United States Patent

[11] 3,619,186

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[54] **PHOTOGRAPHIC DIFFUSION TRANSFER PRODUCT AND PROCESS**
19 Claims, No Drawings

[52] **U.S. Cl.** **96/29,** 96/76
[51] **Int. Cl.** **G03c 5/54**
[50] **Field of Search** ..... 96/29, 52 A

[56] **References Cited**

UNITED STATES PATENTS

2,697,040	12/1954	Parnell	96/52 X
3,093,479	6/1963	Olivares et al.	96/52
3,129,097	4/1964	Van Hoot et al.	96/29 X
3,488,706	1/1970	Cohen et al.	96/29

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ABSTRACT: A receiving layer for use in a photographic diffusion transfer process comprises a proteinaceous colloid binder, a silver precipitant, a water-soluble polyvinyl quaternary salt containing a five or six membered heterocyclic nucleus containing a quaternary nitrogen atom and an iodide. The layer can also contain a silver salt or complex for improving image density and/or a toning agent.

PHOTOGRAPHIC DIFFUSION TRANSFER PRODUCT AND PROCESS

BACKGROUND OF THE INVENTION

This invention relates to receiving layers employing proteinaceous colloid binders for silver precipitants and their use in diffusion transfer products and processes.

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

In carrying out the diffusion transfer process, there have been many problems involved in obtaining a satisfactory image. For instance, many of the prints have a brownish image, lack stability, etc. Therefore, various methods have been proposed to improve the process such as incorporation of toning agents in the processing solution, substitution of various silver precipitants, incorporation of quaternary salts, etc.

A proteinaceous colloid such as gelatin has been recognized as particularly useful as a binder for silver precipitants. However, using gelatin as a vehicle for silver precipitants such as nuclei, especially with certain types of nuclei such as colloidal silver, results in prints having a yellow to light brown color. The problem of obtaining a desirable tone using a proteinaceous colloid such as gelatin has been recognized in the art and various attempts have been made to overcome this problem, as can be seen by Land et al., U.S. Pat. No. 2,774,667 issued Dec. 18, 1956, which describes the use of a silica matrix for silver precipitating nuclei such as colloidal silver to avoid having the prints result in a yellow or light brown color.

It has also been proposed to incorporate certain quaternary salts in receiving sheets to reduce fog and granularity as disclosed in White et al., U.S. Pat. No. 3,314,789 issued Apr. 18, 1967. Polymeric vinyl pyridinium quaternary salts are disclosed in VanHoof et al., U.S. Pat. No. 3,174,858 issued Mar. 23, 1965, for use in a receiving sheet to increase the number of copies obtained in a multiple copy diffusion transfer process. However, the use of a quaternary salt in a receiving layer with a proteinaceous binder such as gelatin may not result in a cold or blue-black tone.

It is recognized that a proteinaceous colloid binder which would behave satisfactorily when used with nuclei to form a receiving layer would be very useful in diffusion transfer processes if it would result in a neutral or black image. It is also recognized that it would be desirable to obtain a proteinaceous binder which could be used with a polymeric vinyl pyridinium quaternary salt to obtain a neutral or black image.

SUMMARY OF THE INVENTION

In accordance with this invention, it has been found that a receiving layer for use in a diffusion transfer process before being in contact with a developing silver halide emulsion and being substantially free from an image, comprises a proteinaceous binder, a silver precipitant, a water-soluble polyvinyl quaternary salt and an iodide. The quaternary salt has a polyvinyl chain, at least one monomeric unit of which is linked directly to a five or six membered heterocyclic nucleus containing a heteroquaternary nitrogen atom. Additional advantages are obtained by also incorporating in the layer a toner and/or a silver salt, such as, e.g., silver nitrate.

In a particularly useful embodiment, the receiving layer contains noble metal nuclei as described in U.S. Pat. No. application entitled "Photographic Diffusion Transfer Product and Process," Ser. No. 796,552 filed concurrently herewith in the name of Rasch.

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.

DESCRIPTION OF PREFERRED EMBODIMENTS

In one embodiment of this invention, colloidal noble metal nuclei are dispersed in a proteinaceous binder such as gelatin, a polyvinyl quaternary salt such as poly(1-methyl-4-vinyl pyridinium methylsulfate) and potassium iodide are added after which the mixture is coated on a suitable support such as paper. After drying, the receiving sheet can then be used in a diffusion transfer process and results in an image of good tone and density.

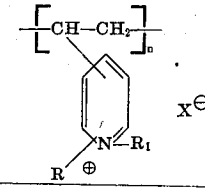
In another embodiment of this invention, colloidal nuclei are dispersed in a binder as described above and the composition coated on a suitable support such as paper. After drying, an unhardened silver halide emulsion is coated over the receiving layer. Particularly useful emulsions are described in Yackel et al., U.S. Pat. No. 3,020,155. The exposed photographic element is processed using a silver halide developing solution containing a silver halide solvent such as sodium thiosulfate. The undeveloped silver halide, complexed with thiosulfate, diffuses to the nucleated underlayer where an image is formed in the silver halide emulsion. Unhardened silver halide emulsion is then removed by washing with warm water.

A significant feature of this invention is the incorporation of an iodide, e.g., potassium iodide, into a receiving layer employing a proteinaceous binder in combination with a polyvinyl quaternary salt. As is illustrated hereinafter by examples 1 and 7, a neutral tone is obtained whereas the presence of potassium iodide in the silver halide emulsion and in the developer does not have the same beneficial effect on the tone.

The binder for the silver precipitant is substantially protein and the binder is typically at least 50 percent, by weight, of a protein as described herein. Gelatin is the preferred binder, but other proteins such as casein, zein, albumin, etc., may be used.

Polymers particularly useful as water-soluble polyvinyl quaternary salts are described in VanHoof et al., U.S. Pat. No. 3,174,858 issued Mar. 23, 1965. These water-soluble basic polymeric quaternary salts have a polyvinyl chain having two to 10,000 monomeric units, at least one monomeric unit of which is linked to a five or six membered heterocyclic nucleus containing a heteroquaternary nitrogen atom.

In one embodiment, the polymer has the following structure:

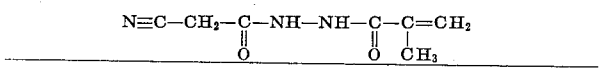


in which n is an integer from two to 10,000 and X is any suitable anion such as $CH_3SO_4^{\ominus}$, para toluene sulfonate, iodide, etc. R represents H, an alkyl group having one to 10 carbon atoms such as, for example, methyl, ethyl, propyl, butyl, etc., halogen, NO_2, NH_2, aralkyl, aryl, etc. R_1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

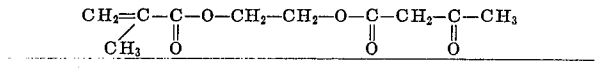
Typical polymeric materials include poly(1,2-dimethyl-5-vinylpyridinium methylsulfate), poly(1-methyl-2-vinyl-

pyridinium iodide), poly(1-methyl-2-vinylpyridinium methylsulfate), poly(1-methyl-4-vinylpyridinium iodide), poly(1-methyl-4-vinylpyridinium methylsulfate), poly(1-vinyl-3-methyl imidazolim iodide) and poly(1-vinyl-3-methyl imidazolium methylsulfate).

In another embodiment, in which the polyvinyl chain has attached thereto at least one monomeric unit linked to a heterocyclic nucleus containing a heteroquaternary nitrogen atom, the chain can contain attached thereto at least one linear group. In preparing a typical polyvinyl quaternary salt, the polymerization mixture can contain a linear compound such as N-cyanoacetyl-N'-methacrylylhydrazine (described in U.S. Pat. No. 2,940,956),



2-acetoacetoxyethyl methacrylate, described in U.S. Pat. application Ser. No. 525,272 filed Dec. 20, 1965 in the name of Donald A. Smith, entitled "Photographic Materials," now U.S. Pat. No. 3,459,790



In a particularly useful coating composition, we employ 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 alkaline iodide, such as, e.g., ammonium, guanidine, sodium, potassium, lithium etc., is 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}. The effect on tone of incorporation in the receiving layer of iodide is particularly striking, since potassium iodide contained in the processing solution in an amount of 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} fails to have this beneficial effect on the tone.

The addition of a silver salt or complex such as, e.g., silver nitrate, to the receiving sheet improves the quality of the transfer, e.g., the image density. Any silver salt or complex can be used, including both organic and inorganic silver compounds. A typical organic silver complex is, for example, silver dipyridyl nitrate. Other silver salts and complexes which are included are described in Gilman et al., U.S. Pat. application Ser. No. 411,594, filed Nov. 16, 1964, now U.S. Pat. No. 3,446,619. Still other silver salts of mercaptotetrazole and triazoles and related heterocyclic mercapto compounds described in U.S. Pat. No. 2,432,864. However, silver nitrate is preferred. The silver compound can be used in an amount of about 0.01 to about 10 mg./ft.^{2}, preferably 0.05 to about 5 mg./ft.^{2}.

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

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, stripping 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.

Suitable silver precipitants for use in the receiving layer include various silver precipitating agents known in the art. As examples of suitable silver precipitating agents and of image-receiving elements containing such silver precipitating agents, reference may be made to U.S. Pat. Nos. 2,698,237, 2,698,238 and 2,698,245 issued to Edwin H. Land on Dec. 28, 1954, U.S. Pat. No. 2,774,667 issued to Edwin H Land and Meroe M. Morse on Dec. 18, 1956, U.S. Pat. No. 2,823,122 issued to Edwin H. Land on Feb. 11, 1958, U.S. Pat. No. 3,396,018 issued to Beavers et al. Aug. 6, 1968 and also U.S. Pat. No. 3,369,901 issued to Fogg et al. Feb. 20, 1968. The noble metals, silver, gold, platinum, palladium etc., in the colloidal form are particularly useful.

Noble metal nuclei are particularly active and useful when formed by reducing a noble metal salt using a borohydride or hypophosphite in the presence of a colloid as described in the above Rasch application. The metal nuclei are prepared in the presence of a porteinaceous colloid, such as gelatin, and coated on the receiving sheet. The same or a different colloid may be added, if desired, providing the colloid is within the scope of our invention. It will be appreciated from the above 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 byproducts 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 used, e.g., gelatin, reducing agent employed, e.g., borohydride, proportions of reagents, etc. Typically about 0.5 percent to about 20 percent, by weight, based on the total reaction mixture of colloid used is used, preferably from about 1 percent to about 10 percent.

In a particularly useful embodiment, 3 to 80 μg./ft.^{2} of an active noble metal nuclei in 80 mg. of colloid (solids basis) is coated per square foot of support. The colloid binder is advantageously coated in a range of about 5 to about 500 mg./ft.^{2}. Suitable concentrations on the receiving sheets of active noble metal nuclei as disclosed above can be about 1 to about 200 μg./ft.^{2}. Other silver precipitants can be coated in a concentration of up to 5 mg./ft.^{2}.

The supports which can be used for coating with the receiving layer are any of those which are suitable and include paper, wood, glass, plastics, etc. A particularly useful support is paper, especially baryta coated paper. However, in a preferred embodiment, a polymeric material which acts as a moisture barrier, such as polyethylene or the like, which is pigmented to provide a white surface is used. Antistain agents, such as acids, etc., can be incorporated in the supports or supporting layers. Typical antistain agents are disclosed in Yungkurth et al., U.S. Pat. No. 3,250,619 and Yungkurth, U.S. Pat. No. 3,326,744. Other polymeric materials which may be used as coatings on paper or as self-supporting webs include polyesters, polyamides, polycarbonates, polyolefins, cellulose esters, polyacetals and the like.

In order to obtain adhesion or to improve adhesion to a receiving support, treatments of the support, e.g., photographic film base, may be carried out including subbing the support, electron bombardment, treating peroxide and the like.

Toning agents are generally present during the diffusion transfer step. For example, various toning agents can be in the processing solution, in the receiving layer, 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-mercatothiazoline, 2-amino-5-mercapto-1,3,4-thiadiazole, 2-thionoimidazolidene, 2,5-dimercapto-1,3,4-thiadiazole, L-cysteine, 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. Other toning agents which may be used include the 5-mercaptotetrazoles of Abbott et al., U.S. Pat. No. 3,295,971 and Weyde, U.S. Pat. No. 2,699,393. Still other toning agents are disclosed in Tregillus et al., U.S. Pat. No. 3,017,270.

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

In carrying out the diffusion transfer process, conventionally a silver halide emulsion is exposed to a light image after which it is contacted with a silver halide developing agent containing a silver halide complexing agent. The exposed emulsion is developed in the light 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. Pat. No. 2,979,477 comprising a mixture vinylpyridine polymer and a hydantoin-formaldehyde condensation polymer.

Suitable print coating compositions may also employ a polymeric material such as methylmethacrylate-methacylic 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 Pat. No. 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. Pat. No. 3,120,795 of Land et al. issued Feb. 11, 1964.

Developing agents and/or developing agent precursors can be employed alone or in combination with each other, as well as with auxiliary developing agents. Suitable silver halide developing agents and developing agent precursors which can be employed include, for example, polyhydroxybenzenes, alkyl substituted hydroquinones, as exemplified by t-butyl hydroquinone, methyl hydroquinone and 2,5-dimethylhydroquinone, catechol and pyrogallol; chloro substituted hydroquinones such as chlorohydroquine 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 six 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-aminorescorcinol
2,4-diaminorescorcinol
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-hydrooxyphenyl hydroxylamine

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

Other silver halide developing agents include ascorbic acid, ascorbic acid ketals, such as those described in U.S. Pat. No. 3,337,342 of Green issued Aug. 22, 1967; **hydroxylamines such as N,N-di(2-ethoxyethyl)hydroxylamine**; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone, including those described in Kodak British Pat. No. 930,572 published July 3, 1963; and acyl derivatives of p-aminophenol such as described in Kodak British Pat. No. 1,045,303 published Oct. 12, 1966.

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. 764,348 (now U.S. Pat. No. 3,548,750) and 764,301 filed Oct. 1, 1968, both entitled "Photographic Compositions and Processes" in the name of Oftedahl. The particularly suitable lactone derivatives provide desired developing activity and reduction of stain without adversely affecting desired maximum density, minimum density, photographic speed and other desired sensitometric properties. Suitable lactone derivative developing agents include those which under neutral, slightly alkaline or acid conditions, i.e., when the pH is lowered to a level of about 9 or lower, i.e., about 2 to about 9, do not have significant developing activity, if any, due to formation of a developing agent precursor.

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

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

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

such as gold, or reduction sensitized with reducing agents or combinations of such materials.

Various photographic silver salts can be used in the practice of the invention. These include photographic silver halides such as silver iodide, silver bromide, silver chloride, as well as mixed halides such as silver bromoiodide, silver chloroiodide, silver chlorobromide and silver bromochloroiodide. Photographic silver salts which are not silver halides can also be employed such as silver salts of certain organic acids such as silver behenate, 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 stripping 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 percent to about 10 percent, by weight, the stripping agents prevent the processing solution from sticking to the receiver. Suitable stripping agents normally are used which have a composition different from the binder used in the silver halide emulsion. Coatings of these agents are relatively thin, having a preferred coverage of about 600 mg./ft.^{2}. However, a useful range may be from 1.0 mg. to 1.0 g./ft.^{2}. It will also be understood that a stripping agent or release agent can be incorporated in the receiving layer along with the nuclei and/or binder used as a carrier for the nuclei.

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

EXAMPLE 1

Effect of Iodide on Tone and Bronzing

A nuclei melt is prepared as follows:

1. 138 g. of 10 percent bone gelatin in 862 ml. of distilled water
2. 19 heat to 50° C. and add 7 ml. of 1.24 percent $PdCl_2$ solution (1 percent HCl)
3. adjust pH to 6.0 with sodium hydroxide
4. add 30 ml. of 0.2 percent $NaBH_4$ solution (60 mg.) to react with the $PdCl_2$ to form colloidal palladium (pH should rise to 8.3–8.5)
5. Stir 10 minutes at 50° C. and adjust pH to 5.5 with 0.1N HCl
6. Add 1,000 g. of 10 percent bone gelatin
7. Stir and chill set as 5.75 percent gelatin

The above nuclei melt is incroporated into coating compositions A and B as follows:

	A	B
Nuclei melt	40 g.	40 g.
Distilled water	183 ml.	183 ml.
10% aqueous gelatin	17 ml.	17 ml.
5% aqueous poly(1,2-dimethyl-5-vinylpyridinium methylsulfate)	1.65 ml.	1.65 ml.
10% aqueous formaldehyde	7.7 ml.	7.7 ml.
15% aqueous saponin	5.0 ml.	5.0
10 % aqueous potassium iodide		7.5 ml.

Receiving sheets are prepared by coating these melts on polyethylene coated paper support at 2.5 ml./ft.^{2} to give a gelatin coverage of 38 mg./ft.^{2}; a nuclei coverage of 6 μg./ft.^{2}; and a potassium iodide coverage of 7 mg./ft.^{2}. Each receiving sheet is tested by placing in contact with a silverbromoiodide emulsion containing iodide in an amount of about 10 mg./ft.^{2} coated on an opaque support, exposed and developed by means of rupture of a viscous pod of the following formulation:

	g./l.
2,4-diamino-6-methyl phenol sulfate	5–10
ter-Butyl hydroquinone	25
$Na_2S_2O_3 \cdot 5H_2O$	60
NaOH	20
KOH	20
KI	0.6–1.6
Hydroxy ethyl cellulose	3–4.5%
K_2SO_3	25–50

The following results are obtained:

Melt	Dmax	Tone	Bronzing
A	1.40	warm	yes
B	1.40	cold	no

EXAMPLE 2

Effect of Iodide and Cold Toner on Tone

Receiver sheets are prepared as in example 1 by preparing the following coating compositions, C and D:

	C	D
Nuclei melt as in example 1	80 g.	80 g.
Distilled water	864 ml.	864 ml.
10% aqueous gelatin	34 g.	34 g.
5% aqueous poly(1,2-dimethyl-5-vinylpyridinium methylsulfate)	3 ml.	3 ml.
10% aqueous formaldehyde	15 ml.	15 ml.
15% aqueous saponin	9.6 ml.	9.6 ml.
10% aqueous potassium iodide		15 ml.
0.1% 2,5-dimercapto-1,3,4-thiadiazole		0.8 ml.

These melts are coated as above at 5 ml./ft.^{2} to give a gelatin coverage of 38 mg./ft.^{2}; a nuclei coverage of 6 μg./ft.^{2}; a potassium iodide coverage of 7 mg./ft.^{2}; and a toner coverage of 0.004 mg./ft.^{2}. They are processed as in example 1 with the following results:

Melt	Dmax	Tone
C	1.66	slightly warm
D	1.50	cold

EXAMPLE 3

Effect of Iodide and L-Cysteine on Tone, Maximum Density and Bronzing

A coating composition is prepared as follows:

720

	g.
Nuclei melt as in example 1	
Distilled water	3,300 ml.
10% aqueous gelatin	304 g.
5% aqueous poly(1,2-dimethyl-5-vinylpyridinium methylsulfate)	30 ml.
10% aqueous formaldehyde	140 ml.
15% aqueous saponin	91 ml.

To portions of this melt are added potassium iodide and L-cysteine as listed in the following table. These melts are coated as above at the same coverages of gelatin, nuclei and KI; the coverage of L-cysteine is listed below.

10% KI	mg./ft.^{2} Cysteine	Dmax	Tone

		1.45	warm Dmax
	.02	1.50	warm Dmax
	.20	1.25	cold
	2.0	1.10	cold
7 ml.		1.45	cold
7 ml.	.02	1.52	cold
7 ml.	.20	1.48	cold
7 ml.	2.0	1.28	cold

The incorporation of potassium iodide prevents the Dmax bronzing that occurs in the control coating; it forms a colder image tone; it reduces the granularity that increases by the addition of cysteine; and it reduces the sensitometric effects of cysteine (i.e., lower Dmax and contrast).

EXAMPLE 4

Iodide Compared with Bromide and Chloride as Tone Modifiers

A nuclei melt is prepared as follows:

1. 138 g. of 10 percent bone gelatin in 862 ml. of distilled water
2. heat to 50° C. and add 7 ml. of 1.24 percent $PdCl_2$ solution (1 percent HCl)
3. adjust pH to 6.0 with sodium hydroxide
4. add 30 ml. of 0.2 percent $NaBH_4$ solution (60 mg.) to react with the $PdCl_2$ to form colloidal palladium (pH should rise to 8.3–8.5)
5. stir 10 minutes at 50° C. and adjust pH to 5.5 with 0.1N HCl
6. add 562 g. of 10 percent bone gelatin and 438 ml. distilled water
7. stir and chill set as 3.5 percent gelatin

A coating composition is prepared as follows, using the nuclei melt above:

	1	2	3	4
Nuclei melt, g	48	48	48	48
Distilled water, ml	252	252	252	252
1% aqueous poly (1,2-dimethyl-5-vinylpyridinium methylsulfate, ml	5	5	5	5
15% aqueous saponin, ml	3	3	3	3
10% aqueous formaldehyde, ml	2.5	2.5	2.5	2.5
10% aqueous potassium iodide, ml	1.3			
7% aqueous potassium bromide, ml		1.3		
4.5% aqueous potassium chloride, ml			1.3	

These are hand coatings at 0.001 in., giving a wet laydown of about 2.5 ml./ft.^{2} and an approximate coverage of 13.25 mg./ft.^{2} of gelatin and equal mole coverage of the halide salts.

The results clearly indicate the superiority of iodide versus the other halides as a tone modifying agent.

EXAMPLE 5

Toners Used Without A Polymeric Salt

A coating composition is prepared as described in example 1, except that the composition contains no polyvinyl polymer or potassium iodide. To portions of the coating composition are added the components as sown in the following table with the resulting maximum density (Dmax) and tone. $AgNO_3$ is added in an amount of 1 mg./ft.^{2} to the coating composition of receiver No. 4.

Receiver	Components	$D_{max.}$	Tone
1	No toner	0.76	Yellow.
2	Phenyl mercaptotetrazole	0.20	Do.
3	KI	0.80	Do.
4	$AgNO_3$	0.76	Do.
5	Poly(1,2,-dimethyl-5-vinylpyridinium methylsulfate).	1.56	Greenish-brownish-blk.
6	Poly(1,2,-dimethyl-5-vinlypyridinium methylsulfate), KI, $AgNO_3$, phenyl mercaptotetrazole.	1.38	Cold neutral.

The following conclusions are found: (a) no one of the following: KI, silver salt or toner, produces a cold tone image without the polymeric quaternary salt; (b) a polymeric quaternary salt in combination with iodide, silver salt and toner produces a cold tone; (c) the cumulative or synergistic results of the combination is unexpected from the results of the individual tests of the ingredients singly.

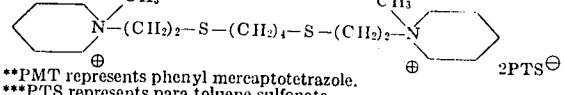
Substitution in receiver No. 6 of poly(1-methyl-4-vinylpyridinium methylsulfate) methylsulfate) or poly(2-vinylpyridinium methyl para toluene sulfonate) results in Dmax values of 1.50 and 1.43 respectively and in a cold tone, indicating that other polyvinyl pyridinium salts are also useful.

EXAMPLE 6

Monomeric Quaternary Salts Compared to Polymeric Quaternary Salts

A coating composition is prepared as in example 5 and components added as shown in the following table:

Quaternary Salt	Mg./ft.^{2} of Q-Salt	Other components	$D_{max.}$	Tone
Poly(1,2-dmethyl-5-vinylpyridinium methylsulfate	0.5	$KI+AgNO_3+PMT$**	1.56	Black.
Salt A*	0.3	None	0.52	Light brown.
Do	0.8	None	0.54	Do.
Do	0.3	$KI+AgNO_3+PMT$	0.61	Do.
Do	0.8	$KI+AgNO_3+PMT$	0.49	Do.
2-hydroxy-4-thiatetradecyl trimethylammonium PTS***	0.3	None	0.54	Yellow.
Do	0.8	None	1.12	Brown.
Do	0.3	$KI+AgNO_3+PMT$	0.96	Light brown.
Do	0.8	$KI+AgNO_3+PMT$	1.04	Brown.
Poly(1,2-dimethyl-5-vinylpyridinium methylsulfate)	0.5	None	1.60	Brownish-black.

* 

**PMT represents phenyl mercaptotetrazole.
***PTS represents para toluene sulfonate.
NOTE.—Substitution of monomeric materials as shown above, including 2-hydroxy-4-thiatetradecyl, trimethylammonium para toluene sulfonate, as described in U.S. Patent 3,314,789 fails to give satisfactory results.

The following results are obtained by processing as in example 1:

Coating No.	Tone
1	cold
2	warm
3	warm
4	warm

EXAMPLE 7

Iodide in Receiver Compared to Iodide in Negative and/or Processing Solution

A coating composition is prepared and processed as in example 1, except that it is modified as shown in the following table:

Toner in Receiver	Tone	Dmax
poly(1,2-dimethyl-5-vinylpyridinium methylsulfate), phenyl mercapto-tetrazole, $AgNO_3$	gray	0.9
poly(1,2-dimethyl-5-vinylpyridinium methylsulfate), phenyl mercapto-tetrazole, $AgNO_3$, KI	black	1.38
poly(1,2-dimethyl-5-vinylpyridinium methylsulfate), phenyl mercapto-tetrazole	gray	1.06
poly(1,2-dimethyl-5-vinylpyridinium methylsulfate), phenyl mercapto-tetrazole, KI	blue-black	1.28

Iodide is present in the negative and in the processing solution, but a major improvement is realized only with the addition of a small amount of iodide to the receiver sheet. These results indicate that potassium iodide in the receiver sheet is quite different than iodide in the negative and/or in the processing solution. Substitution of monomeric material as shown above, including 2-hydroxy-4-thiatetradecyl trimethylammonium para toluene sulfonate, as described in U.S. Pat. No. 3,314,789 fails to give satisfactory results.

EXAMPLE 8

Effect of Silver Dipyridyl Nitrate

Receiver sheets are prepared as in example 1 by preparing the following coating compositions:

	5	6	7	8	9
Nuclei melt of Example 1, g	48	48	48	48	48
Distilled water, ml	252	252	252	252	252
1% aqueous poly(1,2-dimethyl-5-vinyl-pyridinium methyl sulfate), ml	5	5	5	5	5
15% aqueous Saponin, ml	3	3	3	3	3
10% aqueous formaldehyde, ml	2.5	2.5	2.5	2.5	2.5
10% aqueous potassium iodide, ml	1.3	1.3	1.3	1.3	1.3
1% aqueous L-cysteine, ml	1.0				
1% aqueous silver dipyridyl nitrate, ml		5	5	2	2
0.1% 2,5-dimercapto-1,3,4-thiadiazole, ml			1.0		1.0

These melts are coated on polyethylene-coated paper support at 2.5 ml./ft.^{2} giving coverages as follows:

	Per ft.^{2}
gelatin	13.25 mg.
nuclei	6 μg.
polymer	0.4 mg.
potassium iodide	1 mg.
L-Cysteine	0.08 mg.
Silver dipyridyl nitrate	9.4 mg.
Dimercaptothiadiazole	0.009 mg.

The elements are tested as in example 1 with the following results:

No.	Dmax	Tone
5	1.15	cold
6	1.30	cold
7	1.44	cold
8	1.20	cold
9	1.18	cold

EXAMPLE 9

80% Gelatin/20% Polymer as a Vehicle for Palladium Nuclei

	10	11
Distilled water	72 ml	72 ml
Acetone	7 ml	7 ml
10% aqueous gelatin	8 ml.	8 ml
Palladium chloride (1.25 mg./ml. 1:300 Nitric Acid)	2.5 ml.	2.5 ml
pH 6		
10% aqueous Polymer 1*	2 ml.	
10% aqueous Polymer 2**		3 ml.
Sodium Borohydride (1g./20ml. water)	1 ml	1 ml
pH 9.1		
15.3% aqueous Saponin solution	1 ml.	1 ml.
2,5-dimercapto-1,3,4-thiadiazole (1 g./100 ml. 50% aqueous methanol)	0.55 ml.	0.55 ml
10% aqueous formaldehyde	1 ml.	1 ml

These solutions are coated as in example 1 and the resulting receivers tested as in example 1, with the following results:

Coating	Vehicle	Polymer, mg./ft.^{2}	Nuclei, μg.	Mottle	D_{max}	D_{min}	Tone
10	Gel/Polymer 1*	4	85	None	1.3	.01	Black.
11	Gel/Polymer 2**	4	84	None	1.3	.01	Black.

*Polymer 1—copolymer of 1,2-dimethyl-5-vinyl pyridinium methyl sulfate and N-cyanoacetyl-N'-methacrylyl-hydrazine in a 1:1 ratio.
**Polymer 2—copolymer of 1,2-dimethyl-5-vinyl pyridinium methyl sulfate and 2-acetoacetoxyethyl methacrylate in a ratio of 7:3.

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.

We claim:

1. A receiving layer for use in a diffusion transfer process, substantially free from an image, comprising a protein aceous binder, a silver precipitating agent, a water-soluble basic polyvinyl quaternary salt and an alkaline iodide, said quaternary salt having a polyvinyl chain of two to 10,000 monomeric units, at least one monomeric unit of which is linked to a five to six membered heterocyclic nucleus, one of said heteroatoms being a quaternary nitrogen atom.

2. A receiving layer of claim 1 in which said precipitating agent is finely divided noble metal nuclei.

3. A receiving layer of claim 2 in which said noble metal is platinum.

4. A receiving layer of claim 2 in which said metal nuclei are palladium.

5. A receiving layer of claim 2 in which said metal nuclei are gold.

6. A receiving layer of claim 1 in which said polyvinyl salt is poly(1,2-dimethyl-5-vinylpyridinium methylsulfate).

7. A receiving layer of claim 1 in which said polyvinyl salt is poly(1-methyl-4-vinylpyridinium methylsulfate).

8. A receiving layer of claim 1 in which said polyvinyl salt is poly(2-vinylpyridinium methyl para toluene sulfate).

9. A receiving layer of claim 1 which comprises a silver salt or complex.

10. A receiving element comprising a support having thereon said receiving layer of claim 1.

11. A receiving element of claim 10 in which said support is paper.

12. A photographic element comprising a support having thereon said receiving layer of claim 1 and having over said layer an overcoat of a photographic silver halide emulsion.

13. A receiving element according to claim 10 in which said support is plastic film base.

14. A photographic element comprising an image in a proteinaceous receiving layer on a support, said image obtained by a diffusion transfer process, said receiving layer comprising a proteinaceous binder, a silver precipitating agent, a water-soluble basic polyvinyl quaternary salt and an alkaline iodide, said quaternary salt having a polyvinyl chain of two to 10,000 monomeric units, at least one monomeric unit of which is linked to a five to six membered heterocyclic nucleus, one of said heteroatoms being a quaternary nitrogen atom.

15. A process of obtaining an image in a proteinaceous receiving layer comprising diffusing silver complex from undeveloped areas of an exposed and developing silver halide emulsion to said receiving layer, said receiving layer comprising a proteinaceous binder, a silver precipitating agent, a water-soluble polyvinyl quaternary salt and an alkaline iodide, said quaternary salt having a polyvinyl chain of two to 10,000 monomeric units, at least one monomeric unit of which is linked to a five to six membered heterocyclic nucleus, one of said heteroatoms being a quaternary nitrogen atom.

16. a process of claim 15 in which said receiving layer comprises a silver salt or complex.

17. A process of claim 15 in which the said polyvinyl salt is poly(1,2-dimethyl-5-vinylpyridinium methylsulfate).

18. A process of claim 15 in which the said polyvinyl salt is poly(1-methyl-4-vinylpyridinium methylsulfate).

19. a process of claim 15 in which the said polyvinyl salt is poly(2-vinylpyridinium methyl para toluene sulfonate).

* * * * *