxy ether as described in Houck et al. U.S. Pat. 3,062,674 or in Hurwitz U.S. Pat. 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 imbibition 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.

A cellulosic derivative which is particularly useful in an acid reacting layer or as a timing layer over the acid reacting layer is for example, cellulose acetate with fillers as, for example, one-half cellulose acetate and one-half oleic acid; cellulose diacetate which is slowly permeable to alkalis. Another example of suitable cellulose derivatives are hydroxyl propyl cellulose, hydroxypropyl methyl cellulose, and including in a mixture of cellulose derivatives as, for example, a mixture of hydroxy propyl methyl cellulose and hydroxy propyl cellulose.

In order to improve the adhesion of a gelatin containing nuclei layer to an underlayer, a gelatin-cellulose nitrate subbing layer can be used. A particularly useful gelatin-cellulose nitrate subbing composition contains a surfactant such as a copolymer of dimethyl siloxane and polyoxyalkylene ether sold under such trade names as SF 1066 or XF 1066. This surfactant can also be used advantageously in acid layers, particularly in the acid-cellulose ester coating composition.

Precipitating agents which are useful in the receiving sheet of this invention include nuclei which are useful as precipitating agents with a silver halide complex, including all of those nuclei which are commonly useful in the diffusion transfer process. Suitable nuclei 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 heaxy metals with a compound such as thioacetamide, dithiooxamide and dithiobiuret. As examples of suitable silver precipitating agents and of image-receiving element containing such silver precipitating agents, reference may be made to U.S. Pats. 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. The metal nuclei are prepared in the presence of a hydrophilic 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.

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 the particularly active noble metal nuclei 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}.

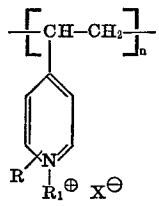
It will also be appreciated that the precipitating agents can be formed in situ or can be applied by precipitating or evaporating a suitable precipitating agent on the surface of the receiving sheet.

Toning agents are generally present during the diffusion transfer step. For example, various toning agents can be contained 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 image blacker or more blue-black include selenotetrazoles, including selenotetrazoles substituted by aliphatic residues, as for example, 1-allyl-5-seleno - 1,2,3,4 - tetrazole, selenotetrazoles substituted by aromatic or heterocyclic residues having 1–12 carbon atoms, as for example, 1-phenyl-5-seleno-1,2,3,4-tetrazole, etc., sulfur compounds such as 2-mercaptothiazoline, 2-amino - 5 - mercapto-1,3,4-thiadiazole, 2-thionoimidazolidene, 2-mercapto-5-methyloxazoline and 2-thionoimid-

azoline. It will be appreciated that these toners can be used either alone or in conjunction with other toning agents.

In a preferred embodiment, a polymeric toner is used. Polymers which are particularly useful are water soluble polyvinyl quaternary salts, as described in Van Hoff et al. U.S. Pat. 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 heteronitrogen 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-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 the polymer 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.

Typically, other 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} either in the receiving layer or coated in the layer on top of the image reeciving layer. A particularly useful combination employs phenyl mercaptotetrazole and potassium iodide in a developer or activator solution. Other toning agents which may be used include 5,5'-dithiabis(1-phenyltetrazole), 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 such as 2-thionothiazolidone, 4-phenyliminothiourazole, 4-phenyl-1,2,4-triazolidene-3,5-dithione, etc

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. 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. 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. 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. 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. 930,572 published July 3, 1963; and acyl derivatives of p-aminophenol such as described in Kodak British Pat. 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 siver halide developing agent.

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.

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 emulsion 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. Pats. 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 addena, 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. 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 senitized 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. These include photographic silver halides such as silver iodide, silver bromine, 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.

Stripping agents can be used either on or in the surface of the silver halide emulsion layer, on or in 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}.

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}.

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. Pats. 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 Chechak U.S. patent application Ser. No. 2,965 filed Jan. 15, 1970 now abandoned.

Various colloids can be used as dispersing agents or as binders for the precipitating agents in the receiving layer. Any suitable colloid 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 to about 5,000 mg./ft.^{2}. Included among suitable colloids are gelatin, preferably coated at a level in the range of about 7–1000 mg./ft.^{2}, polymeric lactices such as copoly(2-chloroethylmethacrylate-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, 3-acryloyloxypropane-1-sulfonic acid, sodium salt and 2-acetoacetoxyethyl methacrylate, in a preferred range of about 10–300 mg./ft.^{2}.

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.

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.

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. The supports for these elements comprise paper coated with polyethylene containing white pigment on which is coated a gelatin-cellulose nitrate sub coat, and a cellulose triacetate layer at a coverage of about 10 grams per square meter. Another gelatin-cellulose nitrate sub coat is applied over the cellulose triacetate layer. One element has contiguous to the nucleated layer an underlayer of colloidal silica in an amount of 160 mg./ft.^{2}. A similar element is prepared wtihout the colloidal silica layer.

Each of the receiving elements described above is placed in contact with an imagewise exposed silver bromoiodide emulsion layer containing silver halide developer, and a viscous developer solution prepared by mixing the following components:

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

Water to 1 liter.

After 30 seconds contact, the receiving sheet and negative are separated. A portion of each is then placed in a light stability chamber illuminated with fluorescent light at an intensity of 300 ft. candles, and having a relative

humidity of 90%, maintained by $ZnSO_4 \cdot 7H_2O$ at its equilibrium vapor pressure in the closed vessel. The temperature inside the container is 80° F. Strips are kept in the chamber for two days.

Characteristic curves plotting density vs. long exposure are prepared from the control and the silver containing element with the following results, both fresh and after two days in a light stability chamber.

Features	Minimum info point [a]	Density loss at 0.6 [b]
Control (no silica)	.30	.30
160 mg./ft.^{2} below nuclei layer	.20	.25

[a] That density value of the fresh coating below which all information is lost on bleaching of the image after two days' keeping in a light stability chamber.

[b] The loss in image density of the coating which is kept for two days in a light stability chamber which is measured at the 0.6 density point of the fresh coating.

The strips having the colloidal silica underlayer show better maintenance of image tone and less bleaching than the control whereas images in the control having a density below .30 are lost.

EXAMPLE 2

Receiving elements are prepared as in Example 1 except that the nucleated layer contains colloidal silica in addition to gelatin and finely divided palladium nuclei. No silica is present in an underlayer. The colloidal silica is varied from the control in which no silica is present to 40 milligrams per square foot and 160 milligrams per square foot of colloidal silica. The receiving sheets are then treated as in Example 1. Characteristic curves plotting density vs. log exposure are prepared from the control sample and each of the test samples with the following results:

Features	Minimum info point [a]	Density loss at 0.6 [b]
Control	.20	.22
40 mg./ft.^{2} silica	.22	.22
160 mg./ft.^{2} silica	.39	.47

[a] That density value of the fresh coating below which all information is lost on bleaching of the image after two days' keeping in a light stability chamber.

[b] The loss in image density of the coating which is kept for two days in a light stability chamber which is measured at the 0.6 density point of the fresh coating.

This example shows that silica in the nuclei layer does not improve the stability.

EXAMPLE 3

Example 1 is repeated except that a layer of alumina is coated in place of the silica at 120 milligrams per square foot. When compared with a control in which the alumina is omitted, the strips having the alumina beneath the nuclei layer show better maintenance of image tone and less bleaching than the control.

EXAMPLE 4

Receiving elements are prepared as in Example 1 except that the polyethylene coated paper has thereon in order, a sub coat, a cellulose triacetate layer, a sub coat, an acid layer containing polyacrylic acid, a timing layer containing cellulose acetate (40% acetyl) and a nuclei layer. This is used as a control compared to a similar element in which a colloidal silica layer coated at 160 milligrams per square foot is located directly under the nuclei layer. Both elements are processed as in Example 1. The silica containing element shows the same maintenance of image tone and less bleaching in comparison with the control as in Example 2. The following results are obtained when characteristic curves applying density against log exposure are prepared from the control and the element of this invention.

Features	Minimum info point	Density loss at 0.6
Control (no silica)	.55	.55
160 mg./ft.^{2} below the nuclei layer	.33	.41

This example shows beneficial results when the element also contains an acid layer.

EXAMPLE 5

Receiving elements are prepared having a nucleated layer comprising a gelatin binder containing finely divided palladium nuclei. In each instance, white pigmented 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.

Receiver I is prepared as follows:

Over the polyethylene surface are coated in order, a gelatin-cellulose nitrate subbing, an acid layer comprising cellulose acetate 400 mg./ft.^{2} and copoly(styrene/maleic anhydride) 200 mg./ft.^{2}, a cellulose acetate timing layer 72 mg./ft.^{2}, a gelatin-cellulose nitrate subbing, a colloidal silica layer 160 mg./ft.^{2}, and the gelatin-nuclei layer 60 mg./ft.^{2} gelatin and 20 mg./ft.^{2} $PdCl_2$.

Receiver II is the same as Receiver I except that it does not contain the colloidal silica layer. Receiver III is the same as Receiver I except that it does not contain the cellulose acetate timing layer and Receiver IV is the same as Receiver I except it does not contain the cellulose ester timing layer or the silica layer.

The receiving sheets are placed in contact with an imagewise exposed silver bromoiodide emulsion coated on a paper base. An image is obtained in each receiving sheet by means of a viscous developer solution having the formulation described in Example 1. After the photosensitive and receiving elements are held in contact for 30 seconds, they are separated.

Light stability is measured by placing the samples in a light stability chamber illuminated with fluorescent light at an intensity of 300 foot candles for six days. The chamber is at 80° F./90% relative humidity. Results below illustrate very little change of image quality in Receivers I and III which show that the colloidal silica layer improves image stability to high humidity and light.

TABLE I

Receiver	Minimum info point [a]	Density loss at 0.6 [a]	$D_{max.}$ Fresh	$D_{max.}$ 6 day keeping
I	0.07	0.13	1.42	1.28
II (control)	0.16	0.30	1.44	1.30
III	0.08	0.14	1.48	1.34
IV (control)	0.20	0.25	1.48	1.16

[a] After six days in the light stability chamber.

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 sheet comprising a support having thereon an image receiving layer and under said layer, a layer containing particulate material comprising colloidal size alumina or silica.

2. An element of claim 1 in which said particulate material is silica.

3. A receiving sheet of claim 1 in which said particulate material is alumina.

4. A receiving sheet of claim 1 in which said support comprises paper.

5. A receiving sheet of claim 1 in which said support comprises a polyolefin.

6. A receiving sheet of claim 1 in which said support comprises polyethylene coated paper.

7. A receiving sheet of claim 1 in which said particulate material is coated in an amount of about 20 to about 450 mg./ft.^{2}.

8. A receiving sheet of claim 1 in which said receiving layer contains palladium nuclei.

9. An element of claim 1 containing an additional layer under the receiving layer comprising a polymeric acid.

10. An element of claim 9 in which said additional layer comprises a mixture of polymeric acid and cellulose ester.

11. A receiving sheet of claim 6 in which said polyethylene is coated on a paper support having a baryta layer on said paper.

12. A receiving sheet of claim 1 in which said receiving layer contains a silver precipitating agent.

13. A receiving sheet of claim 4 in which said image receiving layer comprises silver precipitating nuclei.

14. A process of obtaining an image in a receiving layer by diffusing a silver complex from undeveloped areas of an exposed developing silver halide emulsion to said receiving layer, said receiving layer having an underlayer containing colloidal size inorganic particulate material.

15. An element of claim 1 in which said particulate material is located in a layer contiguous to said image receiving layer.

16. An element of claim 2 in which said silica is located in a layer contiguous to said image receiving layer.

17. An element of claim 3 in which said alumina is located in a layer contiguous to said image receiving layer.

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