

the image is yellowish- or reddish-brown; when the mercapto compound is present, the image is black. The toning of silver diffusion transfer images has been the subject of considerable investigation<sup>56-66</sup> and considerable difference in interpretation. One recent study, by E. H. Land, V. K. Walworth, and R. S. Corley,<sup>67</sup> attributed the difference in image color to the size and structure of the silver deposits, as determined by electron microscopy. According to this investigation, "The brown image deposit (a), is in the form of spheres and ellipsoids 50-100 nm in maximum dimension, with mean diameter 70 nm; many appear to be single crystals. The deposit in the black image, (b), comprises clusters 120-200 nm in maximum dimension with mean 146 nm; an estimated 50 or more particles 10-30 nm across are seen in a typical cluster. Stereoscopic comparison shows separation of the unit particles of the image deposit (a) to be of the order of their diameters (50-100 nm), whereas within the clusters of image (b) typical spacing between the small particles is 1/10 diameter or less ( $\leq 1$  nm)."

Many, many thiol compounds have been found to be suitable for producing black diffusion transfer images. Edith Weyde<sup>68</sup> patented the 5-mercapto-1,2,3,4-tetrazoles, particularly the 1-phenyl-5-mercapto-1,2,3,4-tetrazole, of which 0.05 g was added to a liter of 5% gelatin solution containing 0.05 g of colloidal silver before a sheet of paper was coated to make the receiver material. Tetrahydro-2H-1,3-thiazine-2-thiones,<sup>69</sup> 1,3,4-triazol-4-in-2-thiones<sup>70</sup> or 1,3-oxazolidine-4-on-2-thione,<sup>71</sup> diphenyl iodonium-5-methyl benzotriazole or 5,5-dimethyl-4-thiohydantoin,<sup>72</sup> benzothiazole-2-thiol,<sup>73</sup> 5-chlorobenzotriazole,<sup>74</sup> 5-nitro- and 6-nitrobenzimidazole,<sup>75</sup> and cysteine<sup>76</sup> are only a few representative compounds that have been used as black toners in the diffusion transfer process. Many mercapto compounds, however, have no influence on image tone, and it is difficult to predict the effective agents.<sup>77</sup> A relatively complete listing is given in the book, *Photographic Silver Halide Diffusion Processes*, by André Rott and Edith Weyde, beginning on p. 61.

The usual brown transfer image can be converted into a black image by incorporation into the receiver of compounds such as benzotriazole or its derivatives, 5-nitrobenzimidazole, or 1-phenyl-5-mercaptotetrazole. These compounds form silver compounds of low solubility, decreasing both the rate of development in the negative and the rate of image formation in the receiver. Acceleration of the transfer process has been claimed for black toning agents such as 3-alkyl-benzoxazoline-2-thione, 5,5-dimethyl-4-thiohydantoin, or 5-methyl-3-mercapto-1,2,4-triazole. Black, or blue-black, toning and development acceleration has been claimed for such compounds as 4-amino-3-methyl-1,2,4-triazoline-5-thione or 4-acetamido-1,2,4-triazoline-5-thione.<sup>78</sup> Certain 1,2,4-triazine derivatives, such as 3-thio-1,2,4-triazaspiro[5,5]undecane-3,5-dione, have been patented for this purpose.<sup>79</sup>

An image-receiving layer may be coated from this composition containing this triazine:

Gelatin	40 g
Sodium thiosulfate, crystal	35 g
Colloidal nickel sulfide	$1.28 \times 10^{-3}$ mole
3-Thio-1,2,4-triazaspiro-[5,5]undecane-3,5-dione (0.7% in ethanol)	100 ml
Formaldehyde, 20%	5 ml
Sandozol (sulfonated organic oil) (Sandoz Chemical Works, Inc.)	1 ml
Water to make	1 liter

This suspension is sufficient to cover  $13 \text{ m}^2$  of a paper support.

Developing agents are incorporated in the receiving layer as well as development nuclei and toning agents. A superadditive developing-agent combination has been proposed<sup>80</sup> such that the principal developing agent, hydroquinone, is incorporated in the receiver layer and the secondary developing agent, a 3-pyrazolidone, is incorporated in the light-sensitive material. In the light-sensitive material 1.3 g of silver chloride and 0.1 g of 1-phenyl-3-pyrazolidone are applied to cover  $1 \text{ m}^2$ . One liter of the following composition is coated on  $12 \text{ m}^2$  of paper support:

Water	877.2 ml
Gelatin	40.0 g
Sodium sulfide (10% in water)	2.4 ml
Cobalt nitrate (10% in water)	13.2 ml
Potassium metabisulfite	12.8 g
Hydroquinone	6.4 g
Sodium thiosulfate	48.0 g

The light-sensitive material and the receiver paper are passed through a developing apparatus containing

Water	1 liter
Sodium phosphate	100 g
Sodium sulfite, anhydrous	20 g

The two sheets are laminated together in the machine. After 10 sec contact time, the two sheets are stripped apart to reveal a positive image of the original on the receiver.

### The Processing Solution

The liquid used to bind the light-sensitive negative material in intimate contact with the light-insensitive positive material is an alkaline solution of processing chemicals whose number varies with the composition of the negative and positive layers. The developing agents may be coated in one of the layers of the negative or positive sheets. The silver complexing agent may be coated as part of the receiver. The image-forming nuclei may be part of the processing liquid but usually are coated in the receiving layer. Other variations are possible, but one common combination has the silver complexing agent and nuclei as part of the receiver and the developing agents contained in the liquid. Or the developing agent or agents may be present in the solution with the silver complexing agent to produce a true monobath.

The alkaline processing solution or monobath may contain a number of other compounds, such as sodium sulfite or potassium metabisulfite, to act as an auxiliary silver solvent and to minimize staining due to the oxidation products of the developing agents; restraining agents to minimize fog in the negative; toning compounds to produce a black-toned positive image; development accelerators to speed negative development; sequestering agents to prevent deposition of calcium compounds from hard water or leached from the coated layers; and thickening agents if the processing is carried out in a camera. Viscosity-increasing compounds, such as sodium carboxymethyl cellulose or hydroxyethyl cellulose, in the processing liquid insure even spreading of the thickened liquid and maintain uniform thickness between the negative and receiver sheets. If the processing liquid is subject to continued re-use, as in office copying machines, mercapto compounds to inhibit the sludging of silver from solution may be added to the processing liquid.<sup>81-83</sup>

The most commonly used silver halide solvent for the diffusion transfer process is sodium thiosulfate, sometimes with a small amount of ammonium thiosulfate added. Other solvents, such as calcium thioglycolate, have been<sup>84</sup> proposed for use in the solutions but are little used. The sodium thiosulfate may be present in either the processing solution or the positive material. In either case the quantity of thiosulfate must be maintained at a low level, so that the unstable silver thiosulfates are formed preferentially to the more stable complexes that contain a higher proportion of thiosulfate to silver. When the processing solution contains large amounts of thiosulfate, considerable silver ions are lost to the solution before the positive and negative

are brought together in some office copy machines. Excess thiosulfate coated in the positive material must also be avoided. According to W. Krafft,<sup>85</sup>

The optimum amount of sodium thiosulfate in the positive largely depends on the quantity of silver supplied by the negative, on the activity of the developer and of the nuclei as well as on the swelling properties and absorptivity of the positive. This concentration generally lies between 1 and 3 grams of sodium thiosulfate-5-water per square meter. A real disadvantage of this system is the increase which takes place in concentration of thiosulfate in the developing liquid, when the latter has been used repeatedly. This brings about a reduction in image density, on the one hand by the solution of the silver salts from the negative, which are thus lost to the transfer process, and on the other hand by the formation of stable silver thiosulphate complexes which are no longer capable of being reduced.

Other precautions when incorporating the thiosulfate in the positive involve maintaining the pH of the coated layer at 5.0, at least, to prevent decomposition of the thiosulfate during storage of the positive. The rapid drying of a processed positive that contained incorporated thiosulfate is essential so that silver thiosulfate complexes do not diffuse into the paper base, where later they may decompose and stain the positive image. Baryta underlayers on the positive or nonpermeable barrier layers help to limit the penetration of soluble silver thiosulfates. The use of sparingly soluble thiosulfate compounds was not as practical, because the contact time was greatly lengthened or the amount of image silver was reduced.

The amount of silver halide solvent in the processing solution is also of critical importance if more than one copy is to be obtained from a single negative. A. J. Sievers<sup>86</sup> found that "Silver analysis of the negative material, both before and after transfer, and analysis of the positive image showed that of all the possible limiting factors the action of the silver halide solvent was by far the greatest. While the processing solution was removing 52.1% of the available silver halide in the negative, only 26.8% was actually reduced on the positive sheet. That meant that 25.3% was lost to the processing solution; almost twice the amount required for formation of a positive image. Also 47.9% of the silver halide was left in the negative; enough to form another 3.4 copies." Increasing amounts of silver are transferred as the amount of silver halide solvent is increased. A reduction of 30% from a standard amount normally used in a processing solution removed less silver halide from the negative after forming three copies than solutions containing higher concentrations of sodium thiosulfate.

Multiple copies have been obtained by using the stepwise action of barium thiosulfate although the transfer time may be lengthened (30 sec).<sup>87</sup> Another proposal<sup>88-89</sup> for multiple copies involves the coating of an unhardened

positive layer containing development nuclei on top of a silver halide emulsion layer. After exposure this two-layer element was treated with a solution containing developing agents and a silver halide solvent (sodium thiosulfate). A positive image is formed in the top nucleated layer. This upper layer is then transferred to absorbent sheets to obtain several positive transfers. Water-soluble starch ethers or carboxymethyl cellulose have been suggested<sup>90-91</sup> as binding agents for the positive layer.

For in-camera use, according to E. H. Land in an early patent,<sup>92</sup> sodium thiosulfate, ammonium thiosulfate, sodium thiocyanate, ammonia, or sodium cyanide were suggested as suitable silver complexing agents. In the same patent Land suggested this simple example of the early preparation of a processing solution by taking

Water	1860 g
Sodium carboxymethyl cellulose	117 g
Sodium sulfite	78 g
Sodium hydroxide	74.6 g
Sodium thiosulfate	14.5 g
Citric acid	38.5 g
Hydroquinone	52.0 g

Land stated that the processing solution "is prepared by dissolving the carboxymethyl cellulose, for example the commercially available Hercules 1362 medium viscosity type, in the water in a mixer at room temperature, and the solution is mixed therein for approximately one hour. Thereafter, the sodium sulfite, sodium hydroxide, sodium thiosulfate and citric acid are added to the solution, the addition being effected in an inert atmosphere, for example of nitrogen. Upon dissolution of these materials, the hydroquinone is added and the solution is further mixed for an hour at approximately room temperature in a nonoxidizing atmosphere of nitrogen."

This processing solution was spread uniformly between an exposed negative, such as Kodak Verichrome film, and a receiver sheet having a thin coating of the following composition on a baryta-coated paper base:

Lead acetate, neutral (40% in water)	192 ml
Silica aerogel (Santocel C)	30 g
Sodium sulfide (1% in water)	60 ml
Copper acetate (1% in water)	66 ml
Ascorbic acid (15% in water)	36 ml

A finished positive image, presumably brown or brown-black in color, was said to have been obtained after 1-min contact time of the negative and positive materials.

This illustrative example of early in-camera processing used sodium thiosulfate as the silver complexing agent. The early processing solutions for office copying machines also were based on the use of sodium thiosulfate as the primary silver transfer agent. Some of this thiosulfate or its silver complexes, in addition to the other chemicals contained in the solution, was retained in the print materials. The presence of thiosulfates and oxidized developing agents has a deleterious effect on silver images; indeed, even thorough washing of conventionally processed photographic materials sometimes fails to insure image permanence. Diffusion transfer reversal prints, therefore, must receive special treatment if they are expected to have a long life. Office copies are for short-time use, but in-camera prints must last as permanent records of past events.

An in-camera print is subject to sulfiding due to the decomposition of the retained thiosulfate or due to atmospheric sulfides entering the image layer. The developing agents oxidize with time, staining the background of the print. Oxidized developing agents can cause fading of the silver image. To counteract these deleterious effects, the print has to be overcoated with a thin liquid layer that dries to a protective coating. The coating solution may consist of hydrolyzed gelatin,<sup>93</sup> hydrolyzed polyvinyl butyral,<sup>94</sup> or other acidic polymeric film former, a solvent, a volatile alkali, and certain heavy-metal salts. The substance to be used for the protective coating may be the result of the interaction of an acidic vinyl monomer and a lower alkyl acrylate,<sup>95-96</sup> or a vinylpyridine polymer and a hydantoin-formaldehyde condensation polymer.<sup>97</sup> The organic solvent may be water-miscible solvents such as alcohols (methanol, ethanol, and so on) and ketones (acetone or methylethyl ketone) to solubilize the polymer and to give the coating a quick-drying character.

According to a patent by Edwin H. Land and Meroe M. Morse,<sup>98-99</sup> the incorporation of a volatile alkaline material, preferably ammonia, in fairly substantial quantity in the coating composition provides a material having unexpectedly good stabilizing qualities and does not tend to distort or bleach developed photographic silver images. Although the precise quantity of alkali is not critical, where the developing agent used is acid-sensitive it has generally been found that compositions having a pH of at least about 8 and preferably 9 or higher provide optimum results. Further, although ammonia is the preferred alkaline material owing to its high degree of volatility, other bases which are volatile and which have little or no crystalline or opaque residue which might obscure or disfigure the image

also provide satisfactory ingredients, such as ethylamine, diethylamine, triethylamine, and butylamine.

It is desirable that the coating solution contain an agent capable of becoming dispersed in the protective coating and of protecting the image by reacting with atmospheric sulfides that may penetrate the protective coating. Preferred protective agents or salts, preferably water-soluble, are those containing heavy metal cations which form insoluble sulfides. These salts, for example, are composed of: cations such as zinc, cadmium, zirconium, and tin; and anions such as acetate, sulfate, nitrate, and formate. Since these salts in small quantity are substantially invisible and form invisible sulfides, they and their sulfides do not affect the optical clarity of the protective coating. A salt of zinc is preferred because zinc sulfide is white and does not tend to discolor the highlights of the image on which it is present.<sup>98</sup>

The patent also notes that when the protective coating contains both ammonia and zinc oxide as the salt of the heavy metal,

the zinc oxide and ammonia react to form a zinc ammonium complex which complex, in turn, enters a state of equilibrium with zinc oxide and ammonia. These reactions may be represented as follows:



When the composition is applied as a coating to photographic images, ammonia evaporates, generating additional zinc hydroxide. As zinc hydroxide is formed, however, it reacts with the available acid groups on the chain of the acid film-forming polymer in such a way as to cross-link the polymer.

An example of a protective coating incorporating these chemical constituents has the following composition:

Phthalaldehydic acid partial acetal of polyvinyl alcohol	10 g
Dimethyl hydantoin formaldehyde condensation polymer	13.5 g
Zinc oxide	1.44 g
Water	50 ml
Isopropyl alcohol	30 ml
Ammonia (29.4% solution)	10 ml

The protective coating that had to be applied to freshly processed in-camera prints was essential if the prints were to be protected from rapid fading, but the coating operation required the presence of the applicator and



a smooth surface for the spreading of the liquid.<sup>100-101</sup> The operation was messy and almost impossible to do well under dusty field conditions. The coating of the prints could be avoided if a nonstaining developing agent was present in the developer as well as a nonsulfiding silver solvent. Most developing agents containing a benzenoid structure have staining oxidation products; sodium thiosulfate, with its labile sulfur, strongly attacks any silver image in its presence. In-camera prints of improved stability would then require a departure from conventional diffusion transfer solutions and materials that contain either type of developing agent or sodium thiosulfate or thiocyanate.

Optimistically, Edwin H. Land<sup>92</sup> in 1953 listed the following developing agents, alone or in combination, as being useful for in-camera processing: "hydroquinone, monomethyl-*p*-aminophenol sulfate (Elon, Metol), *p*-aminophenol hydrochloride (Kodolon), *p*-hydroxyphenylaminoacetic acid (Athenon, Glycin), *p*-phenylenediamine, *o*-phenylenediamine, pyrocatechin (pyrocatechol, catechol), diaminophenol dihydrochloride (Amidol), diaminophenol hydrochloride (Acrol), pyrogallol, chlorohydroquinone, dichlorohydroquinone, tetrachlorohydroquinone, bromohydroquinone, toluhydroquinone, xylohydroquinone, *o*-aminophenol, 2-amino-5-diethylaminotoluene hydrochloride, *p*-tertiary-butylcatechol, hydroquinone disulfonic acid (potassium salt), 2,5-ditertiary butyl hydroquinone, and *p*-amino-diethylaniline." The compound 4,6-diamino-ortho-cresol partially oxidized has been claimed to have high energy as a developing agent or auxiliary developing agent.<sup>102,103</sup>

In practice, however, hydroquinone was generally used in a caustic developing-and-silver-solubilizing solution. The hydroquinone was often combined with Phenidone because rapid and complete image development in the negative is essential in order to achieve clean white areas in the positive print. Catechol and pyrogallol developing agents have been suggested. The combination of ascorbic acid, in place of hydroquinone, with Phenidone or its derivatives would be presumed to have a lower staining propensity. One approach involves incorporating the developing agents in the negative layer. These compounds develop the exposed image, but they or their oxidized forms do not diffuse into the transfer solution or to the reception layer. Suitable nondiffusing developing agents include cyclohexyl derivatives of dihydroxybenzenes, such as 1,4-dihydroxy-2-cyclohexyl benzene, or weighted developing agents, such as 1,4-dihydroxy-2-tertiary-butyl benzene.<sup>104</sup> Ascorbic acid is incorporated in the receiver to reduce the transferred silver, the oxidized form of ascorbic acid having low staining tendency. Compounds such as 3,4-dihydroxy diphenyl or lauryl hydroquinone<sup>105</sup> were claimed to be nondiffusing developing agents. Other weighted hydroquinones, such as those containing alkylthio groups<sup>106</sup> or 2,5-bis-ethylenimino groups,<sup>107</sup>



and mono-*N*-benzyl-diamino-phenyl compounds,<sup>108</sup> have also been proposed for minimizing the stain of oxidized developer in the positive image. *p*-Aminophenoxyhydroquinone,<sup>109</sup> 1,5-bis(2',5'-dihydroxyphenyl)-3-pentylamine,<sup>110</sup> 2- $\gamma$ -amino-propylamino-1,4-dimethoxy-benzene,<sup>111</sup> and 2-hydroquinone-amino-4-chloro-6-hydroxy-s-triazine<sup>112</sup> have been patented for diffusion transfer processes. A hydrazine derivative, bis-benzene-sulfonyl hydrazide, was patented<sup>113</sup> as early as 1954 as a colorfree developing agent but probably did not have sufficient activity for general use.

Ascorbic acid and isoascorbic acid have oxidation products of low color, but the compounds alone may not possess sufficient activity for a diffusion transfer system. The acid ketals and acetals of either ascorbic or isoascorbic acids may be used alone but are said<sup>114-115</sup> to be most effective when used with other developing agents—for example, a very small amount of an active developing agent such as 2,6-dimethoxy-4-aminophenol—or with ascorbic or isoascorbic acids. The use of large quantities of a weak developing agent such as ascorbic acid with extremely small quantities of a high-energy developing agent, such as 2,4-diamino-ortho-cresol, was claimed to form a combination that eliminated the need for overcoating the transferred image. An uncoated image was reported to have resisted silver image fading or background coloration for over two years standing at room temperature and humidity (actual conditions not stated). These results were achieved with a solution of the following composition that was spread between a silver iodobromide negative film and a "surface hydrolyzed cellulose acetate spreader sheet" for 40 sec:<sup>116</sup>

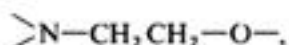
Water	902.0 ml
Hydroxyethyl cellulose	41.5 g
Sodium sulfite, desiccated	33.0 g
Potassium thiosulfate	14.0 g
Ascorbic acid	60.0 g
2,4-Diamino-ortho cresol	2.0 g
Cysteine	2.2 g
Diethylamine	50.0 ml
Sodium hydroxide	25.0 g

The diethylamine and the sodium hydroxide are the alkaline components of the solution. The diethylamine contributes a considerable amount of the alkalizing action. Diethylamine is a volatile alkalizing agent whose evaporation from the positive print will result in a reduction of the alkalinity of the print, so that overcoating of the print after processing is not needed.<sup>117</sup>

A nonvolatile salt of the amine, such as diethylamine sulfate, may be incorporated in the receiver, the hydroxide ions of the processing solution freeing the volatile amine, which is then free to evaporate and lower the alkalinity of the positive print.<sup>118</sup> The cysteine in the processing fluid is said<sup>76</sup> to provide "a considerably more neutral tone in the resulting print than would exist in its absence." Cysteine in combination with an amine such as diethylamine<sup>119</sup> has been claimed to prevent thiosulfate complexes from being reduced in the negative, providing a usable negative without washing.

The need for low-staining developing agents for reducing staining and fading of the positive print has resulted in the patenting of a number of potential compounds for this purpose.<sup>120-121</sup> Anhydro dihydro hexose reductones were said<sup>122</sup> to combine desired activity with improved stability and colorless or low-colored oxidation products. The incorporation of an aminomethyl hydroquinone developing agent, such as 2-methyl-5-morpholinomethyl hydroquinone, in the light-sensitive layer and the use of the anhydro dihydro hexose reductone in the processing fluid was claimed to be an especially suitable arrangement.<sup>123-124</sup>

In highly alkaline solution, hydroxylamine is an active developing agent with colorless oxidation products. *N*-Alkyl and *N*-alkoxyalkyl substituted hydroxylamines have been proposed<sup>125-133</sup> for diffusion transfer processes. These compounds, however, were reported to lose effectiveness after storage in the highly alkaline processing solution. The shelf life of such a solution containing a hydroxylamine developing agent, such as *N,N*-diethyl hydroxylamine, was said<sup>134-135</sup> to be substantially improved by the presence of certain amines containing the oxyethylamino grouping,



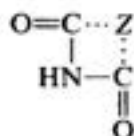
as in triethanolamine. The combination of a considerable quantity of a hydroxylamine such as *N,N*-diethylhydroxylamine, or an ascorbic acid, with a small amount of an aminophenol, for example, 2,6-dimethoxy-4-aminophenol hydrochloride, was said to give reduced developer stain in the positive image as well as improved image stability.<sup>136</sup> Another proposal<sup>137</sup> had a nondiffusing developing agent, for example, 4'-methylphenylhydroquinone, in the emulsion layer of the light-sensitive material and the *N,N*-diethylhydroxylamine in the processing solution. The *N,N*-diethylhydroxylamine volatilized from the receiver layer, yielding transferred images of less stain and better stability without after treatment.

In summary, the necessity of swabbing a freshly formed receiver image can be avoided if (1) a nondiffusing developing agent is coated in the light-sensitive layer and the low-staining or volatile auxiliary developing agent is contained in the processing fluid, or if (2) an extremely small amount of an

active developing agent is combined in the solution with a large quantity of a volatile, low-staining developing agent, such as *N,N*-diethylhydroxylamine. This latter compound is necessary to reduce the silver that is transferred to the nuclei of the receiver, but its oxidation products, or the unoxidized compound, volatilize from the layer, leaving the image free from stain or later attack on the silver image. The use of a volatile alkali as part of the alkali of the processing solution also helps lower the alkalinity of the transferred image layer.

The choice of the most suitable developing agent and alkali is essential for compounding a transfer fluid that makes aftertreatment of the transferred image unnecessary, but the image still may deteriorate because some of the usual silver solvent, sodium or potassium thiosulfate, would be contained in the positive image, resulting in sulfiding of the silver of the image. Obviously, thiosulfate should be replaced by a more stable silver solvent that does not attack silver images. A number of nonthiosulfate silver complexing agents have been proposed. Dicyanamide was found to be effective in diffusion transfer systems by Grant Haist, James King, and Lance Bassage.<sup>138</sup> Bis(methylsulfonyl)methane is an active silver halide solvent at high pH but is inactive when the pH of the print is reduced to a lower value.<sup>139</sup>

One particularly useful approach was suggested by a research team at the Polaroid Corporation.<sup>125-127</sup> Two associated complexing agents were found to be more effective together than each used alone, and the combination was suitable for the production of transferred images.<sup>132-137</sup> Cyclic imides characterized by the following general formula



where Z represents enough atoms to complete a ring of from five to six atoms, of which from one to three are nitrogen and the remainder carbon, were used in combination with nitrogenous bases. The cyclic imides could be, for example, compounds such as uracil or amino urazole, although triazines, barbiturates, hydantoins, glutarimides, glutaconimides, succinimides and maleimides were also suggested. The nitrogenous bases consisted of amines, hydroxylamines, or hydrazines, and their various derivatives. Such a suitable amine is aminoethylethanolamine.<sup>140</sup>

The selection of a cyclic imide-nitrogenous base as the silver complexing agent, and a suitable low- or no-staining development agent of the hydroxylamine type, provides a diffusion transfer system that avoids most of the chemical reasons that required aftertreatment of the transferred image. According to U. S. Patent 2,857,274, "If the associated complexing agents

and developer are judiciously chosen, the reaction product residue of the composition and silver halide will remain substantially colorless when present on the silver image either as a trace remaining after the processing composition layer has been separated from the silver image or within the protective coating formed when the processing composition has been permitted to remain upon the silver image." Thus, modern in-camera silver prints are able to avoid the chemical attack so common to the early instant prints when no aftertreatment of the freshly processed image was given. Various other chemical addition agents, such as sulfonamides,<sup>141</sup> imidazolidine-2-thiones,<sup>142</sup> and polyethyleneglycols,<sup>143</sup> are added to the processing fluid to increase the rate of silver transfer and image density so that high-quality transfer prints are available in seconds under a variety of environmental conditions.

## VARIATIONS OF THE DIFFUSION TRANSFER PROCESS

The ease with which positive images are produced by the diffusion transfer technique has led to the investigation of various modifications of the basic process, including some which do not involve the transport of silver ions from the negative to the receiver. Some of these ingenious variations are well worthy of mention.

### The Use of Water or an Alkaline Solution as the Transfer Fluid

Usually, the diffusion transfer reversal process has an alkaline, sometimes caustic, transfer solution with a silver complexing agent, often sodium thiosulfate, contained in the liquid or incorporated as part of the receiver layer. The thiosulfate or other silver solvent is necessary because the undeveloped silver halide of the negative image is insoluble in water or alkaline solution. The silver complexing agent makes possible the transfer of the silver ions from the negative to the positive layers. This silver solvent might not be needed if a light-sensitive silver salt of greater water solubility was used in place of the silver halide of the negative material.

Grant Haist<sup>144</sup> appears to have been the first to recognize that a separate silver solvent in the diffusion transfer system would be unnecessary if water-soluble, light-sensitive organic silver salts were used in the negative material to replace completely the silver halide. Earlier, Curt B. Roth<sup>145</sup> has used tap water to transfer the soluble silver salts normally present in very slow printout emulsions to a receiver, preferably with silver halide present. In one example, dark-brown letters on a dark background was obtained. Most light-sensitive inorganic silver salts are either insoluble or unsuitable, but silver-containing