This invention relates to the silver halide diffusion transfer process of photography and more particularly to methods for increasing the speed of the process and density of reproductions obtained thereby.

In the well-known silver halide diffusion transfer process of photography, an exposed emulsion layer is developed in the presence of a silver halide solvent, the emulsion layer being for at least a portion, or for the whole of the development period in effective contact with a receiving sheet, the surface of which generally carries a quantity of a silver precipitant which may comprise either physical development nuclei such as colloidal silver or silver sulfide or a chemical precipitant for silver ions, such as zinc sulfide. Development of the emulsion layer proceeds and is followed immediately by complexing of the residual unexposed silver halide with a silver halide solvent also present in the developer composition, and imagewise diffusion of the resulting silver complex to the receiving sheet where the silver precipitant causes the formation of an argentate (or containing silver) image.

We have discovered that when the silver halide diffusion transfer process is carried out in the presence of certainonium compounds including certain quaternary ammonium and ternary sulfonium salts, a number of improvements are unexpectedly obtained. These improvements include increase in density of the positive image, appreciable increase in emulsion speed and rate of development, and change in tone of the positive image from a warm brown to a neutral black color. These effects are separate and distinct from the effects of amines and the lower quaternary ammonium hydroxides in silver halide solvent transfer processes. Furthermore, in the presence of the onium compounds an increase in solvent action of the silver halide solvent is observable. Accordingly, it is possible to use an appreciably smaller amount of the silver halide solvent or a weaker silver halide solvent in such solution wherein the conventional sodium thiosulfate in the process without experiencing loss of density in the positive image. Also, the effect of the quaternary nitrogen compounds and ternary sulfonium compounds in the diffusion transfer process has been found to be separate and distinct from comparable usage of the compounds in connection with emulsions subjected to the older methods of simple development and fixation. For example, in the Piper U.S. patent application Serial No. 550,495, filed December 1, 1955, now U.S. Patent No. 2,886,437, granted May 12, 1959, quaternary ammonium compounds are utilized together with polyalkylene oxides to increase emulsion sensitivity over that attributable to the polyalkylene oxides themselves. However, when such quaternary nitrogen compounds are used in the present invention as illustrated hereinafter, emulsion speeds generally as high or higher are obtained in the absence of the polyalkylene oxide compound.

We have further discovered that in addition to effecting the mentioned improvements in the silver halide diffusion transfer processes, when the quaternary ammonium salts are employed in the diffusion transfer processes in conjunction with certain tone-modifying compounds, pronounced improvement in image tone of the argentate images formed in the processes is obtainable even though the processes are carried out at moderately low pH. That is, the silver halide diffusion transfer processes are ordinarily carried out using developer solutions having relatively high pH of the order of 12 so as to maintain a high development rate necessary for the proper functioning of the process. It is desirable to operate the diffusion transfer processes at lower pH partly because the developers of low alkalinity produce less skin irritation, are less costly, handle better, and the print quality is improved. However, at moderately low pH of the order of 10, the tone of the argentate image is characteristically warm brown. This is true even if tone-modifying compounds such as the mercaptotetrazoles are employed in the emulsion, the developer or both. Accordingly, when the quaternary salt compounds and certain tone-modifying compounds described hereinafter are present at the time the argentate image is being formed in the receiving sheet, a profound improvement of the image tone is obtained, i.e., shift in color of the argentate image from brown to black, and this effect is obtainable even when carrying out the diffusion transfer processes with stable alkaline developer compositions of pH of the order of about 10 to 10.4. This degree of improvement in image tone cannot be obtained in such solutions by use of the quaternary salt alone in any concentration or by use of the tone modifying compound alone in any concentration.

The objects of the invention therefore include providing means for increasing the effective speed of diffusion transfer processes, means for improving the tone of the prints obtained in the diffusion transfer processes and means for carrying out the diffusion transfer processes at moderate pH. Other objects of our invention will become apparent from the following description thereof.

These objects of the invention are accomplished in part by providing suitable emulsions, developer solutions and receiving layers and carrying out diffusion transfer processes therewith in the presence of quaternary ammonium or ternary sulfonium compounds alone or additionally in the presence of certain tone modifying compounds.

The onium compounds of the invention which are used in the diffusion transfer processes are quaternary ammonium and ternary sulfonium compounds, the onium radical of which has attached to it a chain containing at least 7 atoms such as carbon atoms, oxygen atoms, etc. Included among the onium compounds are the following representative groups of compounds:

(A) Trialkyl sulfonium salts in which one of the alkyls contains at least 7 carbon atoms. These sulfonium salts have the general structure

\[ R_1 \]

\[ R_2 \]

\[ X \]

\[ R_4 \]

where:

- \( R_1 \) and \( R_4 \) represent alkyl groups, e.g., methyl, carboxymethyl, ethyl, propyl, butyl, etc., or aralkyl groups, e.g., benzyl,
- \( R_2 \) represents an alkyl group of at least 7 atoms, e.g., heptyl, nonyl, decyl, dodecyl, tetradecyl, cetyl, etc., and
- \( X \) represents an anion, e.g., chloride, bromide, iodide, perchlorate, p-toluene sulfonate, alkyl sulfate, etc.

Specific compounds having the above formula are:

- Sulf. I Dimethyl n-dodecyl sulfonium p-toluene sulfonate
- Sulf. II Dimethyl n-heptyl sulfonium p-toluene sulfonate
- Sulf. III Dimethyl n-nonyl sulfonium p-toluene sulfonate
- Sulf. IV Dimethyl n-decyl sulfonium p-toluene sulfonate
- Sulf. V Dimethyl n-tetradecyl sulfonium p-toluene sulfonate
Sulf. VI Dimethyl n-octadecyl sulfonium p-toluene sulfonate
Sulf. VII Carboxethoxymethyl methyl dodecyl sulfonium p-toluene sulfonate
Sulf. VIII (z,y-Diketo-butyl) dodecyl methyl sulfonium p-toluene sulfonate
Sulf. IX (1,3-di-methylbutyral) hydrazido - methyl - methoxyethyl-sulfonium p-toluene sulfonate
Sulf. X Carboxoxymethyl dodecyl methyl sulfonium p-toluene sulfonate
Sulf. XI Carboxoxymethyl-dodecyl-methyl-sulfonium inner salt
Sulf. XII Diethyl n-dodecyl sulfonium p-toluene sulfonate
Sulf. XIII Benzyl ethyl n-dodecyl sulfonium ethanesulfonate

Other useful compounds having the above general formula are described in the Carroll and Allen U.S. Patent 2,275,727, granted March 10, 1942.

(B) Polysulfonium salts having the general structure

wherein R, R1, R2 and Z are as above indicated and Z represents a bivalent organic radical such as the ethylene-bis-oxy-methyl radical present, for example, in the compound ethylene-bis-(oxymethyl dodecyl methyl sulfonium p-toluene sulfonate)

Sulf XIV 

Other suitable polysulfonium salts are disclosed by the Carroll and Allen U.S. Patent 2,288,226, granted June 30, 1942.

(C) Tetraalkyl quaternary ammonium salts having the general formula

in which X is an anion or acid radical, for example, halide, p-toluene sulfonate, alkyl sulfate or perchlorate, R, R1, R2 and R3 are alkyl groups of which at least one has a chain or seven or more atoms such as carbon atoms, carbon atoms plus oxygen atoms, sulfur atoms or nitrogen atoms and ring systems, while the remaining R groups are alkyl such as methyl, ethyl, butyl, and benzyl as exemplified hereinafter.

In addition, the quaternary nitrogen atom may be linked through one of the R groups to a second quaternary nitrogen atom in the bis-quaternary ammonium salts having the general structure

wherein R, R1 and R3 are as just mentioned and Z is a bivalent radical as exemplified by those radicals disclosed in U.S. Patent 2,288,226, for example, the decamethylene radical.

(D) Quaternary ammonium salts in which the quaternary nitrogen atom is a part of a ring system and which have the general formula

where X is as above mentioned and R represents a chain of at least seven atoms and Z represents the atoms necessary to complete a cyclic structure such as a pyridyl, u-picoly, piperidyl or morpholinyl nucleus. R may contain a second quaternary nitrogen atom as present in the bis-quaternary ammonium compounds having the structure

(F) Bis-quaternary salts whose quaternary nitrogen atoms are connected by means of a linear chain containing less than 34 atoms such as bis-amide, bis-urethane, bis-urea, bis-ester, etc. compounds having the following general formulas:

Q(RNHC(O)O)n.R'OCONHANHCOR', [OOCNR]n-1.Q'

Q(RNHCOOA)(OOCNR')n-.Q'

QRCNH(A)n-NHCOR'Q

QRCNHAQ'

QROOCA(COOR')n-1.Q'

wherein Q and Q' represent organic radicals containing quaternary nitrogen atoms, R and R' represent alkyl or aromatic groups, R2 represents an alkyl group of from 1 to 4
carbon atoms, \( n \) represents a positive integer of from 1 to 2, \( A \) represents a chain of atoms of the class consisting of carbon, nitrogen, oxygen and sulfur atoms, there being less than 34 atoms present in the linear chain connecting \( Q \) to \( Q' \).

These compounds are described in more detail in the Beavers, Wilson and Graham U.S. patent applications Serial Nos. 699,197, 699,198 and 699,199, filed November 27, 1957, now respectively U.S. Patents 2,940,851 granted June 14, 1960, 2,944,896 granted July 12, 1960, and 2,940,855 granted June 14, 1960. Representative compounds of this class are as follows:

\[
\begin{align*}
CH_3-\text{CONH}(CH_2)NH\text{CONH}(CH_2)NH_2 &\quad \text{C}_{20}H_{20}O_2, \\
CH_3-\text{CONH}(CH_2)NH\text{CONH}(CH_2)NH_2 &\quad \text{C}_{20}H_{20}O_2, \\
CH_3-\text{CONH}(CH_2)NH\text{CONH}(CH_2)NH_2 &\quad \text{C}_{20}H_{20}O_2, \\
(CH_3)\text{CONH}(CH_2)\text{CONHCH}(CH_2)NH_2 &\quad \text{C}_{20}H_{20}O_2, \\
(CH_3)\text{CONH}(CH_2)\text{CONHCH}(CH_2)NH_2 &\quad \text{C}_{20}H_{20}O_2, \\
(CH_3)\text{CONH}(CH_2)\text{CONHCH}(CH_2)NH_2 &\quad \text{C}_{20}H_{20}O_2, \\
(CH_3)\text{CONH}(CH_2)\text{CONHCH}(CH_2)NH_2 &\quad \text{C}_{20}H_{20}O_2, \\
\end{align*}
\]

The anion of the above ammonium and sulfonium compounds may be any acid radical not injurious to photographic emulsions, for example, p-toluene sulfonate, chloride, bromide, iodide, perchlorate or alkyl sulfate.

The introduction of halide anions into photographic silver halide emulsions alters the halide concentration in the emulsion and compensating changes in the emulsion may be desirable if such salts are employed. For this reason, it is ordinarily preferred to employ compounds containing anions other than halides. Perchlorates and p-toluene sulfonates are advantageous employed.

The use of the quaternary ammonium compounds in various ways in different solvent transfer processes will now be illustrated by means of the following examples:

In the examples the quaternary nitrogen compounds whose use is illustrated are referred to for convenience as follows:

Quat. I — Tetradecamethylene-bis (pyridinium perchlorate)

Quat. II—7,18-diaza-6,19-dioxotetracosenone-1,2,4-bis (pyridinum perchlorate) (Beavers-Wilson invention above)

Quat. III—5,6,9,12,15,18,21,24,27,30-hexacosane-1,2,4-bis (pyridinum perchlorate) (Carroll et al. U.S. Serial No. 627,135, filed December 10, 1956)

Quat. IV—\( \alpha \)-Picolinium-\( \beta \)-phenyl-ethyl bromide

In the examples when comparing the effectiveness of the quaternary nitrogen compounds present in the emulsion, developer or receiving sheet, the particular emulsion is exposed on an intensity-scale densitometer and development then initiated at room temperature with a developing solution of the following composition unless otherwise indicated:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Grams per mole</th>
<th>Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. Hydroquinone</td>
<td>32.8</td>
<td>396</td>
</tr>
<tr>
<td>Sodium sulfite (anhydrous)</td>
<td>75.0</td>
<td>410</td>
</tr>
<tr>
<td>Sodium thiosulfate</td>
<td>14.0</td>
<td>428</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>26.7</td>
<td>440</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>0.12</td>
<td>504</td>
</tr>
<tr>
<td>Water to make 1.0 liter.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

If desired, p-phenylenediamine may replace the hydroquinone and thiosulfate in the formula since it functions both as a developing agent and as silver halide solvent in the processes described hereinafter.

Following initiation of development the emulsion is then rolled into contact with a receiving sheet containing a suitable silver precipitant and left in contact until an argential image has formed on the sheet from the silver halides transferred thereto.

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Unless otherwise indicated, the receiving sheet in the examples was prepared as follows: The following solutions were provided:

Solution A—

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>246</td>
</tr>
<tr>
<td>0.5 molar lead acetate</td>
<td>2.0</td>
</tr>
<tr>
<td>0.5 molar zinc nitrate</td>
<td>0.36</td>
</tr>
<tr>
<td>0.1 molar silver nitrate</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Solution B—

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>246</td>
</tr>
<tr>
<td>0.5 molar sodium sulfide</td>
<td>1.2</td>
</tr>
<tr>
<td>0.5 molar sodium metasilicate</td>
<td>5.0</td>
</tr>
<tr>
<td>1.0 molar nitric acid</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Jet streams of the two solutions were passed at equal rates into a funnel for rapid mixing, and thereafter the mixture was allowed to trickle through a column packed with glass helices over a period of approximately 12 seconds allowing the mixture to fall into a gelatin solution being stirred rapidly, the gelatin solution comprising 15 grams of gelatin, 90 cc. of water, the temperature being 40° C. The mixing of the solutions required about 5 minutes. To 200 cc. of the resulting dispersion which had been stirred for 1 hour were added 2.8 grams of lead acetate. After 15 minutes of stirring, the pH was adjusted to 3.0 with 6 molar nitric acid and thereafter the composition was coated at a coverage of 2 cc. per square foot on a film base.

The densities of the transferred positive images obtained on the receiving surfaces were read by transmission and from the resulting characteristic curves speeds were measured in units of 100 (1-log E) where E is the exposure in meter-candle seconds required to produce a density of 0.3 above fog. Since the densities were read by transmission and the positive images were designed for viewing by reflection, the effective densities are higher than those shown in the examples. From the data in the examples it will be observed that the maximum effectiveness of the quaternary nitrogen compounds in increasing speed occurs when these compounds are used in the emulsion.

EXAMPLE 1

Addition of quaternary ammonium salt to the emulsion

An extremely high-speed bromoiodide emulsion optically sensitized with methyl-3,3'-diethyl seleno carbocyanine iodide and chemically sensitized with gold and sulfur compounds was provided. Also there was added to the emulsion 2 grams per mole of silver halide of 4-hydroxy-6-methyl-1,3,4a,7-tetraazaindene (indicated as "AZA" hereafter). The amounts of the quaternary nitrogen compound indicated in the following table were then added to samples of this emulsion and the samples tested as described above:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Grams per mole</th>
<th>Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quat. III</td>
<td>0.1</td>
<td>396</td>
</tr>
<tr>
<td>Quat. III</td>
<td>0.2</td>
<td>410</td>
</tr>
<tr>
<td>Quat. III</td>
<td>0.3</td>
<td>428</td>
</tr>
<tr>
<td>Quat. III</td>
<td>0.4</td>
<td>434</td>
</tr>
<tr>
<td>Quat. III</td>
<td>0.5</td>
<td>440</td>
</tr>
<tr>
<td>Quat. III</td>
<td>0.6</td>
<td>440</td>
</tr>
</tbody>
</table>

EXAMPLE 2

Addition of quaternary ammonium salt to the developer

An emulsion similar to that of Example 1 was provided except that decamethylene-bis-benzoiazolium perchlorate was used instead of the azaindene stabilizer. The diffusion transfer process described above was car-
ried out using portions of the above standard developer to which the following additions had been made:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Grams per liter Developer</th>
<th>Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quat. I</td>
<td>0</td>
<td>325</td>
</tr>
<tr>
<td>Quat. II</td>
<td>0.06</td>
<td>326</td>
</tr>
<tr>
<td>Quat. III</td>
<td>0.12</td>
<td>341</td>
</tr>
<tr>
<td>Quat. IV</td>
<td>0.12</td>
<td>341</td>
</tr>
<tr>
<td>Quat. V</td>
<td>0.5</td>
<td>343</td>
</tr>
<tr>
<td>Quat. VI</td>
<td>1.0</td>
<td>350</td>
</tr>
<tr>
<td>Quat. VII</td>
<td>1.0</td>
<td>350</td>
</tr>
<tr>
<td>Quat. VIII</td>
<td>0</td>
<td>353</td>
</tr>
<tr>
<td>Quat. IX</td>
<td>0.5</td>
<td>353</td>
</tr>
<tr>
<td>Quat. X</td>
<td>0.12</td>
<td>353</td>
</tr>
<tr>
<td>Quat. XI</td>
<td>0.12</td>
<td>353</td>
</tr>
<tr>
<td>Quat. XII</td>
<td>0.5</td>
<td>353</td>
</tr>
<tr>
<td>Quat. XIII</td>
<td>1.0</td>
<td>353</td>
</tr>
</tbody>
</table>

Compared to Example 1, the data show that the quaternary compounds are somewhat less effective in the developer than in the emulsion.

**EXAMPLE 3**

*Addition of quaternary ammonium salt to the emulsion*

The emulsion of Example 2 was used and the following amounts of quaternary nitrogen compounds were incorporated into samples of the receiving sheet:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Milligrams per 60 ft. receiver</th>
<th>Transmission, D max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quat. I</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>Quat. II</td>
<td>0.12</td>
<td>1.14</td>
</tr>
<tr>
<td>Quat. III</td>
<td>1.0</td>
<td>1.15</td>
</tr>
</tbody>
</table>

When the quaternary ammonium salt is incorporated in the receiver, its action on the development of the negative takes place only after contact has been made between the receiver and the negative which has previously been wet with developer.

**EXAMPLE 4**

*Addition of quaternary ammonium salt and stabilizing agent to the emulsion*

The emulsion of Example 1 was used to which had been added the azaindene compound "AZA" above, and cadmium chloride in the amount shown in the following table:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Grams per mole AgX</th>
<th>Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZA</td>
<td>2.0</td>
<td>360</td>
</tr>
<tr>
<td>AZA</td>
<td>2.0</td>
<td>360</td>
</tr>
<tr>
<td>AZA</td>
<td>0.4</td>
<td>420</td>
</tr>
<tr>
<td>AZA</td>
<td>0.4</td>
<td>420</td>
</tr>
<tr>
<td>AZA</td>
<td>0.4</td>
<td>420</td>
</tr>
<tr>
<td>AZA</td>
<td>0.4</td>
<td>420</td>
</tr>
<tr>
<td>Quat. II</td>
<td>0.4</td>
<td>420</td>
</tr>
<tr>
<td>Quat. III</td>
<td>0.4</td>
<td>420</td>
</tr>
<tr>
<td>Quat. IV</td>
<td>0.4</td>
<td>420</td>
</tr>
<tr>
<td>Quat. V</td>
<td>0.4</td>
<td>420</td>
</tr>
<tr>
<td>Quat. VI</td>
<td>0.4</td>
<td>420</td>
</tr>
</tbody>
</table>

**EXAMPLE 5**

*Addition of a sulfonium salt to the developer and quaternary ammonium salt to the emulsion*

To a high-speed bromide emulsion optically sensitized as in Example 1 and chemically sensitized with sulfur and gold compounds, were added 2 grams of AZA, 0.4 gram Quat. II and 10 grams of cadmium chloride per mole of silver halide. To the standard developer composition given above was added 2.0 grams of 1-phenyl-3-pyrazolidone and 50 grams of xylene sulfonate per liter. A sulfonium compound dimethyl-ethyl-sulfonium-p-toluene sulfonate (Sulf. III) was also added to one sample of the developer as shown in the following table:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Grams per liter Developer</th>
<th>D max.</th>
<th>Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulf. III</td>
<td>0</td>
<td>0.42</td>
<td>437</td>
</tr>
<tr>
<td>Sulf. III</td>
<td>0.2</td>
<td>0.77</td>
<td>437</td>
</tr>
</tbody>
</table>

From these data it is apparent that the addition of the sulfonium compound to the developer did not greatly increase speed much but this speed increase was real as substantiated by other tests.

**EXAMPLE 6**

*Addition of quaternary ammonium salt to the emulsion and use of high energy developer*

The emulsion of Example 5 was used, a quaternary nitrogen compound being added to one sample of the emulsion as shown in the table following. In this example the standard developer was modified as follows to obtain maximum development activity:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Grams per liter AgX</th>
<th>D max.</th>
<th>Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quat. II</td>
<td>0</td>
<td>0.76</td>
<td>438</td>
</tr>
<tr>
<td>Quat. III</td>
<td>0.4</td>
<td>0.76</td>
<td>438</td>
</tr>
</tbody>
</table>

As illustrated in the above examples, useful results are obtained with about 0.03 to 1.0 gram of the quaternary nitrogen compound per mole of silver halide in the emulsion or per liter if in the developer.

The following examples illustrate usage of the ternary sulfonium compounds in diffusion transfer processes.

As mentioned above, the ternary sulfonium compounds themselves have little solvent action on silver halide but when employed with a silver halide solvent such as hypo, sodium sulfite, potassium thiocyanate or potassium bromide, the rate of solution of the silver halide through complexing with the solvent is increased considerably. Accordingly, in the process a greater amount of the silver halide is made available for formation of the positive image on the receiving sheet. Thus, better reproductions are obtained and a smaller amount of silver halide solvent or a weaker silver halide solvent can be used in the system. For example, a developer may be used containing 1/2 to 3/4 of the usual amount of hypo and a speed increase of about 0.45 log E is obtained when theonium compound is also present. Similar effects are obtainable when sodium thiocyanate and to a lesser extent high concentrations (50–200 grams per liter) of potassium bromide are substituted for hypo. A weak image can even be obtained with sodium sulfite in the presence of the onium compound. When the onium compound is used in the developer in concentrations of the order of 1.0 gram per liter, an increase in speed of about 0.15 to 0.30 log E is readily obtainable. At much higher concentrations a warmer toned image is obtained with loss of maximum density partly because of development of fog in the negative layer which tends to reduce the amount of silver halide available for transfer. When employed in the emulsion, it is preferred to maintain fog at a low level by use of antifogulant such as the azaindines provided below.

The maximum effectiveness of the ternary sulfonium
3,017,370

9 compounds occurs when they are used in the developer compositions and is generally accompanied by either no change or an increase in maximum density of the transferred positive image as compared to a developer free of the sulfonium compound.

EXAMPLE 7
Sulfonium compound in developer

The receiving sheet was prepared as follows: A solution containing 100 cc. of water and 1 cc. of 0.5 molar sodium sulfide was added in 1 minute and 20 seconds to a solution of 1 cc. of 0.5 molar zinc nitrate and 0.5 cc. of 10 percent gelatin solution in 375 cc. of water at 40°C. Twenty-five cc. of a 10 percent gelatin solution were then added and 1.5 grams of lead acetate and a suitable gelatin hardening agent. The resulting composition was then coated at a coverage of 6 cc. per square foot upon a film support.

The emulsion used was a medium-speed bromoiodide emulsion.

The developer had the same composition as the standard hydroquinone developer given preceding Example 1 except that the hypo was reduced from the normal level of 14 grams to 7.5 grams per liter and 0.95 gram of di-methyl - n - dodecyl sulfonium - p - toluene sulfonate was added per liter. The diffusion transfer process of Example 1 was carried out with the result that a speed increase of 0.3 log E in the shoulder regions, a 0.6 log E increase in the toe regions of the characteristic curve, and a maximum density increase of about 0.15 and a slightly colder tone was obtained compared to the same emulsion processed in the standard hydroquinone developer free of the sulfonium compound and containing the higher level of hypo. By transmission the increase in density was 0.42.

EXAMPLE 8
Sulfonium compound in developer

A receiver was prepared by first mixing rapidly a solution comprising

Water ----------------------------- cc. 1200
0.5 M sodium sulfide ---------------- cc. 6.0

with a solution comprised of—

Water -------------------------------- cc. 4750
Gelatin -------------------------------- g. 0.5
0.5 M zinc nitrate ------------- cc. 6.0
0.5 M lead acetate ------------- cc. 3.0

at 40°C. To 2000 cc. of this solution was added after 20 minutes of stirring 20 grams of gelatin. To 600 cc. of the resulting solution was added after one hour of stirring 10.5 cc. of a 0.5 M lead acetate solution. This solution was adjusted to a pH of 3.5 with nitric acid, a coating aid and a hardening agent were added, and then the solution was coated on film support at 6.0 cc. per square foot.

The negative consisted of a gelatino-silver bromoiodide emulsion containing 6.3 mole percent iodide, optimally sensitized with methyl-3,3'-diethyl-seleno-carbocyanine iodide, and containing the antifoggent 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene. The emulsion was coated on film support so as to obtain 0.09 g. silver and 0.50 g. gelatin per square foot.

The developer was the same as the standard hydroquinone-control developer except that 0.5 gram per liter of the sulfonium compound of Example 7 was used. When processing was carried out as above, a speed gain of 0.45 log E was realized over the same process in which the sulfonium compound was omitted from the developer. The increase in D max. was 0.15 (by reflection) and 0.07 (by transmission).

EXAMPLE 9
Sulfonium compound in emulsion

The receiving sheet of Example 8 and the standard hydroquinone developer of Example 1 were used. The emulsion was a high-speed bromoiioide emulsion free of optical sensitizing dye and to which had been added 0.25 gram of the sulfonium compound of Example 7 and 2.0 grams of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene per mole of silver halide. The above diffusion transfer process yielded a positive image showing an increase in maximum density of 0.15 by reflected light compared to a comparable process carried out with a sample of the emulsion free of the sulfonium compound. D max. by transmission was 0.25.

EXAMPLE 10
Sulfonium compound in receiving sheet

The emulsion, developer and procedure of Example 7 were employed with the receiving sheet of Example 8 above to the coating of which had been added 1.0 gram of the sulfonium compound of Example 7. An increase in density of 0.15 was obtained in the positive compared to the control process where the sulfonium compound was absent from the receiving sheet. D max. (transmission) 0.13.

EXAMPLE 11
Sulfonium compound in receiving sheet

The process of Example 10 was carried out except that the receiving sheet consisted of a water resistant paper sheet carrying a gelatin coating containing colloidal silver and 15 milligrams of the sulfonium compound of Example 7 per square foot. The image obtained in the positive was brown in color and of significantly higher density compared to a light yellow image contained in the control process using the same receiving sheet free of sulfonium compound. D max. (transmission) 0.37.

EXAMPLE 12
Sulfonium compound in developer

The process of Example 11 was carried out except using 2.0 grams per liter of the sulfonium compound only in the developing solution. The same improvement in image tone was obtained. The maximum density (transmission) was 0.73, compared with 0.16 for the control.

EXAMPLE 13
Sulfonium compound in developer

The receiving sheet of Example 1 and a fast bromoiodide emulsion were used in the process. The standard hydroquinone developer contained 0.4 gram per liter of Sulf. I. In the transfer process, a speed gain of 0.15 log E was obtained compared to the control process using no sulfonium compound in the developer.

When 1.0 gram per liter of 1-phenyl-3-pyrazolidone was further added to the developer composition containing the sulfonium compound, an additional 50 percent increase in speed was obtained in the process.

EXAMPLE 14
Use of thiocyanate as the silver halide solvent

Medium-speed panchromatic bromoiodide emulsion was used with the receiving sheet of Example 1 and the following developer composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroquinone</td>
<td>35</td>
</tr>
<tr>
<td>Sodium sulfite</td>
<td>80</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>28.5</td>
</tr>
<tr>
<td>Sodium thiocyanate</td>
<td>20</td>
</tr>
<tr>
<td>Water to 1 liter</td>
<td></td>
</tr>
</tbody>
</table>

Addition of 0.2 gram of Sulf. I produced an increase
in maximum density of 0.15 in the transferred positive image.

EXAMPLE 15

Sulfonium compound in developer

The emulsion and receiving sheet of Example 14 were employed. The standard hydroquinone developer of Example 1 was used except reducing the hypo concentration by \( \frac{1}{2} \), to 10 grams per liter, and 0.5 gram per liter of the different sulfonium compounds shown in the following table were added to samples of the developer. The speed was evaluated as mentioned above and the improvement compared to the control developer free of sulfonium compound is indicated in the table as \( \Delta \log E \).

### Sulfonium Salt | Speed Increase, \( \Delta \log E \)
--- | ---
I | +0.05
II | +0.06
III | +0.08
IV | +0.14
V | +0.16
VI | +0.09
VII | +0.10
VIII | +0.10
IX | +0.10
X | +0.10
XI | +0.07
XIV | +0.07

From similar tests it has been ascertained that when the sulfonium compounds are present in amounts up to about 2.0 grams per liter of developer, the most significant improvements in speed and other characteristics of the process are obtained. The choice of elements of the process will naturally be found to also influence the optimum amount of sulfonium compound to use and similarly for the above quaternary ammonium compounds.

The azaindene stabilizing agents suitable for use in the invention as indicated above are those such as described in the Carroll et al. U.S. patent application Serial No. 627,135, filed December 10, 1956, as follows: 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, 5 - carboxy-4-hydroxy-1,3,3a,7-tetraazaindene (Reynolds et al. U.S. Patent 2,756,147, granted July 24, 1956), 1,2-bis(4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene - 5 - yl)ethane, 1,2,3,4-tetraakis(4-hydroxy - 6 - methyl-1,3,3a,7-tetraazaindene-5-yl)butane, 2-amino - 5 - carboxy-4-hydroxy-1,3,3a,7-tetraazaindene, 4 - hydroxy - 2 - \( \beta \) - hydroxyethyl-6-methyl-1,3,3a,7-tetraazaindene, 5 - carboxy-4-hydroxy-1,3,3a,7-tetraazaindene (Reynolds et al. invention above), 7 - hydroxy - 1,2,3,4,6 - pentaazaindene, 4 - hydroxy-2-\( \gamma \)-hydroxypropyl-6-methyl-1,3,3a,7 - tetraazaindene and 4-hydroxy-2-(4-pyridyl)-6-methyl-1,3,3a,7 - tetraazaindene.


In those cases where the diffusion transfer process involves the development of dye images by means of the paraphenylenediamine type of developing agents, suitable colored or colorless coupler compounds of the phenolic hydroxyl, pyrazoline and open-chain reactive methylene types may be employed in the emulsion, receiving sheet, or developer.

The quaternary ammonium and ternary sulfonium compounds indicated are similarly beneficial for use with other types of diffusion transfer processes such as that disclosed in the Yackel et al. U.S. patent application Serial No. 867,705, filed May 23, 1956, wherein a unitary element is provided having, for example, a removable cellulose ether phthalate silver halide emulsion layer coated upon a receiving layer containing a silver precipitant. The quaternary ammonium or ternary sulfonium compound may be present in either the receiving layer or the developer solution. The element is exposed in a suitable manner, development initiated in the presence of a silver halide solvent and a positive image formed in the receiving layer accompanied by removal of the overlying emulsion layer containing the negative image.

Additional well-known silver precipitating agents for use in the processes of the invention of the nature disclosed in the above Yackel et al. invention give useful results in the present process.

When the indicated quaternary ammonium salts are used in the process of the Yackel et al. invention, it is advantageous to also employ one of the azaindene stabilizing compounds preferably together with a tone modifying agent. That is, when a high speed coarse-grained emulsion is to be used containing the cellulose ether phthlate vehicle and a minimum of gelatin, the stability of the emulsion is increased by adding an azaindene compound as mentioned in Example 9 above. The stability conferred by this compound is greater than obtainable with antifogging compounds of the benzothiazole and mercaptotetrazole types; however, a loss in \( D_{\text{max}} \) is sustained and it is desirable to further add a quaternary nitrogen compound such as Quast. If above the receiving layer \( D_{\text{max}} \) is sustained and preferably also 2-mercaptop-5-phenyl-1,3,4-oxadiazole to improve the tone of the image.

3-pyrazolidone silver halide developing agents which may be employed in the developer composition alone or in conjunction with other silver halide developing agents such as hydroquinone may be suitably employed in the composition. The pyrazolidone compounds may be alone or in conjunction with ascorbic acid for the purposes disclosed in the patent. Also, the silver halide developing agents may be present in the emulsion layer rather than in the alkaline solution containing the silver halide solvent. Thus developer compositions comprising the combination of a silver halide solvent, a 3-pyrazolidone developing agent, a hydroquinone such as hydroquinone, per se, toluidywhole, and chlorobenzene, and one of the mentioned quaternary ammonium salts, especially the cyclammonium quaternary salts are especially useful in the diffusion transfer processes.

As mentioned previously, when the quaternary salts are employed in the diffusion transfer processes in conjunction with certain tone modifying compounds, pronounced improvement in image tone is obtainable even when the processes are carried out at moderately low pH. Suitable quaternary salts are those mentioned above. The following quaternary salts are representative cyclammonium quaternary salts, which are particularly effective in combination with the tone modifying compounds.

- Tetraendecamethylene-bis (pyridinium perchlorate)
- \( \alpha \)-Dimethyldihydrocarbamate-N-methyl pyridinium p-toluenesulfonate
- Decamethylene-\( \alpha,\alpha\)-bis (oxyethyl pyridium perchlorate)

13
1-methyl-2-nonanoyl pyridinium -p-toluen sulfonate
Heptoxymethyl-2,4,6-trimethyl pyridinium chloride
Tetradecamethylene-bis-(trimethyl ammonium perchlorate)
3-methyl-2-phenethyl isoquinolinium bromide
1-phenethyl-n-picolininium bromide
4,4,10,10 - tetraoxo - 4,10 - dithiatriecane - bis - (pyridinium perchlorate)

A quaternary ammonium base, β-hydroxy ethyl trimethyl ammonium hydroxide has been used as a agent for promoting photographic quality in solvent transfer processes. However, this compound and other similar quaternary ammonium bases and salts which consist of an onium radical attached to short chain aliphatic groups such as tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, tetra-n-propyl ammonium hydroxide, etc are not suitable for the purposes of this invention.

The mentioned tone modifying compounds which are useful in combination with the quaternary salts, and which are particularly useful in combination with the cyclammonium quaternary salts given immediately above, are the following cyclic and open chain sulfur and nitrogen-containing compounds which are characterized as being organic compounds forming with silver ion, such as present during the transfer of dissolved silver halide, a silver compound less soluble than silver bromide in water and solutions of silver halide solvents. It is known that some of these organic compounds are useful in controlling the tone of silver images but as mentioned above and shown in the examples hereafter pronounced improvement in tone results when these organic sulfur and nitrogen-containing compounds are used in combination with the onium compounds compared to using either compound alone.

2-mercapto-1-phenyl-tetrazole

2-mercapto-5-phenyl-1,3,4-oxadiazole

Dihydro-1,4-benzothiazin-3-one

2-γ-pyridylbenzothiazoline hydrochloride

5-t-butyl-6-methyl-1,2,3a,7-tetrazaindene-4-thiol

14
7-seleno-1,3,4,6-tetrazaindene

2,6-dimethyl-1,3,3a,7-tetrazaindene-4-thiol

5-ethyl-6-methyl-1,2,3a,7-tetrazaindene-4-thiol

bis-(5-p-hydroxyphenyl-1,3,4-oxadiazolyl) disulfide

2-mercapto-5-(p-hydroxyphenyl)-1,3,4-oxadiazole

μ-Thiolfuctoxazoline

4-oxo-2,3,3a,4,5,6-hexahydro-1,3a-diazo-7-thiaindene

5-aminobenzotriazole

S-thiobenzoythioglycolic acid

4-aminobenzotriazole-HCl

S-carbobenzoxy-L-cysteine
19

2-mercapto-5-(o-tolyl)-1,3,4-oxadiazole

\[
\begin{array}{c}
\text{NH} \\
\text{O} \\
\text{S} \\
\text{N} \\
\text{O} \\
\text{H}
\end{array}
\]

2-mercapto-5(o-methoxyphenyl)-1,3,4-oxadiazole

\[
\begin{array}{c}
\text{NH} \\
\text{O} \\
\text{S} \\
\text{N} \\
\text{OCH_3} \\
\text{O}
\end{array}
\]

2-mercapto-5(p-methoxyphenyl)-1,3,4-oxadiazole

\[
\begin{array}{c}
\text{NH} \\
\text{O} \\
\text{S} \\
\text{N} \\
\text{OCH_3} \\
\text{O}
\end{array}
\]

2-mercapto-5-(p-nitrophenyl)-1,3,4-oxadiazole

\[
\begin{array}{c}
\text{NH} \\
\text{O} \\
\text{S} \\
\text{N} \\
\text{NO_2} \\
\text{O}
\end{array}
\]

2-mercapto-5-(m-nitrophenyl)-1,3,4-oxadiazole

\[
\begin{array}{c}
\text{NH} \\
\text{O} \\
\text{S} \\
\text{N} \\
\text{NO_2} \\
\text{O}
\end{array}
\]

\(\beta\)-mercapto-propionic acid

\[
\begin{array}{c}
\text{HS} \\
\text{CH_2COOH}
\end{array}
\]

1-phenyl-2(1)-thioquinolone

\[
\begin{array}{c}
\text{N} \\
\text{S}
\end{array}
\]

2-mercapto-\(\beta\)-naphthoxazole

\[
\begin{array}{c}
\text{N} \\
\text{S}
\end{array}
\]

3-phenyl rhodanine

\[
\begin{array}{c}
\text{S} \\
\text{N} \\
\text{O} \\
\text{H}
\end{array}
\]

1-cyclohexyl-5-mercaptotetrazole

\[
\begin{array}{c}
\text{S} \\
\text{N} \\
\text{N} \\
\text{N}
\end{array}
\]

Dimethylcarbamyldimethyl-thiocarbamylsulfide

\[
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{S} \\
\text{S}
\end{array}
\]

Sym-tetra-\(\alpha\)-pyridyl-bis-(formamidine)-disulfide

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{C} \\
\text{N}
\end{array}
\]

3,017,270

20

5-(\(\gamma\)-pyridyl methyldiene)-2-thiono-thiazolidone

\[
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{O}
\end{array}
\]

\(\psi\)-1,5-diphenyl-3-mercapto-4-methyl-1,2,4-thiazole

\[
\begin{array}{c}
\text{H} \\
\text{O}
\end{array}
\]

2-mercaptobenzoxazole

\[
\begin{array}{c}
\text{O} \\
\text{S}
\end{array}
\]

3 - amino-6-keto-4-methyl-1-phenyl-2-thiono-1,2,3,6-tetrahydropyrimidine

\[
\begin{array}{c}
\text{O} \\
\text{S}
\end{array}
\]

2-thionothiazolidone

\[
\begin{array}{c}
\text{H} \\
\text{S}
\end{array}
\]

2-mercaptobenzothiazole

\[
\begin{array}{c}
\text{H}
\end{array}
\]

\(\beta\)-picolyldimethylthiocarbamate

\[
\begin{array}{c}
\text{H}
\end{array}
\]

Thiobenzanilide

\[
\begin{array}{c}
\text{O}
\end{array}
\]

3-hydroxymethyl-2-thio-benzothiazolone

\[
\begin{array}{c}
\text{H}
\end{array}
\]

bis-2-thiazolyldisulfide

\[
\begin{array}{c}
\text{N}
\end{array}
\]

2-aminothiazoline

\[
\begin{array}{c}
\text{H}
\end{array}
\]
Phenacylodithiocarbohydrazide

21 Phenacylodithiocarbohydrazide

1-mercapto-phthalazine

2-((β-phenethylthio)-5-mercapto-1,3,4-thiazolone

4-mercapto-1-thia-3,5,7-triazaindene

α-picolylidimethylthiocarbamate

5-nitro indazole

1,8-dibenzoyl-1,2,7,8-tetraza-4,5-dithia-3,6-dithionooctane

Aminothiatrazole

bis-(5-m-tolyl-1,3,4-oxadiazolyl) disulfide

The above cyclic and open chain sulfur and nitrogen-containing tone modifying compounds share the common property, when employed in combination with the quaternary ammonium salts in the diffusion transfer processes, of causing the precipitation of the silver-containing images in a state of aggregation such that the images are neutral in color rather than brown or some other color. It is not apparent from the structures of these compounds nor from the structures of the host of other compounds, which are ineffective in combination with the quaternary salts, to what factor the favorable result should be attributed. However, the tone-modifying effect does appear to be related to the fact that in the diffusion transfer processes the compounds all form with the silver halide of the emulsion, silver salts less soluble in water than silver chloride or silver bromide.

Representative developer compositions containing the combination of quaternary salt and tone modifying compound are given below.

**EXAMPLE 16**

<table>
<thead>
<tr>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-methyl-p-aminophenol sulfate</td>
</tr>
<tr>
<td>Hydroquinone</td>
</tr>
<tr>
<td>Sodium sulphite, des.</td>
</tr>
<tr>
<td>Sodium carbonate, 1H₂O</td>
</tr>
<tr>
<td>Sodium thiosulphate, 5H₂O</td>
</tr>
<tr>
<td>5-bromo-6-methyl, 1,3,3a,7-tetrazaindene-4-thiol</td>
</tr>
<tr>
<td>Tetradecamethylene-bis-pyridinium perchlorate</td>
</tr>
<tr>
<td>Water to 1 liter</td>
</tr>
</tbody>
</table>

The first five materials are dissolved in the above order in approximately 750 cc. of water at 90° F. The 5-bromo-6-methyl, 1,3,3a,7-tetrazaindene-4-thiol is dissolved in 50 cc. of warm water to which has been added 3 drops (0.15 cc.) of 30% sodium hydroxide. The tetradecamethylene-bis-pyridinium perchlorate is dissolved in 50 cc. of warm water. Both solutions are added to the bulk solution which is then made up with water to one liter. The solution has a pH of approximately 10.1.

This solution is particularly suited to use in a develop-
ment of the sensitive elements of the above Yackel et al. invention, neutral toned images being obtained by development for two minutes at 68° F.

If either one or both of the organic materials, 5-bromo-6-methyl 1,3,5,7-tetrazaindene-4-thiol and tetradecamethylene-bis-pyridinium perchlorate, are omitted from the developer formula, a warm brown-toned image results.

**EXAMPLE 17**

<table>
<thead>
<tr>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-methyl-p-aminophenol sulfate</td>
</tr>
<tr>
<td>Hydroquinone</td>
</tr>
<tr>
<td>Sodium sulphide, des.</td>
</tr>
<tr>
<td>Sodium carbonate, H2O</td>
</tr>
<tr>
<td>Sodium thiosulphate, H2O</td>
</tr>
<tr>
<td>Benzoiazolium methyl metho sulfate</td>
</tr>
<tr>
<td>Tetradecamethylene-bis-pyridinium perchlorate</td>
</tr>
</tbody>
</table>

The first five materials are dissolved in approximately 750 cc. of water at 90° F. The benzoiazolium methyl metho sulfate and the tetradecamethylene-bis-pyridinium perchlorate are dissolved in 50 cc. of warm water. The solutions are then added to the bulk solution which is then made up to one liter with cold water. The solution has a pH of approximately 10.1.

When this solution is employed in the same manner as the solution of Example 16, a neutral-toned image is obtained.

If either one or both of the organic materials, benzoiazolium methyl metho sulfate and tetradecamethylene-bis-pyridinium perchlorate are omitted from the developer formula, a warmer toned image results.

**EXAMPLE 18**

A 10% gelatin solution (250 cc.) was diluted with 750 cc. water. 2.5 cc. of 1 N Na2S were then added to the solution. 250 cc. of water containing 2.6 cc. of 1 N zinc nitrate were added slowly to the sulfide solution through a jet, resulting in the formation of a colloidal dispersion of zinc sulfide. To this dispersion were added 10 liters of a 3% gelatin solution, 300 cc. of a 7.6% saponin solution and 134 cc. of a 10% formaldehyde solution. The mixture was dispersed at 40° C. and then coated on a photographic paper support at a coverage of 2 lbs. of solution per 100 sq. ft. of coated surface and dried, forming the silver precipitating layer.

Over the silver precipitating layer was coated a 1% aqueous solution of the sodium salt (or other alkali metal salt) of cellulose ether phthalate (an ethyl cellulose containing 45.8% ethoxy phthalylated to 22.7% phthalyl) at a concentration of 0.3 lb. per 100 square foot.

To 1 liter of a positive speed, sulfur sensitized, high contrast chlorobromide emulsion containing approximately 30 g. of gelatin and one mole of silver halide per liter, were added the following ingredients: (Such emulsions containing low gelatin content can be prepared by the procedures described in the MacWilliam U.S. patent application Serial No. 440,822, filed June 29, 1954, now U.S. Patent 2,756,148 granted July 24, 1956, and the Yutzy and Frame U.S. Patent 2,614,928, granted October 21, 1952).

30 cc. of a 50% aqueous solution of glycerine
30 cc. of a 7.6% saponin solution
12½ cc. of a solution containing 2 gm. of 1-carboxymethyl-5-[(3-ethyl-2-3-benzoxazolylidene)-ethylidene]-3-phenyl-2-thiolydantoin in 30 cc. of MeOH+1 drop of triethylamine.

To the above mixture were added 5 liters of a 4% solution of the ammonium salt of the cellulose ether phthalate just mentioned dissolved in methyl alcohol.

The mass was stirred at 30° C., thoroughly dispersed and then coated over the sodium salt of cellulose ether phthalate interlayer at a coverage of 600 sq. ft. per mole of silver halide and dried in the conventional manner.

After exposure to a subject the sensitive element was processed for 60 to 120 seconds at 68° F. in the following developer solution:

<table>
<thead>
<tr>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mononethyl-p-aminophenol sulfate</td>
</tr>
<tr>
<td>Hydroquinone</td>
</tr>
<tr>
<td>Sodium sulfite, anhydrous</td>
</tr>
<tr>
<td>Sodium carbonate monohydrate</td>
</tr>
<tr>
<td>Sodium thiosulfate, 5H2O</td>
</tr>
<tr>
<td>5-Nitroindazole</td>
</tr>
<tr>
<td>3,6,9,12,15,18,21,24-octoxahexacosane,1-26-bis-(5-ethyl-2-methylpyridiniummethane sulfonate)</td>
</tr>
</tbody>
</table>

Water to 1 liter.

followed by washing with water at 35° C. for 20 to 30 seconds to remove the emulsion layer leaving a neutral-toned positive image on the receiving layer. If either the tone modifying compound, 5-nitroindazole, or the quaternary ammonium salt, 3,6,9,12,15,18,21,24-octoxahexacosan e,1-26-bis-(5-ethyl-2-methylpyridiniummethylammonium sulfonate), is omitted from the developer solution, an unacceptable, warm-toned positive image is obtained.

**EXAMPLE 19**

The process of Example 18 was carried out using the same developer solution but in which 5-nitroindazole was replaced by benzoiazolium methyl metho sulfate in like amount to also obtain a neutral-toned image. The omission of either of the nitrogen-containing compounds from the developer solution yields a warm-toned positive image.

**EXAMPLE 20**

The procedure of Example 18 was carried out with a number of developer solutions in which the pyridinium salt was replaced with the same amount of each of the following cyclammonium quaternary salts:

Decamethylenec-α,ω-bis-(oxyethyl pyridinium perchlate)
2-β-phencylisoquinolinium bromide
1-β-phencylisoquinolinium bromide
3,14-dioxahexadecane-1,16-bis-(pyridinium methane sulfonate)
3-methyl-2-β-phencyl isoquinolinium bromide
3-methyl-2-β-phencyl isoquinolinium bromide

In each case the image obtained was neutral-toned. The substitution of quaternary ammonium bases or salts which consist of an onion radical attached to short chain aliphatic groups instead of the compounds listed above, does not give the desired results. Formulas containing e.g. β-hydroxethyl trimethyl ammonium-p-toluen sulfo nate, tetramethyl ammonium bromide, tetramethyl ammonium bromide or tetra-n- propyl ammonium bromide in concentrations ranging from 0.2-0.4 g./l. produced images having very warm tone and low maximum density.

**EXAMPLE 21**

The procedure of Example 18 was carried out with a number of developer solutions in which 5-nitroindazole was replaced by the same amount of benzoiazolium methyl metho sulfate and the pyridinium salt replaced by one of the following cyclammonium quaternary salts:

Tetradecamethylene-bis(pyridinium perchlate)
α - Dimethyldiiodocarbaethoethyl - N - methyl pyridinum-p-toluen sulfonate
Decamethylenec-α,ω-bis-(oxyethyl pyridinium perchlate)
2-β-phencylisoquinolinium bromide
3,14-dioxahexadecane-1,16-bis-(pyridinium methane sulfonate)
1-methyl-2-nonanoyl pyridinium-p-toluen sulfonate
Heptoxymethyl-2,4,6-trimethyl pyridinium chloride
Tetradecamethylene-bis-(trimethyl ammonium perchlate)
3-methyl-2-β-phencyl isoquinolinium bromide
The results given in Table I also demonstrate another new and unexpected result. Those solutions containing the quaternary ammonium salts marked with an asterisk (*) produced colder and more neutral image tone than is produced by the control developers. This effect is quite striking in some cases where tone is changed from a yellow brown to a cold black tone. This effect was not as great, however, when a tone modifying compound such as the 5-nitroindazole is not present during processing. The results also show that unexpectedly the quaternary salts exhibit a substantial increase in D max.

**EXAMPLE 23**

The inadequacy of the short chain quaternary ammonium salts to improve the tone of the solvent transfer images was demonstrated by carrying out the procedure of Example 18 except using tetramethylammonium chloride, tetra-n-propylammonium chloride and trimethylphosphine hydroxide, respectively, as the "quaternary salt" in the following solution, development being carried out for 2 min. at 65° F.

<table>
<thead>
<tr>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomethy1-p-aminophenol sulfate</td>
</tr>
<tr>
<td>Hydroquinone</td>
</tr>
<tr>
<td>Sodium sulfite</td>
</tr>
<tr>
<td>Sodium carbonate hydrate</td>
</tr>
<tr>
<td>Sodium thiourea hydrate</td>
</tr>
<tr>
<td>Quaternary ammonium salt</td>
</tr>
<tr>
<td>Benzothiazolium methyl metho sulfate</td>
</tr>
</tbody>
</table>

The results were that the tone of the image was still yellow-brown the same as when the short chain quaternary salt was absent from the solution.

It is possible in solvent transfer processes such as described above to use an acidic rather than alkaline developing solution thereby effecting improvements such as reduction in stain on the transfer prints. For this purpose the acidic solution may contain a metal salt as tita
nious chloride, a metal ion chelating compound such as ethylenediamine tetraacetic acid and a silver halide solvent such as hypo as follows:

<table>
<thead>
<tr>
<th>Acidic Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium trichloride solution (20%)</td>
</tr>
<tr>
<td>Ethylenediamine tetraacetic acid</td>
</tr>
<tr>
<td>Sodium thiourea sulfate H2O</td>
</tr>
<tr>
<td>Water to make</td>
</tr>
<tr>
<td>pH adjusted to 4.0</td>
</tr>
</tbody>
</table>

A suitably exposed emulsion is immersed in the solution briefly, then squeezed in contact with a receiving sheet such as described above until a silver image is formed in the receiving layer. Other chelating agents such as iminotriacetic acids, oxalate, tarteric, etc. may be substituted in the developer solution.

Another method for preparing developer compositions which are appreciably less alkaline than those prepared with caustic alkali or alkali carbonate, includes using an organic alkaline buffer compound as the source of alkali. The buffer compound is reaction products of sulfur dioxide and amino alcohols such as 2-diethylaminol ethanol sulfite, 2-aminoethanol sulfite, 2-ethylaminoethanol sulfite, 2-methylaminoethanol sulfite, 2-ethanol sulfite. One advantage of the use of the buffer compounds lies in the fact that they permit the preparation of highly concentrated developer solutions which can be diluted with as much as forty parts of water without appreciable loss in activity.

A representative formula containing the buffer compounds is as follows:

- 4-methyl-1-phenyl-3-pyrazolidone ———— grams ———— 1.6
- Hydroquinone ———— do ———— 12.2
- 2-diethyl amino ethanol sulfite ———— do ———— 44.4
- 2-methyl amino ethanol thiosulfate ———— do ———— 11.4
- Benzoimidazolium methyl metho sulfite ———— do ———— 0.4
- Ammonium hydroxide (28 percent) ———— ml ———— 4.6

The composition can be diluted to one liter for use and as such has a pH of 9.8.

In a parallel investigation of other compounds effective in improving the tone of the argentals images, it has been found that when certain common organic solvents such as the lower alcohols, ketones, amides, and water soluble ethers are employed in the developer solutions containing silver halide solvent in sufficient concentration of the order 7 to 20% by volume, in combination with one of the many cyclic and open chain sulfur and nitrogen-containing compounds above, a pronounced improvement in tone of the argentals images is obtained which effect is comparable to that obtained by the combination of quaternary salt and the tone-modifying compounds. Examples of the preferred compounds are: alcohols-methyl alcohol, ethyl alcohol, ethylene glycol, glycerol; ketones-acetone; amides-formamide, acetamide; ethers-dioxane.

It has further been observed that certain water soluble amines are effective in darkening the tone of the argentals images in silver halide diffusion transfer processes. The effective amines include the primary aliphatic amines containing a linear carbon chain of from 4 to 6 carbon atoms, that is, amines of the normal butyl to hexylamine series. Surprisingly, lower and higher members of the series e.g., propylamine and heptylamine, are ineffective. Other amines which are effective are the a-o-alkylene diamines containing from 8 to 12 carbon atoms in the alkylene chain separating the amino groups, as in the series from a-o-oclylene diamine to a-o-dodecylene diamine. Also, one of the amino groups of the diamine may be replaced by a hydroxyl group as in the alkanolamines.

In addition, benzylamine and cyclohexylamine are useful for the same purpose.

These amines are advantageously used in the developing solutions containing developing agent and silver halide solvent used for initiating development of the sensitive element, in concentrations up to about 0.5%.

Representative aliphatic amines thus useful are as follows:

- 1,8-diamino-n-octane
- 1,12-diamino-n-dodecane
- 1-amino-11-hydroxy-n-undecane
- n-Butylamine
- Benzylamine
- n-Amylamine
However, if one employs in the diffusion transfer system one of the above group of approximately 100 sulfur and nitrogen containing cyclic and open chain toning compounds in combination with the mentioned sulfur and nitrogen containing cyclic and open chain toning compounds.

4-di-N-butylaminobutylamine
3,3'-diaminodipropylamine
11-amino-3,6,9-triazoundecanol
14-amino-3,6,9,12-tetrazatedecanol
3,6,9,10-tetraza-1,4-tetradecanediol
3,6,9,12-pentaza-1,17-heptadecanediol
2-aminoethanol
2-methyldiminoethanol
Methylmimo-bis-propylamine

A preferred group of toning compounds useful with the above amines are the following:

2,3-dihydro-2,5-dimethyl-1-phenyl-1,2,4-triazole-3-thione
2-mercapto-5-phenyl-1,3,4-oxadiazole
5-aminobenzotriazole
4-aminobenzotriazole
5-chlorobenzotriazole
5-bromobenzotriazole
1-phenyl-2-mercaptotetrazole
Benzothiazolium methyl metho sulfate

The amines, and combinations of amines with the above large number of tone modifying compounds, are especially useful for producing black-toned images in the processes of the mentioned Yakkel et al. U.S. patent application Serial No. 586,705.

A representative developer composition especially useful in those processes is as follows:

Monomethyl-p-aminophenol sulfate 1.25 Grams
Hydroquinone 5.0 Grams
Sodium sulfite, des 20.0 Grams
Sodium carbonate, anhydrous 25.0 Grams
Potassium bromide 0.4 Grams
Sodium thiosulfate 5H2O 25.0 Grams
Sodium hydroxide 12.0 Grams
n-Butylamine 2.5 Grams
Water to 1 liter

In other developer formulas containing silver halide developing agent and silver halide solvent, butylamine may be replaced in similar quantity by other amines such as disclosed above or one of the amines in combination with one of the above-mentioned sulfur and nitrogen containing tone modifying compounds.

Examples of the use of an amine in combination with one of the tone modifying compounds are as follows:

The following developer solution was prepared:

4-methyl-1-phenyl-3-pyrazolidone 1.6 Grams
2-ethylaminoethanol sulfite addition compound* 35.2 Grams
2-aminoethanol 2.5 Grams
5-bromo-5-methyl-1,3,3a,1-tetrazaindene-4-thiol 0.2 Grams
5-bromo-6-methyl-1,3,3a,1-tetrazaindene-4-thiol 0.2 Grams
Water to 1 liter.

* Prepared by reacting 1 mole of sulfur dioxide with 4 moles of 2-ethylaminoethanol.

The sulfite addition compound can be replaced by sodium sulfite by adjustment of the developing agent and silver halide solvent concentrations. When the above solution was used to develop sensitive elements such as shown in the examples of Yakkel et al. U.S. patent application Serial No. 586,705 for 2 minutes at 68°F, neutral toned images are obtained. The omission of either 2-aminoethanol or the tetrazaindene compound from the developing solution results in images of inferior toning and contrast.

The following formula may also be used in the same manner to produce neutral toned images:

4-methyl-1-phenyl-3-pyrazolidone 1.6 Grams
Hydroquinone 11.2 Grams
2-ethylaminoethanol sulfite addition product* 35.2 Grams
Sodium thiosulfate 9.2 Grams
Methylmimo-bis-propylamine 4.0 Grams
Benzothiazolium methyl methosulfate 0.2 Grams
Water to 1 liter.

* Preparated by reacting 1 mole of sulfur dioxide with 4 moles of 2-ethylaminoethanol.

If the tone modifying compound benzothiazolium methyl metho sulfate is omitted, a weak positive image is obtained. If, on the other hand, the methylmimo-bis-propylamine is omitted, no positive image is obtained.

What we claim is:

1. In a process for the direct production of positive images in which a silver halide emulsion layer is developed, to produce a silver image and the residual undeveloped silver halide is caused to diffuse image-wise to a receiving stratum, and an argental image is formed in the stratum for said residual silver halide in the presence of a silver precipitating agent, the step of forming said argental image in continuity with quaternary ammonium salt having a linear chain of at least seven atoms attached directly to a quaternary nitrogen atom and a compound of the class consisting of:

2-mercapto-1-phenyl-tetrazole
2-mercapto-5-phenyl-1,3,4-oxadiazole
Dihydro-1,4-benzothiazin-3-one
2-pyrindylbenzothiazolone hydrochloride
4-butyli-5-methyl-1,2,3a,7-tetrazaindene-4-thiol
7-seloeno-1,3,4,6-tetrazaindene
2,6-dimethyl-1,3,3a,7-tetrazaindene-4-thiol
5-ethyl-6-methyl-1,2,3a,7-tetrazaindene-4-thiol
Bis-(5-p-hydroxyphenyl-1,3,4-oxadiazolyl) disulfide
2-mercapto-5-(p-hydroxyphenyl)-1,3,4-oxadiazole
μ-Thiolfructoxazolone
4-oxo2,3,3a,4,5,6-hexahydro-1,3a-diaza-7-thiindene
5-aminobenzotriazole
5-thiobenzothioglycolic acid
4-aminobenzotriazole-HCl
5-carboxybenzox-L-cystine
5-chloro-1,2,3-benzotriazole
Bromobenzotriazole
Ethylene thiourea
Ethylene thiocyanate
4,6-trimercapto-1,3,5-triazine
4,6-dimercapto-1,3,5-pyrimidimine
2,4,6-trihioamidate
2,4,6-trihioamidate
Bis-(2,3-dihydroxypropyl)-disulfide
3-amino-5-mercapto-1,2,4-triazole
4-aminomethyl-2-mercaptoimidazol
1-(p-hydroxyethyl)-3-methylthiourea
3-p-anilyl-1,2-dihia-cyclopentenem-5-thione
2-mercapto-5-amino-1,3,4-thiadiazole
3-mercapto-5-methyl-1,2,4-triazole
3-mercapto-1,2,4-triazole
2-mercapto-5-(m-toly)-1,3,4-oxadiazole
2-mercapto-5-(ο-tolyl)-1,3,4-oxadiazole
2-mercapto-5-(p-methoxyphenyl)-1,3,4-oxadiazole
2-mercapto-5-(p-nitrophenyl)-1,3,4-oxadiazole
β-Mercapto-propionic acid
1-phenyl-2(1)-thioxoquinolone
2-mercapto-5-naphthoxazole
3-phenyl rhodanine
8,017,270 29 1-cyclohexyl-5-mercaptotetrazole
Dimethylcarbamylmethylthiocarbamylsulfide
Sym-tetra-o-4-pyridyl-bis-(formamidine)-disulfide
5-(γ-pyridyl methyliden)-2-thiono-thiophosphorolidone
2,1,5-diphenoxy-3-mercapto-4-methyl-1,2,4-thiazole
2-mercaptobenzoxazole
3-amino-6-keoto-4-methyl-1-phenoxy-2-thiono-1,2,3,6-tetrahydropyrimidine
2-thionothiazolidone
2-mercaptobenzothiazole
β-Picolyl-dimethylthiocarbamate
Thiobenzaldehyde
3-hydroxymethyl-2-thio-benzothiazolone
Bis-2-thiazolylsulfide
2-aminothiazoline
Bis-2-benzoxyazoysulfide
3,5-dimethyltetrahydro-1,3,5,2H-thiadiazine-2-thione
4-methyl-1,2,3a,7-tetrazaindene-6-thiol
2-(6-methyl-1,3,3a,7-tetrazaindene-4-yl-thio)-ethyliothiuro-nium bromide
6-methyl-1,2,3a,7-tetrazaindene-4-thiol
4,6-diaza-1-diethylamin-5-thioacene
Tetrapropyl thiuram disulfide
1-benzyl-3,3-dimethylthiourea
Thioglycolic dihydrozide
3-β-pyrindinopropylmethylthiocarbamate
5-bromo-6-methyl-1,3,3a,7-tetrazaindene-4-thiol
2,4,6-tris(diethylamino-ethylamin)-s-triazine-3HCl
4-hydroxy-1,3,8-triazanaphthalene
4-thione-4-a-naphthalencene
2-mercapto-5-furyl-1,3,4-thiadiazole
2-mercaptobenzimidazole
2-mercapto pyridine-N-oxide
2-isothiourido pyridine-N-oxide
2-mercapto-5-methyl-4H,1,3,4-thiadiazine
2,3-dihydro-2,5-dimethyl-1-phenyl-1,2,4-triazole-3-thione
4,5-dihydro-1-(4,5-dihydroimidazolide-2-y)-2-thioimido-
dazole
Ethylene trithiocarbionate
3,4-diphenyl-5-mercapto-1,2,4-triazole
Dimethylcyclohexadienethiocarbodiiboic acid
5-p-dimethylaminobenzylidine-2-thio-2,4-oxazolidindione
6-hydroxy-2-mercapto-4-methylpyridylidine
3-β-formamido-5-mercapto-1,2,4-triazole
1-γ-hydroxypropyl-3-methylthioureien
2-imino-5-thio-1,3,4-thiadiazolidine
5-imino-3-thiazolurazide
Bis-[2-(4-pyridyl)-ethyl]-sulfide
Phenacyloxythiocarbodiiboic acid
1-mercapto phthalazine
2-(β-phenethyhiho)-5-mercapto-1,3,4-thiadiazole
4-mercapto-1-thia-1,5,7-triazaindene
α-Picolyl dimethylthiocrbamate
5-nitro indazole

3,017,270 30 2-pyridine carboxaldehyde thiosemicarbazone
Benzothiazolium methyl metho sulfate
1-methyl-2-mercaptoimidazole
3,4-diamino-5-mercapto-1,2,4-triazole
4-hydroxy-6-methyl-1,2,3a,7-tetrazaindene-3-thiol
5-phenyl-1,2,3a,4-tetrazaindene-7-thiol
4-phenyliminothiouarazole
5-methyl-1,2,3a,4-tetrazaindene-7-thiol
1,8-dibenzyloxyl-1,2,7,8-tetrazo-4,5-dithia-3,6-dithiooctane

Aminothiatriazole
Bis-(5-m-tolyl)-1,3,4-oxazoliodylsulfide, and
5-ethyl-3-mercapto-4-phenoxy-1,2,4-triazole.
2. The process of claim 1 wherein the quaternary ammonium salt is a cyclammonium quaternary ammonium salt.
3. The process of claim 1 wherein the quaternary ammonium salt is a member of the class consisting of:
Tetradecamethylene-bis-(pyridinium perchlorate)
α-Dimethylthiocarbamatoethyl-N-methyl pyridinium p-toluene sulfonate
N-methyl-2-N-propyl mercapto pyridinium perchlorate
Decamethylene-bis-(oxyformyl pyridinium perchlorate)
2,3,6,9,12,15,18,21,24-octaoxahexacosane-1,26-bis-(5-ethyl-2-methyl pyridinium methane sulfonate)
2-β-phenethyloquinolinium bromide
1-β-phenethyloquinolinium bromide
3,14-dioxahexacosane-1,16-bis-(pyridinium methane sulfonate)
1-methyl-2-β-nonanoyl pyridinium-p-toluene sulfonate
Heptoxymethyl-2,4,6-trimethyl pyridinium chloride
Tetradecamethylene-bis-(trimethyl ammonium perchlorate)
3-methyl-2-β-phenethylo isoquinolinium bromide
3-β-phenethyl-α-picolinium bromide
4,4,10,10-tetraoxo-4,10-dithiatridecane-βs(pyridinium perchlorate)
2-β-hydroxyethyl-1-ethyl quinolinium iodide

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