United States Patent

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[54] **PHOTOGRAPHIC PROCESSES, COMPOSITIONS AND PRODUCTS**
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96/66
[51] Int. Cl... G03c 5/54
[50] Field of Search... 96/29, 76,
50, 60, 66, 95, 107

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ABSTRACT: Development solubilization photographic processes are disclosed wherein silver halide is preferentially dissolved from developing silver halide grains. Processing compositions employed in such processes include at least one silver halide complexing agent capable of forming a soluble silver complex, and preferably contains a second silver halide complexing agent capable of forming a less soluble silver complex. The dissolved silver halide may be transferred to another stratum to provide a visible image, preferably a silver transfer image which is a negative image of the photographed subject matter.
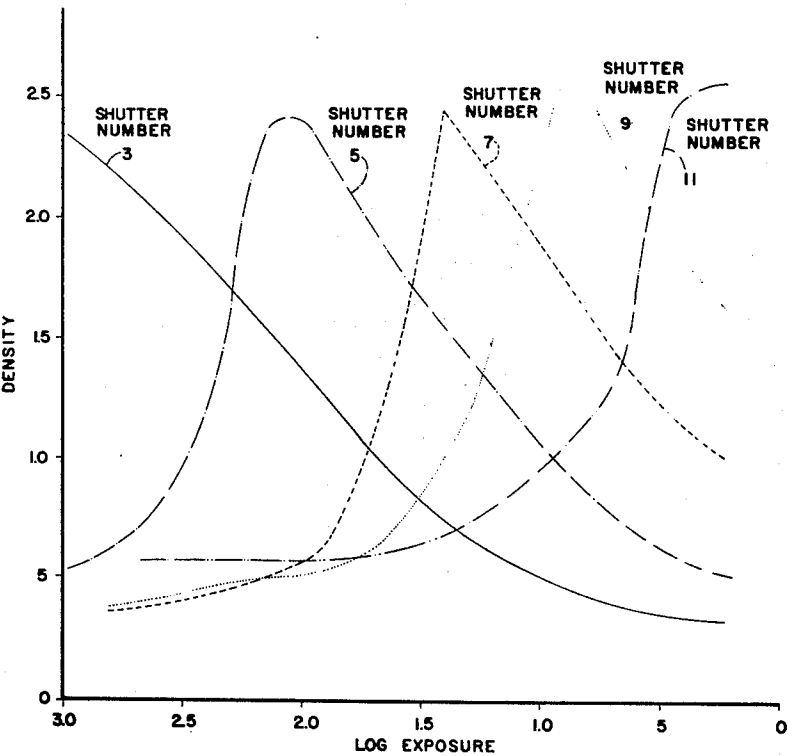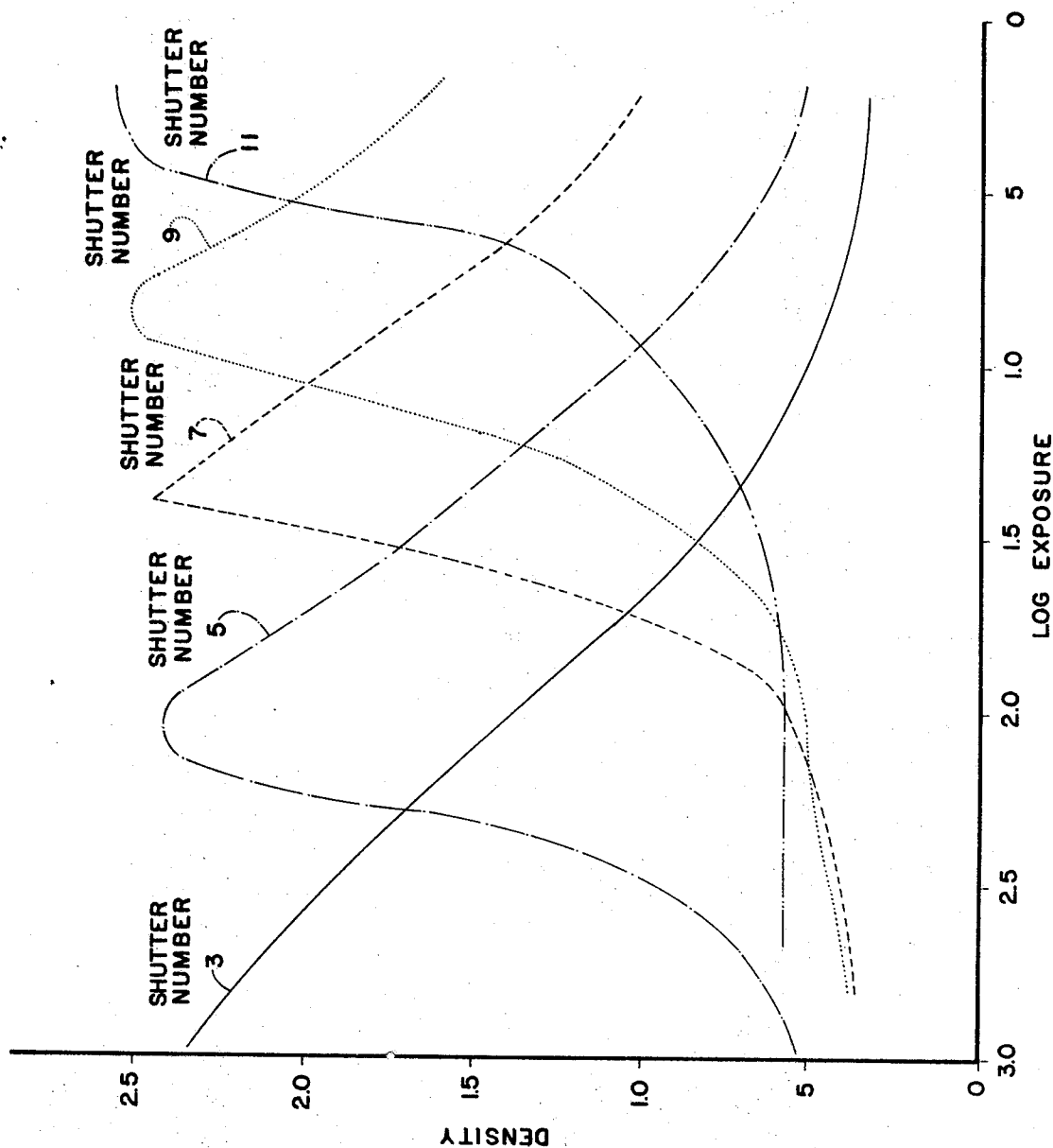
FIG. I

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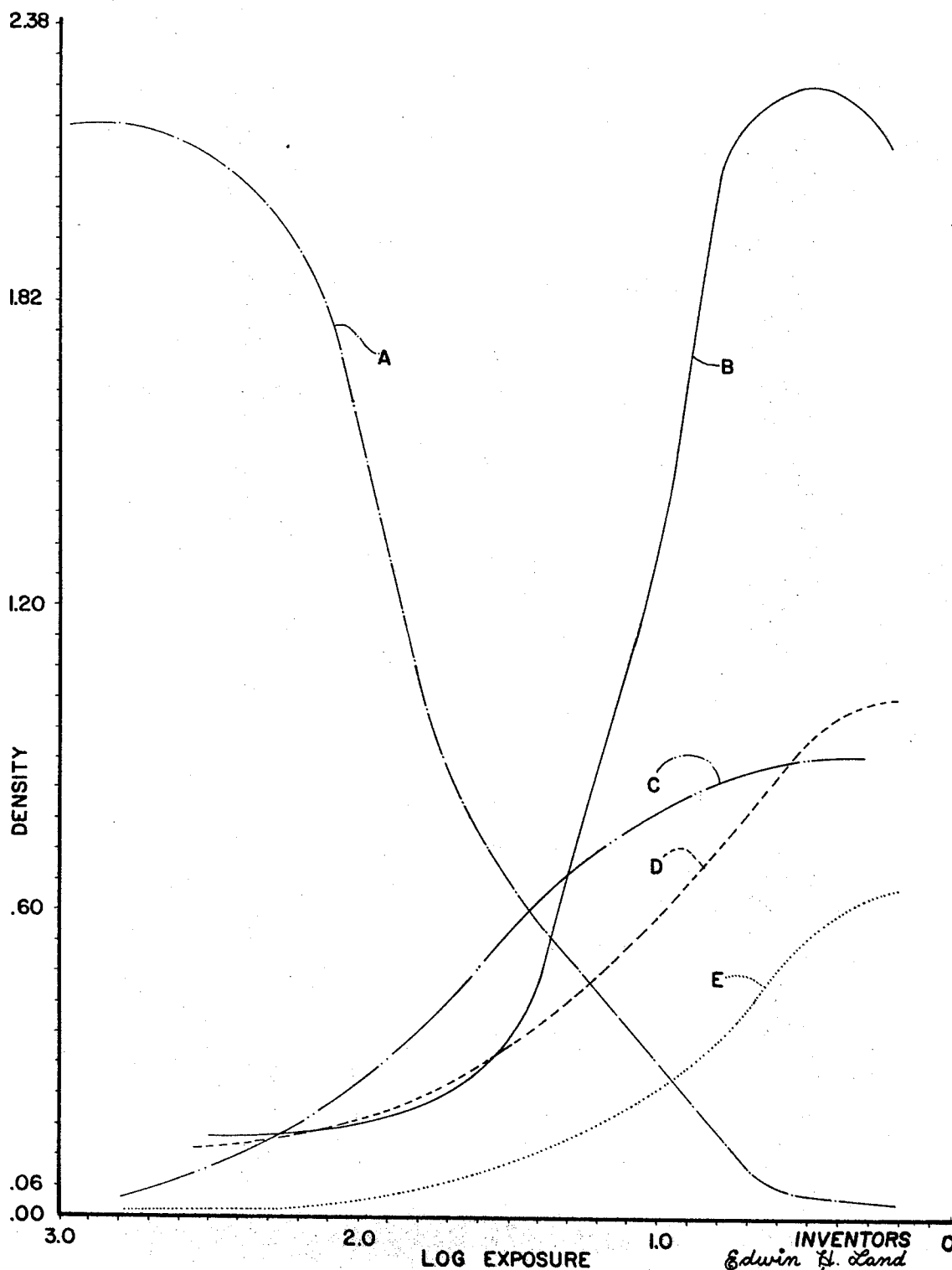BY
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3,615,438

FIG. 2

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PHOTOGRAPHIC PROCESSES, COMPOSITIONS AND PRODUCTS

This invention relates to photography and, more particularly, to a novel photographic process wherein silver halide in exposed areas is preferentially solubilized during development of said exposed areas of an exposed silver halide emulsion.

Throughout the history of photography, the most useful photosensitive materials have been the silver halides, i.e., silver chloride, silver bromide, silver iodide and mixtures thereof. No photosensitive material is as efficient and as generally useful as silver halide. No other photosensitive media offer the multitude of advantages exhibited by silver halides, e.g., the responsiveness to light of various colors, the stability of the resulting images, the multiplication effect obtained when one develops an exposed silver halide emulsion, etc.

Silver halide emulsions are of two general types: (a) developing out and (b) printing out. In a "developing out" emulsion, an invisible or latent image is formed by photoexposure, and that latent image is rendered visible by chemical development, i.e., by preferentially reducing or "developing" the exposed silver halide to silver. A "printingout" emulsion, on the other hand, produces a visible image simply by prolonged exposure to light. This invention is concerned with silver halide emulsions of the "developing out" type, and takes full advantage of the latent image formed by photoexposure.

An integral part of almost all photographic processes utilizing silver halides has been the ability to preferentially dissolve the unexposed silver halide, and thus remove the unexposed silver halide from the stratum containing the exposed silver halide emulsion, either contemporaneously with or subsequent to development. The preferential solubilization of unexposed silver halide substantially contemporaneously with development of the latent image has given life to a family of photographic processes generally referred to as silver diffusion transfer processes (see, for example, U.S. Pat. No. 2,543,181, issued Feb. 27, 1951; "A new One-Step Photographic Process," by Edwin H. Land, *Journal of the Optical Society of America*, Vol. 37, pp. 61–77, Feb., 1947; "One-Step Photography" by Edwin H. Land, *The Photographic Journal*, Jan., 1950, pp. 7–15). The dissolved silver complex may be transferred to a different stratum and there precipitated, e.g., reduced, to provide a transfer image in silver which is positive with respect to the negative image formed by development of the exposed silver halide containing the latent image.

We now have discovered that if a given grain of silver halide has received an exposure sufficient to render it developable in a given processing composition, and said processing composition contains a silver halide solvent in addition to a silver halide developing agent and the other usual components, then there is a competition is said grain between development and solubilization of the silver halide of that grain. We have further discovered that we can so adjust the relative rates of developability and solubility of a given grain of developing silver halide so that where incipient development occurs, we will obtain preferential solubilization of silver halide from said developing grain, i.e., silver halide in the developing grain will be dissolved at a rate much greater than the solubilization rate of silver halide in unexposed and, hence, undeveloping grains. This new process we call "development solubilization," since solubilization of silver halide is effected, within the predetermined processing time period, substantially only in silver halide grains which have started to develop, and the silver halide in unexposed grains is substantially insoluble in said processing composition within said predetermined time.

As noted above, we have discovered that we can adjust the relative rates of development and solubilization so that silver halide in a developing grain is preferentially dissolved in the processing composition. We have found that such an adjustment in the relative rates of development and solubilization may be effected by using an appropriate concentration of the silver halide solvent. The difference between the relative rates of development and solubilization may be relatively narrow in any given situation, as, for example, when one relies primarily upon the relative concentration of the silver halide solvent to obtain development solubilization. We have further discovered, however, that the differential between the relative rates of solubilization and development of a given developing grain may be desirably modified, and superior images obtained, if development is effected in the presence of a reagent which we call a "development solubilization promotor"; this reagent will be discussed in more detail hereinafter.

It is a unique characteristic of our invention that conventional silver halide emulsions are employed, and that such conventional silver halide emulsions are given normal exposures, and, in many instances, exposures substantially less than said normal exposure; the silver halide in exposed areas is then preferentially solubilized as a function of the development of the latent image formed by said exposure.

Thus, by utilizing this discovery that a developing grain of silver halide may be dissolved more rapidly than a grain which is not developing, and by dissolving such silver halide in preference to developing it, one may employ conventional silver halide emulsions in a host of new and extremely useful ways to provide images which are either negative or positive, or even partially negative and partially positive, with respect to the latent image formed by photoexposure. This discovery is particularly useful in forming images by diffusion transfer, as will be described in detail hereinafter.

Accordingly, it is a primary object of this invention to provide novel photographic processes wherein silver halide in exposed areas is more rapidly dissolved in a processing composition than is silver halide in unexposed areas.

Additional objects of this invention are to provide novel photographic processing compositions in which exposed silver halide is more rapidly dissolved than is unexposed silver halide, and to provide novel photographic products embodying and employing said novel photographic processing compositions.

A further object of this invention is to provide diffusion transfer images in terms of a novel complex of exposed silver halide and one or more complexing agents, which complex may be precipitated to provide a visible image, which image may be in silver.

Another object of this invention is to provide photographic processes wherein silver halide grains which have received the minimum exposure necessary to render them developable are rendered dissolvable and silver halide grains which have received a lesser exposure than said minimum exposure are not dissolved in said processing composition.

STill another object of this invention is to provide a novel complex of exposed silver halide and one or more complexing agents, which complex is stable to reduction by a silver halide developing agent in the absence of a silver precipitating agent.

Another object of this invention is to provide a novel complex of exposed silver halide, which complex is soluble in aqueous alkali and which complex is transparent to visible light but absorbs ultraviolet light.

A further object of this invention is to provide photographic processes which produce images at very small exposures.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the processes involving the several steps and relation and order of one or more of said steps with respect to each of the others, and the product and composition possessing the features, properties and the relation of elements, which are exemplified in the following detailed disclosure, and the scope of the application which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

The figures illustrate characteristic curves of silver transfer images obtained in accordance with this invention.

The terms "exposed silver halide" and "unexposed silver halide" are used herein in their accepted and usual meaning in the photographic art. A given silver halide grain is considered to be "exposed" if it has received an amount of exposure sufficient to cause it to be developed when treated with an appropriate developer composition; the developability of a given silver halide grain thus is a function, inter alia, of the number of quanta absorbed. It is believed that individual silver halide grains actually receive gradations of exposure as a function of the incident exposure; an individual silver halide grain therefore may be said to be composed of both exposed and unexposed areas. Thus, in somewhat more precise terms, the instant invention may be said to involve the preferential solubilization of silver halide in or from the exposed grains of the exposed silver halide emulsion, this preferential solubilization being imagewise as a function of the development of exposed grains, the amount of silver halide dissolved and diffused away from a given developing grain being a function of the degree of exposure.

Most photographic systems employing silver halide require, and depend upon, rendering the exposed silver halide insoluble, as by preferentially and selectively reducing the exposed silver halide to silver. These systems employ the latent image formed upon exposure to catalyze this discriminatory reduction of the exposed silver halide. Special silver halide emulsions, e.g., the so-called "internal latent image emulsions," have been described which exhibit the property of having the unexposed silver halide develop at a faster rate than does the exposed silver halide; silver halide emulsions of this type require special processing conditions and exhibit, relatively speaking, low sensitivity to light and hence are said to be "low speed" materials.

The invention herein described and claimed, however, makes full utilization of conventional silver halide emulsions and the classical latent image formed therein by exposure. Ordinary silver halide emulsions, ordinary silver halide developing agents, ordinary alkalis, and ordinary silver halide complexing agents or solvents may be used in practical applications of this invention.

As stated above, it has been discovered that the relative rates of developability and solubility of a given grain of silver halide may be so adjusted that at a given exposure incipient development of exposed silver halide will result in the solubilization of silver halide in exposed grains at a rate much greater than the solubilization rate of unexposed silver halide grains. Increasing the exposure beyond the amount necessary to make the grain developable and, hence, beyond the amount necessary for said incipient development, will lead to fuller development of the silver halide of that grain into silver in the silver halide stratum. Thus, at a given exposure, an unexposed and, hence, and undeveloped, grain is insoluble in the processing reagent within the processing time, but exposed grains that begin to develop are also rendered soluble. Whether the resulting dissolved silver halide is reduced to silver at the same locus or it is diffused to another locus is a function of the amount of exposure received by the grain, i.e., the amount of silver halide which will diffuse to another locus after being dissolved inversely proportional to the amount of exposure received by the exposed grain. The particular property most valuable in this new process, e.g., in the formation of a negative transfer image, is the solubilization of the silver halide grain by the combination of he minimum exposure necessary to make it developable, plus the first stages of actual development. This minimum exposure is very small indeed, and is frequently less then what is ordinarily specified for a given negative material for ordinary photographic processes.

As noted above, the relative rates of developability and solubility of a given silver halide grain may be so adjusted that as a result of incipient development of solubilization of silver halide is, in effect, catalyzed where development occurs so that silver halide in exposed grains is preferentially dissolved, i.e., dissolved at a much greater rate than is silver halide in unexposed grains. These relative rates may be adjusted in vari-

ous ways to achieve the requisite balance. In general, the desired relationship may be obtained by employing a processing composition containing a silver halide developing agent and at least one reagent which is capable of forming a soluble silver halide complex. The concentration of this soluble silver complex former (i.e., silver halide solvent) by itself or in combination with a reagent which is capable of forming a relatively insoluble silver halide complex. This latter reagent we call a "development solubilization promotor." The preferred method of adjusting the relative rates of developability and solubility is to effect development of the latent image in the presence of a combination of a silver halide solvent and a development solubilization promoter. Such a combination is effective to dissolve silver halide more rapidly where development has started that it dissolves silver halide in unexposed areas.

A "development solubilization promoter" is a compound which, under appropriate conditions, cooperates with a silver halide solvent to lead to the preferential solubilization of exposed silver halide, i.e., silver halide of a silver halide grain which has received a predetermined, small exposure sufficient to render it incipiently developable in the processing composition. The mechanism by which the development solubilization promoter performs this function is not precisely known. A large variety of compounds have been found to be capable of acting as development solubilization promoters. Examination of the properties of these compounds, when employed in conventional wet photographic processes, shows a number of common characteristics. It will be understood that all of these properties need not, and may not, be exhibited by a given development solubilization promotor. Nevertheless, the recognition that one or more of these properties is present may be advantageously used to select additional compounds for use as development solubilization promoters. One such property is the ability to form a salt or complex with silver ion or silver halide; many of these compounds are reported in the photographic literature to form substantially water-insoluble silver salts. Many development solubilization promoters contain the grouping

$$-N{=}C{-}N{-}, \quad -N{=}C{-}O{-}, \quad \text{or} \quad -N{=}C{-}S{-}$$
$$\overset{|}{SH} \qquad \overset{|}{SH} \qquad \overset{|}{SH}$$
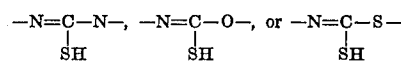
(or the tautomeric forms thereof). A property exhibited by most of these compounds is the ability to act, in appropriate concentrations, as a development restrainer and/or as an antifoggant. A number of the compounds found by us to be useful as development solubilization promoters have previously been proposed for use as toning agents in the formation of positive silver diffusion transfer images. In general, the concentrations in which such compounds are employed as development solubilization promoters are greater then the concentrations in which they would be employed as antifoggants, toning agents, etc. A useful test by which a test compound may be screened for activity as a development solubilization promoter is to add the test compound to a diffusion transfer processing composition containing a silver halide solvent, preferably an alkali metal thiosulfate, and effective to form a positive silver transfer image at a normal exposure. If a development solubilization promoter is subjected to this test, it is found that as its concentration is increased, a concentration is found at which transfer of unexposed silver halide is essentially stopped but negative development is not prevented. At this point, the concentration of the silver halide solvent is increased and the imbibition time is increased until a negative or a negative-positive silver transfer image is obtained. If a negative-positive transfer image is obtained, reducing the exposure will give a negative silver transfer image.

Another useful test by which a test compound may be screened for activity as a development solubilization promoter is to prepare a processing composition containing a silver halide developing agent and a silver halide solvent and effective

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to dissolve and diffusion transfer unexposed silver halide. The test compound is added to the processing composition in incremental amounts until unexposed silver halide is no longer dissolved and transferred. The processing composition is then used to process an exposed photosensitive element, e.g., a photosensitive stratum exposed at its usual "equivalent A.S.A. exposure index" (as defined hereinafter). If the test compound is useful as a development solubilization promoter, a silver transfer image will be obtained, which image will be positive or partially negative/partially positive with respect to the latent image. If the exposure is then reduced, the scale of silver transfer image will become more "negative."

Although we may employ as development solubilization promoters compounds which exhibit the property of restraining development, and we may employ such compounds in concentrations much greater than if they were being used to restrain development in a conventional photographic system, the silver halide remains developable, and generally with a gain in sensitivity, although the rate of development may be slowed down.

After a conventional silver halide emulsion has been exposed, preferably at greater than the ordinary exposure index for said silver halide emulsion, the exposed silver halide emulsion is subjected to the novel processing reagent of this invention, which processing reagent *quite rapidly dissolves the silver halide in exposed and developing areas* but only very slowly dissolves the silver halide in unexposed areas. The thus-formed soluble complex exposed silver halide will precipitate silver, e.g., it will be reduced to silver, in the presence of a silver precipitating environment, such as that provided by the silver precipitating environments of the well-known silver transfer processes. As a result, the silver halide dissolved in exposed areas of the silver halide emulsion may be precipitated in a different locus, and particularly in a different plane, from that occupied by the original silver halide grain at the time of exposure. There are many advantages to this transfer—for example, it provides a fixed negative image of high density and high contrast from a layer of silver halide emulsion so thin that if developed in the ordinary way the density and contrast would be relatively low. The solubilization of silver halide from the exposed areas of the silver halide emulsion leaves behind the unexposed silver halide, possibly in complex form but still light sensitive. If the so processed silver halide emulsion then is stopped and fixed in the dark, a negative image may be obtained in the silver halide emulsion layer in addition to the negative transfer image formed from dissolved and transferred silver halide. Alternatively, if the unexposed silver halide remaining in the silver halide emulsion is exposed to environmental light after removing the exposed silver halide through this new development solution process, a positive image may be formed in the silver halide emulsion layer without utilization of reagents beyond those originally applied following the original photoexposure; if desired, a separate and conventional developing bath can be used to develop the originally unexposed silver halide to a positive image in the original silver halide emulsion layer. The residual unexposed silver halide may be rendered developable in other ways than by exposure to light; indeed, it may be reduced to silver simply by application of a suitable reducing agent, which reducing agent need not be a silver halide developing agent.

It is an extraordinary characteristic of this new process that when the conditions have been established to preferentially dissolve and transfer silver halide from a given exposed silver halide grain at a given exposure, increasing the exposure will lead to the development of more of the silver halide of that grain and one can reach a level of exposure which will result in the development of substantially all of the silver halide of that same grain in the silver halide stratum, thus preventing the transfer of any silver halide from that grain. It is a remarkable further characteristic of this new process that when this greater exposure has been established which prevents such transfer, a change in the processing composition, e.g., a reduction in the concentration of the silver halide solvent or an in-

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crease in the concentration of the development solubilization promoter, will again make possible the transfer of at least a portion of the exposed silver halide grain at this greater exposure. This interrelationship between the various factors, i.e., exposure, processing time, concentration of silver halide solvent, concentration of development solubilization promoter, etc., permits a great deal of flexibility and latitude and enables one to establish the processing conditions which will result in any desired image scale.

Based on the experimental evidence, it is possible to describe this new process as follows: In the processing reagent, unexposed and, hence, undeveloped silver halide grains are quite insoluble, but incipiently developed silver halide grains are highly soluble. From this it would follow that in this new process an unexposed silver halide grain would not dissolve and thus would not transfer, and that increasing the exposure in any region would lead to full development of the silver halide in the silver halide stratum and hence no transfer from those regions. It also follows that prolonged imbibition or immersion in the processing reagent could dissolve the unexposed silver halide grains and, if transferred, lead to high density in the transfer image. It further follows that at a given exposure, only those grains which undergo development have the capability of contributing silver halide which may be preferentially dissolved and transferred to another locus. The amount of silver halide which may be dissolved and transferred is proportional to the exposure received by a given grain and the size or volume of that grain. Combining these factors and observations, proper exposure to a normal scene will result in the preferential solubilization of exposed silver halide and, if performed in a diffusion transfer process, will lead to the formation of a negative transfer image. It will further be seen that this new process is capable of producing a transfer image which has both a negative and a positive scale, the highest density of the positive scale being produced at approximately the same exposure as the highest density of the negative scale.

It will be helpful in understanding this invention if, at this point, we examine what happens in this development solubilization process with just two grains of silver halide, one grain which is unexposed and one grain which has received a little exposure.

The unexposed grain is not dissolved because its rate of solubilization in the processing composition is too slow for any significant dissolving to occur within the predetermined period. The silver halide grain which has been exposed begins to develop. In accordance with the previous discussion, the grain which has begun to develop also starts to dissolve. It is also true that the amount of insoluble silver formed by development of a given grain increases with the amount of exposure the grain has received; up to a crossover point in the relative rates of development and solubilization, this formation of silver by development does not increase as rapidly as the solubilization and/or diffusion rates of the dissolved silver halide. Thus there is an exposure so great that the rate of development becomes great enough that essentially all of the silver halide of such an exposed grain is reduced to silver, i.e., essentially all soluble complex of silver halide formed from such a heavily exposed grain is reduced to silver in the same locus and is not transferred to a different locus. It is believed that such heavy exposures create nucleation sites in a quantity proportional to exposure and that these nucleation sites are effective to "abstract" the silver halide dissolved from that grain and cause it to be precipitated essentially in the same locus. It therefore follows that the amount of silver halide which can be solubilized and transferred from an exposed grain can be plotted against exposure, to give a type of characteristic curve for each grain.

An insight into the mechanism of the development solubilization process has been obtained by the study of movies of developing silver halide grains. In these studies, a monodisperse silver bromide emulsion, i.e., a silver bromide emulsion all the grains of which are substantially the same

size, was exposed and developed with a silver halide developing agent and a mixture of sodium thiosulfate and 1-phenyl-5-mercaptotetrazole. Development was observed in a microscope under infrared light. The silver bromide grains were cubic and approximately 2 microns large. Development was observed to initiate from a particular point on the cubic grain, presumably the latent image speck. From this point silver ions were dissolved with great force, and one could actually see the original grain recoil from this stream and move back through the gelatin binder. Based upon these and other experimental observations, it is believed that the silver halide complexer(s) initially form a "skin" of less soluble silver halide except where a latent image speck has been formed by exposure, thus preventing solubilization of unexposed silver halide grains. The presence of the latent image speck, however, permits the silver halide developing agent to contribute electrons. The resulting forces generated at and within the grain cause the silver halide to be dissolved. If the thus-dissolved silver halide can be diffused away without becoming involved with a nucleation site provided by exposure or by already developed silver, it is free to be transferred to another locus, e.g., a superposed image-receiving stratum.

At any given exposure there will be a set or family, or several families, of silver halide grains of like grain size and/or sensitivity, which will be incipiently developable, and the scale of the transfer image will reflect the "mix" of such sets or families of grains which are developing. It must also be noted that the scale of the transfer image formed by development solubilization processing is determined by the volume, i.e., size, of a given grain and the amount of exposure of that grain; in contrast, the scale in conventional photography is obtained from the grain size distribution, and only a high contrast image is obtained in conventional photography if a homogeneous grain size emulsion is employed. In our invention, we can superpose these two scale producing systems.

Accordingly, the scale of transfer images obtained by development solubilization may be extended by mixing families of grain sensitivities. Each new set or family of lower sensitivity grains will extend the length of the negative scale of the transfer image before the scale reverses to positive. To obtain this extended negative scale, it is desirable to have the relative rates of solubilization and development substantially the same for grains of different size or different sensitivity. An all large grain emulsion of varying sensitivity grains may be obtained by mixing sensitized and unsensitized grains of the same size.

The development solubilization process may produce a transfer image which is negative, positive, or a combination of negative and positive scales. It is important to remember that the positive transfer image obtained by development solubilization is formed by a different mechanism than that employed in the now conventional positive silver transfer process. In the latter, the positive is formed from unexposed silver halide, exposure removing silver halide from the domain of solubility. In the development solubilization process, all silver transferred is made available for transfer by exposure and the initiation of development of the exposed grains.

In any silver halide emulsion, at any given incremental exposure, there is a number of "population" of silver halide grains which, by virtue of their size and/or sensitization, will receive an exposure sufficient to be rendered developable by an appropriate developer composition. If one plots the number of grains rendered developable by each incremental increase in exposure against the exposure scale, a typical camera speed silver halide emulsion will show a generally bell-shaped grain-sensitivity distribution curve. This curve shape follows from the fact that at the lowest exposure, a small or minimum number of grains will be exposed, i.e., rendered developable; these grains are the most sensitive grains present. As the amount of exposure increases, the number of additional grains rendered developable by each incremental increase in exposure will increase until a maximum in grain population (representing a medium sensitivity) is reached, after which each further incremental increase in exposure will

render fewer and fewer additional grains incipiently developable until a new minimum in grain population is reached; the latter grains are the least sensitive grains. To obtain a negative transfer image by development solubilization, we use an exposure range whose minimum will render some grains incipiently developable and whose maximum is the exposure at which the population of incipiently developable grains becomes a maximum. To obtain a positive transfer image by development solubilization, we use an exposure range whose minimum is where said population is a maximum. We note then that the positive transfer image in our new process is formed by having its maximum density derive not from all the grains in the silver halide emulsion, as in the conventional silver transfer process, but from that fraction of the grains that run from the high population of medium sensitivity to the low population of lowest sensitivity. The decrease in transfer density with increasing exposure for the positive mode of the process thus is due to two factors: first, the development to silver, at their original site, of an increasing number of grains; and second, the diminishing population, together with their decreasing volume, of grains present which can be made developable by incipient development with increasing exposure.

Thus the same chemistry, i.e., the same developing composition, can give either a negative or a positive transfer image, depending upon the population distribution of incipiently developable grains. For every grain, there exists a critical exposure, i.e., a useful but reasonably small exposure range, which makes some portion of that grain dissolve and transfer. At any given exposure, only the developing grains contribute density to the transfer image and therefore transfer density is a function of the population ordinate of the grain-sensitivity distribution curve, i.e., the "altitude" or height of the distribution curve of grains according to size and sensitivity; thus, transfer density at a given exposure is a function of the total number of grains of a given size and/or sensitivity. Thus, we can vary the shape of the characteristic curve of the transfer image by changing the population of silver halide grains of any given size and sensitivity.

It is a unique characteristic of this new process that the solubilized exposed silver halide need not be reduced to silver. In fact, this novel complex of exposed silver halide has been found to be quite stable to reduction by silver halide developing agents, even in the presence of alkali. This complex may be reduced to silver, however, by bringing it into a silver precipitating environment of the type found so useful in silver transfer processes.

The terms "latent image," "negative image" and "positive image" are used herein in their conventional, classical meanings. Thus, the latent image is a negative image of the subject to which the silver halide emulsion was exposed. The imagewise distribution of soluble exposed silver halide complex also is a negative image of the photographed subject matter and a positive image of the latent image, i.e., it is not reversed, in the positive-negative sense, with respect to the latent image. It will therefore be understood that if the silver halide emulsion is exposed to actinic light through a negative transparency, the latent image formed will be a positive image, and the silver image formed by precipitation of the transferred soluble complex of exposed silver halide also will be a positive image.

As stated above, this new process may employ any silver halide developing agent, such as:

hydroquinone
4-N-methylamino-phenol [Metol]
ascorbic acid
isoascorbic acid
2,6-dimethyl-4-amino-phenol
toluhydroquinone
2,6-dimethyl-hydroquinone
2-methyl-4-amino-6-methoxy-phenol
2.6-dimethoxy-4amino-phenol
2.5-dimethyl-hydroquinone
2,4,6-triamino-phenol
2,4-diamino-phenol [Amidol]

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N,N-diethyl-hydroxylamine
N,N-bis-methoxyethyl-hydroxylamine
4,6-diamino-ortho-cresol

The processing reagent includes a silver halide complexer or solvent of the type employed in conventional, i.e., positive, silver transfer processes, i.e., a reagent which will form a diffusible complex with unexposed silver halide, such as sodium thiosulfate, potassium thiosulfate, barbituric acid, uracil, etc. The usual alkalis, e.g., sodium hydroxide, potassium hydroxide, diethylamine, etc., may be used.

In accordance with the preferred embodiments of this invention, as stated above, the processing composition or reagent also includes a development solubilization promoter. As previously noted, a characteristic of many compounds useful as development solubilization promoters is their ability to act as development restrainers or antifoggants in conventional processes. Indeed, many compounds found useful in this invention, e.g., 1-phenyl-5-mercaptotetrazole, have been employed or proposed for employment in positive silver transfer processes in very small quantities, as is conventional in the normal use of development restrainers and antifoggants in photographic processing. In addition, some compounds herein used as development solubilization promoters have been used or suggested for use as toning agents in positive silver transfer processes; again, in such instances, they are used in relatively minute quantities. In this invention, these compounds frequently are employed in quantities substantially greater than fog-inhibiting or image-toning quantities.

Useful development solubilization promoters may be mercapto heterocycles, e.g.,
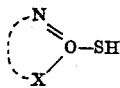
wherein X=O, N or S, and the heterocyclic radical is a member of the tetrazole, oxadiazole, oxazoline, imidazole, benzoxazole, purine, triazole, thiadiazole, thiazoline, thiazole, benzothiazole or pyrimidine series, or the corresponding disulfide; an acyclic mercaptan, such as thiourea or 2-mercaptoethyl sulfide or the corresponding acyclic disulfide, or a nitrogen heterocycle, such as a member of the triazole, xanthine, imidazole, indazole or purine series.
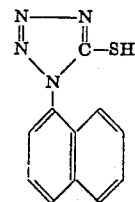
As examples of development solubilization promoters useful in practicing this invention, mention may be made of:
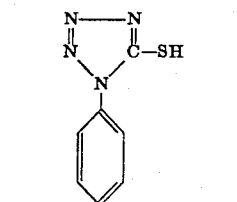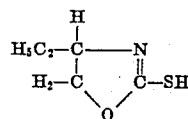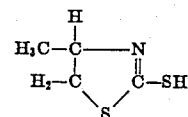
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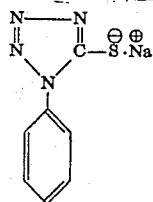
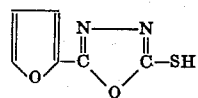1-phenyl-1H-tetrazole-5-thiol sodium salt
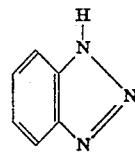
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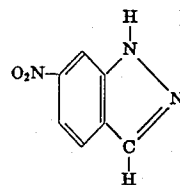
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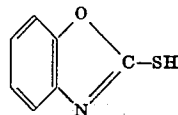
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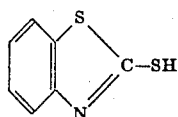
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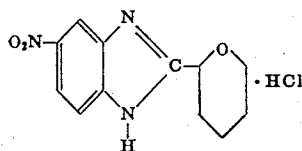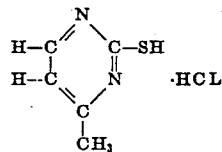
benzotriazole

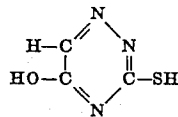6-nitroindazole

2-benzoxazole thiol

2-mercaptobenzothiazole

6-nitro-2-(2'-oxacyclohexano)-benzimidazole hydrochloride

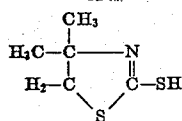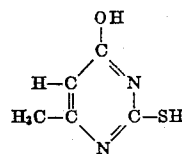2-mercapto-4-methyl-pyrimidine hydrochloride
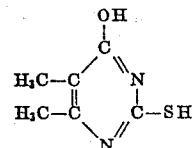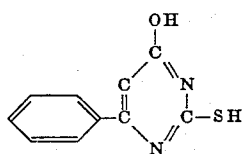
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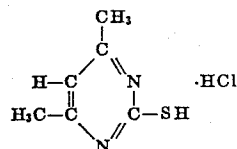
11

CH₃

4,4-dimethyl-2-thiothiazoline

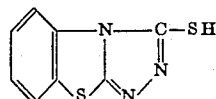4-hydroxy-2-mercapto-6-methyl-pyrimidine
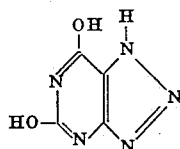
5,6-dimethyl-4-hydroxy-2-mercapto-pyrimidine

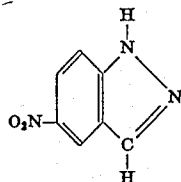4-hydroxyl-2-mercapto-6-phenyl-pyrimidine

4,6-dimethyl-2-mercapto-pyrimidine hydrochloride

3-mercapto-8-thia-1,2,3-a-triazacyclopent(a)-indene

8-azaxanthine

5-nitroindazole
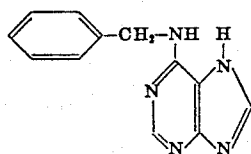
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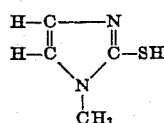
2-mercapto-1-methyl-imidazole

12
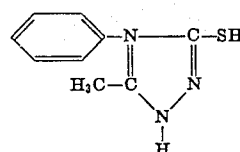
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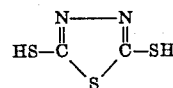
2,5-dimercapto-1,3,4-thiadiazole

$HS-CH_2-CH_2-S-CH_2-CH_2-SH$
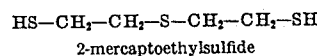
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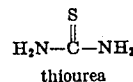
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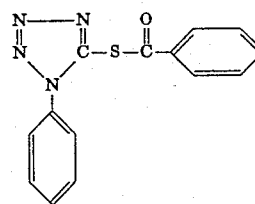
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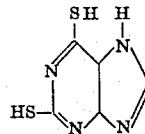
2,6-dimercaptopurine

40 The desired preferential solubilization of exposed silver ha-
lide may be effected by using an appropriate quantity of a
silver halide solvent, such as sodium thiosulfate. This embodi-
ment, however, is not as effective as the use of a combination
of a silver halide solvent and a development solubilization
45 promoter. The latter embodiment has been found to be more
generally applicable with various negatives and silver
precipitating agents, and to give the highest transfer densities
and film speeds.

Reference is frequently made herein to "film speed" and
50 "exposure index." It is therefore appropriate to briefly discuss
these terms and how they are used. The "speed" of a
photosensitive material comprises generally an empirically
derived relative measurement which may be defined as a value
representing the reciprocal of the exposure required to
55 produce a given result. Over the years, the American Stan-
dards Association has established standards for rating sensi-
tive materials for speed. Under these standards, emulsion
speed is considered as a value inversely proportional to the
60 minimum exposure which must be incident upon the negative
material, from the scene element of minimum brightness in
which detail is visible, in order that a print of excellent quality
can be made from the resultant negative. These standards
specify techniques for plotting the characteristic H & D curve
65 of a negative material, that is, the curve relating the logarithm
of the original exposure of the negative to density in said nega-
tive. The value of speed derived from the standard charac-
teristic curve so determined is specified as equal to the
reciprocal of the exposure, E, on the characteristic curve at
70 which the slope is 0.3 times the average slope for a log expo-
sure range of 1.5 of which E is the minimum exposure. (See,
ASA Publication PH 2.5—1954, "American Standard Method
for Determining Photographic Speed and Exposure Index".)

The A.S.A. speed rating is to be distinguished from what is
75 termed the A.S.A. Exposure Index, for use with exposure me-

ters and calculators. The A.S.A. Exposure Index is determine by the formula A.S.A. Exposure Index = A.S.A. speed/4. The exposure index so obtained indicates, generally, the corre exposure rating to which an A.S.A. calibrated exposure meter must be set in order that it give correct exposure data for producing pictures of satisfactory high quality.

The A.S.A. speed rating is to be further distinguished from what may be termed "Diffusion Transfer Process Exposure Index." In diffusion transfer processes, the exposure index may be based on a curve relating original exposure of the negative to the density in the resultant transfer positive. It has been experimentally determined that the Diffusion Transfer Exposure Index of a silver transfer process may be determined by plotting a characteristic curve of the reflection (or transmission) density of the transfer image as a function of the log exposure of the negative emulsion, determining the exposure in meter-candle-seconds (mcs) at the point on this curve corresponding to a density of 0.50 (above base density if reflection densities are being measured and above $D_{min.}$ if transmission densities are being measured), and dividing the constant 4.0, by the exposure so determined. The exposure index so obtained indicates generally the correct exposure rating of a silver transfer process to which an exposure meter, calibrated to the A.S.A. Exposure Index, must be set in order that it give correct exposure data for producing transfer prints of satisfactory high quality, and is sometimes referred to as the "equivalent A.S.A. exposure index."

This invention finds principal applicability and utility in the formation of images by diffusion transfer processing techniques, and such uses constitute the preferred embodiments of this invention. Full utilization thus may be made of the existing apparatus, whether in cameras or otherwise, for performing the well-known positive diffusion transfer process. Thus, in the preferred embodiments, a photosensitive element containing a photosensitive silver halide stratum is exposed, and the latent image is developed employing a processing composition which may be applied before or after said exposure has been effected. In the preferred embodiments, the processing composition is applied in a relatively thin layer between the exposed photosensitive element and a second sheet which may serve as a support for the stratum in or on which the transfer image is formed. This support may comprise an opaque material where a reflection print is desired or it may comprise a transparent material where a transparency is desired. The processing composition preferably includes a high molecular weight film-forming, viscosity-increasing material which is stable to alkali over long periods of time, e.g., sodium carboxymethyl cellulose or hydroxy ethyl cellulose. The processing composition may conveniently be applied by distribution in a substantially uniform manner between said elements, for example, in accordance with the procedures disclosed in U.S. Pat. No. 2,543,181. For example, the processing composition may be contained in a rupturable container or pod which is attached to one of said elements, or otherwise positioned therebetween, so that upon application of pressure to said container the processing composition is released for spreading in a substantially uniform layer between and in contact with the opposed faces of said elements. Rupture of the container and spreading of its contents may be accomplished, for example, by advancing said elements in superposed relationship, and with said container appropriately positioned therebetween, between a pair of opposed, suitably gapped rollers. After said processing composition has been applied, the superposed elements are maintained in superposed relationship until the appropriate imbibition time has elapsed for formation of the desired diffusion transfer image. At the conclusion of this time interval, the image-receiving layer and its support are separated from the photosensitive layer as, for example, by manual stripping. The details and variations of such processing techniques, etc., are well known.

The image-receiving stratum preferably includes one or more silver precipitating agents or nuclei, whose presence during the transfer process facilitates the conversion of the

transferred silver complex into a visible image, and has a desirable effect on the amount and character of the silver precipitated during formation of the transfer image. As examples of silver precipitating materials, mention may be made of metallic sulfides and selenides, certain colloidal metals such as colloidal silver and gold, thiooxalates and thioacetamides. These preferably are distributed in a macroscopically continuous film that consists of submacroscopic agglomerates of minute particles of a suitable water-insoluble, inorganic, preferably siliceous, material such as silica aerogel. Materials of the foregoing types are more specifically described in U.S. Pat. Nos. 2,698,237 and 2,698,245 both of which issued to Edwin H. Land on Dec. 28, 1954, and U.S. Pat. No. 2,774,667 issued Dec. 18, 1956 to Edwin H. Land. The image-receiving stratum may also be provided by dispersing the silver reduction or precipitation agents or initiators in the processing fluid, so that the solidified layer of said fluid contains the desired silver transfer image, in accordance with the principles of U.S. Pat. No. 2,662,822, issued to Edwin H. Land on Dec. 15, 1953. In addition, processing may be effected in the presence of reagents adapted to render the tone of the silver transfer image more blue-black or neutral, as is now well known in silver transfer processes, e.g., as described in U.S. Pat. No. 2,984,565 issued May 16, 1961 to Meroe M. Morse.

It is a unique characteristic of this process that negative transfer images are obtained using exposure indices which are usually one to two or more stops faster than the normal recommended exposure index for obtaining positive silver transfer images by diffusion transfer processing of a given silver halide emulsion. In the illustrative examples given below, the exposure is given in terms of "shutter numbers." These numbers represent combinations of lens apertures and shutter speeds such that the shutter numbers differ by a full stop exposure, with higher numbers giving lower exposures; thus, the higher the exposure index the higher the shutter number at a given brightness level. Illustrative shutter numbers and their equivalent shutter speeds and lens apertures are given in the following table:

Shutter Number	Shutter Speed	Lens Aperture
1	1/25	f/5.6
2	1/25	f/8
3	1/25	f/11
4	1/25	f/16
	1/100	f/8
5	1/25	f/22
	1/500	f/5.6
6	1/25	f/32
	1/500	f/8
7	1/25	f/45
	1/500	f/11
8	1/25	f/45
	1/500	f/22
9	1/100	f/45

By way of illustration, at a scene brightness level of 200 candles/sq. ft., i.e., a normal outdoors exposure condition, a diffusion transfer film with an A.S.A. equivalent exposure index of 200 usually would be exposed at shutter number 6, while a film with an A.S.A. equivalent exposure index of 1600 usually would be exposed at shutter number 9. In the examples given below, unless otherwise indicated, the exposures were through a step tablet to a cold grid; a diffusion transfer film with an A.S.A. equivalent exposure index of 200 would be exposed at shutter number 2 under these conditions.

The following examples are given only for the purpose of illustrating this invention, and are therefore not intended to be limiting. In these examples, the sodium thiosulfate employed was the pentahydrate, i.e., $Na_2S_2O_3 \cdot 5H_2O$, the sodium sulfite was anhydrous, and the potassium thiosulfate was anhydrous. The silver coverages were determined by X-ray fluorescence, and may be converted to equivalent silver halide coverages by

multiplying by the ratio of the molecular weight of the silver halide to the atomic weight of silver (107).

EXAMPLE 1

An Eastman Kodak Royal X Pan negative (average silver coverage 912 mg. Ag/sq. ft.) was exposed at Shutter 6 and processed by spreading a layer of the processing fluid, approximately 0.0020 inch thick, between the exposed negative and a surface hydrolyzed sheet of cellulose acetate. The processing fluid comprised:

Water	9.1 cc.
Hydroxyethyl cellulose	0.41 g.
Sodium hydroxide	0.26 g.
Sodium sulfite	0.33 g.
Potassium thiosulfate	0.14 g.
Diethylamine	0.5 cc.
Ascorbic Acid	0.6 g.
4,6-diamino-ortho-cresol	0.02 g.
Aqueous solution of sodium sulfide (156 mg. Na₂S/cc.)	0.011 cc.
Aqueous solution of lead acetate and cadmium acetate (100 cc. H₂O, 2.9 g. lead acetate; 2.1 g. cadmium acetate)	0.34 cc.
1-phenyl-5-mercaptotetrazole	0.03 g.

After an imbibition period of 3 minutes, the cellulose acetate sheet was separated from the exposed negative, and a negative silver transfer image was present in the solidified layer of processing fluid adhered to the hydrolyzed surface of the cellulose acetate sheet.

EXAMPLE 2

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 1 was repeated exposing an Eastman Kodak Super Panchro Press B negative (average 643–657 mg. Ag/sq. ft.) at Shutter 5, employing a layer of said processing fluid 0.0018 inch thick.

EXAMPLE 3

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 1 was repeated exposing an Eastman Kodak RS Pan negative at Shutter 5, employing a layer of said processing fluid 0.0026 inch thick.

EXAMPLE 4

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 1 was repeated exposing an Eastman Kodak Portrait Pan negative (average 790 mg. Ag/sq. ft.) at Shutter 3, employing a layer of said processing fluid 0.0026 inch thick.

EXAMPLE 5

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 1 was repeated exposing an Eastman Kodak Super XX Panchromatic negative (average 683 mg. Ag/sq. ft.) at Shutter 5, employing a layer of said processing fluid 0.0026 inch thick.

EXAMPLE 6

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 1 was repeated exposing an Ansco Versa Pan negative at Shutter 3, employing a layer of said processing fluid 0.0026 inch thick.

EXAMPLE 7

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of ex-

ample 1 was repeated exposing an Eastman Kodak Royal Ortho negative (average 660 mg. Ag./sq. ft.) at Shutter 6, employing a layer of said processing fluid 0.0015 inch thick, and the processing fluid contained 0.07 g. of 1-phenyl-5-mercaptotetrazole.

EXAMPLE 8

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 1 was repeated exposing an Eastman Kodak "Commercial Film" 4×5 negative (average 659 mg. Ag/sq. ft.) at Shutter 3, employing a layer of said processing fluid 0.0022 inch thick and the processing fluid contained 0.09 g. of 1-phenyl-5-mercaptotetrazole.

EXAMPLE 9

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 1 was repeated exposing a DuPont T-508 X-ray negative (average 1054 mg. Ag/sq. ft.) at Shutter 5, employing a layer of said processing fluid 0.0020 inch thick, the imbibition period being 5 minutes, and the processing composition contained 0.07 g. of 1-phenyl-5-mercaptotetrazole.

EXAMPLE 10

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 1 was repeated exposing an Eastman Kodak Gravure Copy negative (average 458 mg. Ag/sq. ft.) at Shutter 4, employing a layer of said processing fluid 0.0020 inch thick, the imbibition period being 4 minutes, and the processing composition contained 0.12 g. of 1-phenyl-5-mercaptotetrazole.

EXAMPLE 11

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 1 was repeated exposing an Ansco Super Hypan negative (average 1 mg. Ag/sq. ft.) at Shutter 5, employing a layer of said processing fluid 0.0026 inch thick, the processing fluid comprising:

Water	124 cc.
Sodium sulfite	5 g.
Sodium carboxymethyl cellulose	5.5 g.
Ascorbic Acid	9 g.
4,6-diamino-ortho-cresol	0.3 g.
Diethylamine	7.5 cc.
Sodium hydroxide	3.85 g.
Potassium thiosulfate	7.2 g.
Aqueous solution of sodium sulfide (156 mg. Na₂S/cc.)	0.177 cc.
Aqueous solution of lead acetate and cadmium acetate (100 cc. H₂O, 2.9 g. lead acetate; 2.1 g. cadmium acetate)	5.25 cc.
1-phenyl-5-mercaptotetrazole	0.38 g.

EXAMPLE 12

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 1 was repeated exposing a high speed panchromatic negative (average silver coverage of 96–108 mg. of silver per square foot) at Shutter 8½, employing a layer of said processing fluid 0.0012 inch thick, and the processing fluid contained an additional 0.1 g. of potassium thiosulfate.

EXAMPLE 13

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 12 was repeated except that the sodium hydroxide and

diethylamine were omitted from the processing fluid, and 0.35 g. of potassium hydroxide was added.

EXAMPLE 14

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 12 was repeated, except that the sodium hydroxide was omitted from the processing composition, and the diethylamine concentration was increased to 1.6 cc.

EXAMPLE 15

A negative silver transfer image was obtained in the solidified layer of processing fluid when the procedure of example 12 was repeated, except that the diethylamine was omitted from the processing composition.

EXAMPLE 16

A high-speed panchromatic silver halide negative (average 96–108 mg. Ag/sq. ft.) was exposed at Shutter 5, and the exposed negative processed by spreading a layer of processing fluid 0.0026 inch thick between the exposed negative and a superposed surface hydrolyzed cellulose acetate sheet. The processing fluid comprised:

Water	920 cc.
Sodium carboxymethyl cellulose	38.9 g.
Sodium hydroxide	25.8 g.
Sodium sulfite	33 g.
Potassium hydroxide	10 g.
Potassium thiosulfate	48 g.
Hydroquinone	10 g.
1-phenyl-5-mercaptotetrazole	3 g.
Metol	30 g.
Diethylamine	50 cc.

There were no silver precipitating agents anywhere in this system. After an imbibition period of 4 minutes, the cellulose acetate sheet having the solidified layer of processing fluid adhered to its surface was separated from the developed negative. The still wet layer of processing fluid was totally transparent to the eye, and it was immediately placed in an enlarger and an exposure was made through the still wet layer of processing fluid on to conventional enlarging paper, the light source being strong in ultraviolet light. Conventional wet development of the thus exposed printing paper gave a positive image, indicating that the invisible, transferred silver complex in the solidified processing layer absorbed, i.e., was opaque to, ultraviolet light, thus functioning as a negative.

EXAMPLE 17

The procedure of example 16 was repeated except that the solidified layer of processing fluid adhered to the cellulose acetate sheet was allowed to dry, resulting in the precipitation of the silver complex transferred from the exposed areas of the exposed negative, thereby forming a visible image in terms of a white precipitate. The precipitated complex is relatively opaque to the transmission of light and also reflects and scatters light, so that the areas containing the precipitated complex appear white by reflected light and black by projected light. In general appearance and utility, the image thus obtained is similar to a vesicular image.

EXAMPLE 18

The procedure of example 16 was repeated, except that the separated cellulose acetate sheet was immediately superposed on a silver receptive stratum containing silver precipitating agents, so that the surface of the still wet solidified layer of processing fluid was in contact with the surface of the silver receptive stratum. After a few seconds, a negative silver image began to form in the silver receptive stratum by precipitation of the silver halide complex originally transferred to the layer processing fluid from exposed areas of the negative. The for-

mation of this negative silver transfer image was observed through the back of the transparent cellulose acetate sheet, and the image-receiving stratum separated after the transfer image had developed to adequate density; the duration of this second imbibition step varies, but good results have been obtained in about 5 to 10 minutes.

EXAMPLE 19

A high speed panchromatic negative (average 138 mg. Ag/sq. ft.) was exposed at Shutter 6 and processed by spreading a layer of the processing fluid, approximately 0.0022 inch thick between the exposed negative and an image-receiving element of the type used in Type 47 Polaroid Land Film. The processing fluid comprised:

Water	850 cc.
Hydroxyethyl cellulose	32.5 g.
Sodium sulfite	53.3 g.
Sodium thiosulfate	19.3 g.
Sodium hydroxide	40.5 g.
Toluhydroquinone	35.6 g.

to which was added 1 drop or 0.05 cc. of 2-mercaptoethylsulfide per 10 cc. of processing fluid. After an imbibition period of 2 minutes, the image-receiving element was separated from the exposed negative, to reveal a negative silver transfer image.

EXAMPLE 20

A negative silver transfer image was obtained in the image-receiving element when the procedure of example 19 was repeated exposing the negative at Shutter 8 and imbibing for 1½ minutes, the 2-mercaptoethylsulfide being replaced by 0.06 g. of 2-mercapto-5-furyl-1,3,4-oxadiazole per 10 cc. of processing fluid.

EXAMPLE 21

A negative silver transfer image was obtained in the image-receiving element when the procedure of example 19 was repeated exposing the negative at Shutter 8 and imbibing for 5 minutes, the 2-mercaptoethylsulfide being replaced by 0.07 g. of 2-mercapto-4-methyl-pyrimidine hydrochloride per 10 cc. of processing fluid.

EXAMPLE 22

A silver halide emulsion was prepared as follows: using constant agitation, 60 cc. of a solution of 30 g. of silver nitrate dissolved in 360 cc. of water at 60° C. was dumped into a solution formed by dissolving 54.6 g. of ammonium bromide, 6.1 cc. of a 15 percent potassium iodide solution, 4.5 cc. of a 28 percent ammonium hydroxide solution, and 30 g. of inert gelatin (limed ossein type) in 660 cc. of water at 70° C. After a pause of 8 minutes, the remainder of the silver nitrate solution was dumped in. After a pause of 5 minutes, one-half of a solution of 60 g. of silver nitrate dissolved in 360 cc. of water at 60° C. was added over a period of 1 minute. After a pause of 10 minutes, the remainder of the second silver nitrate solution was added over a period of 1 minute. After a pause of 2 minutes, the reaction mixture was cooled rapidly to below 20° C. The emulsion was flocculated for washing by adding a 50 percent by weight ammonium sulfate solution. The flocculate was washed until the supernate had a conductivity of 500 micro ohms/cm. 33 g. of an active gelatin then were added to the washed flocculate. After swelling the gelatin was dissolved and the flocculate melted at 35° C., the emulsion volume being adjusted to 800 cc. The pH was adjusted to 6.0 and the pAg to 8.9. The temperature was raised to 60° C. and 1 cc. of aurous thiocyanate sensitizer containing 0.25 mg. Au and 10 mg. ammonium thiocyanate was added. The emulsion ripened to optimum speed in 95 minutes, after which the pAg was adjusted to 9.10 and emulsion chilled. This emulsion had a silver to gelatin ratio of 1 and a silver concentration of 66.2 mg./cc.

A coating solution of this emulsion was prepared by adding 3 g. of gelatin to 10 g. of this emulsion, 40 cc. of water, and 0.25 cc. of a 25 percent aqueous solution of Triton X–100 wetting agent. This coating solution was applied to a cellulose acetate film base (8 feet long, 5 inches wide) on a loop coater at a speed of 10 feet per minute. The excess coating solution weighed 15.5 g. This negative then was exposed at Shutter 5 and processed by spreading a layer of processing fluid 0.0020 inch thick between the exposed negative and a conventional image-receiving element of the type used in Type 47 Polaroid Land Film. The processing fluid comprised:

Water	9.2 cc.
Sodium carboxymethyl cellulose (medium viscosity)	0.15 g.
Sodium carboxymethyl cellulose (high viscosity)	0.26 g.
Sodium sulfite	0.33 g.
Sodium hydroxide	0.26 g.
Potassium hydroxide	0.1 g.
1-phenyl-5-mercaptotetrazole	0.05 g.
Amidol	0.60 g.
Potassium thiosulfate	0.48 g.
Diethylamine	0.5 cc.

After an imbibition period of 4 minutes, the image-receiving element was separated, and adhered processing fluid was washed off. A negative silver transfer image was present in the image-receiving element.

EXAMPLE 23

A photosensitive element having a layer of a low speed fine grain X-ray type emulsion (average 174 mg. Ag/sq. ft.) was exposed at Shutter 4 and processed by spreading a layer of processing fluid 0.0018 inch thick, between the exposed photosensitive element and a surface hydrolyzed sheet of cellulose acetate. The processing fluid comprised:

Water	920 cc.
Sodium carboxymethyl cellulose	38.9 g.
Ascorbic Acid	60 g.
4,6-diamino-ortho-cresol	2 g.
Diethylamine	50 cc.
Sodium hydroxide	25.8 g.
Potassium thiosulfate	42 g.
Aqueous solution of sodium sulfide (156 mg. Na₂S/cc.)	1.18 cc.
Aqueous solution of lead acetate and cadmium acetate (100 cc. H₂O, 2.9 g. lead acetate; 2.1 g. cadmium acetate)	35.5 cc.
Sodium sulfite	33 g.
1-phenyl-5-mercaptotetrazole	2.2 g.

After an imbibition period of 3 minutes, the cellulose acetate sheet was separated from the exposed photosensitive element in the dark, and a negative silver transfer image was present in the solidified layer of processing fluid adhered to the hydrolyzed surface of the cellulose acetate sheet. The thus processed photosensitive element was rinsed off in the dark, after which the lights were turned on and the thus re-exposed photosensitive element was placed in a tray of Kodak Dektol developer (undiluted). Development was followed visually, and the photosensitive element was removed when maximum density had apparently been reached (about 1 to 2 minutes). The photosensitive element was placed in a "Rapid Fix" acid fixing bath to harden it; there was no evidence of actual fixing. The photosensitive element then contained a *positive* silver image ($D_{max.}$ 1.80, $D_{min.}$ 0.88 by transmission).

EXAMPLE 24

Silver precipitating agents (colloidal gold) were added to a silver halide emulsion which was then coated on baryta paper. The resulting photosensitive element was exposed at Shutter 2 and processed by spreading a layer of processing fluid 0.0026 inch thick between the exposed photosensitive element and a

surface hydrolyzed sheet of cellulose acetate. The processing fluid comprised:

Water	9.1 cc.
Sodium carboxymethyl cellulose	0.39 g.
Sodium hydroxide	0.257 g.
Potassium thiosulfate	0.28 g.
Sodium sulfite	0.33 g.
Ascorbic acid	0.6 g.
4,6-diamino-ortho-cresol	0.02 g.
Diethylamine	0.5 cc.
1-phenyl-5-mercaptotetrazole	0.022 g.

After an imbibition period of 3 minutes, the photosensitive element was separated in the dark and placed in a fixing bath for 3 minutes. Examination of the resulting image showed a very dense negative silver image of $D_{max.}$ 3.05 and $D_{min.}$ 0.4 (base density = 0.25), and no image in the unexposed areas even though a silver precipitating agent was present throughout the silver halide emulsion layer. A control silver halide emulsion processed under the same conditions except that the silver precipitating agent was omitted gave a negative image of $D_{max.}$ 0.85 and $D_{min.}$ 0.33 (base density = 0.25) and much lower film speed.

EXAMPLE 25

Five sheets of high speed panchromatic negative (average 138 mg. Ag/sq. ft.) were exposed at Shutters 3, 5, 7, 9 and 11, respectively. Each exposed negative then was processed by spreading a layer of the processing fluid, approximately 0.0018 inch thick, between the exposed negative and an image-receiving element prepared as described later in this example. The processing fluid comprised:

Sodium carboxymethyl cellulose (medium viscosity)	13.9 g.
Sodium carboxymethyl cellulose (high viscosity)	25 g.
Potassium thiosulfate	48 g.
Sodium sulfite	33 g.
Potassium hydroxide	10 g.
Metol	30 g.
Hydroquinone	10 g.
Diethylamine	50 cc.
Sodium hydroxide	25.8 g.
1-phenyl-5-mercaptotetrazole	3 g.
Water to make 1 liter	

After an imbition period of 3½ minutes, the image-receiving element was separated from the exposed negative, and the characteristic curves of each of the silver transfer images plotted. These characteristic curves are reproduced in FIG. 1, each curve being identified by the Shutter Number at which the corresponding exposure was made. The transmission densities, scales, and exposure indices for said scales of each of the transfer images are set forth in the following table:

Shutter number	Scale	Transmission densities		Exposure index	
		$D_{max.}$	$D_{min.}$	Positive scale	Negative scale
3	Positive	2.49	0.33	500	
5	Positive plus negative.	2.50	0.37	550	23,000
7	do	2.43	0.35	1,600	16,000
9	do	2.48	0.35	1,100	32,000
11	Negative	2.55	0.58		30,000

The indices were determined at a point 0.5 density units above $D_{min.}$ based on transmission density. Particularly significant are the general similarity of these characteristic curves, the consistency of the maximum density regardless of the positive or negative scale of the transfer image, and the remarkably greater speed of the negative scale as compared with the positive scale obtained at the same exposure. As indicated, all processing conditions and components were kept constant except for the stated changes in exposure.

The image-receiving elements employed in example 25, were prepared as follows: gold wire was evaporated in a rotat-

ing bell jar chamber, under vacuum (approximately 10^{14} mm. Hg), onto 50 g. of cellulose triacetate flakes; chemical analysis showed that the product contained 2.6 percent gold by weight. A coating solution was prepared by dissolving 11 g. of this mixture in 109 cc. of ethyl acetate, 36 cc. of methanol and 3 cc. of water. This coating solution was applied to baryta paper to provide a layer approximately 0.00035 inch thick. The thus formed cellulose acetate layer was treated with a hydrolyzing solution in accordance with the procedure described in Ostberg U.S. Pat. No. 3,078,178, issued Feb. 19, 1963, the hydrolyzing solution being applied to the surface of the cellulose acetate layer and being effective to hydrolyze the cellulose acetate to cellulose to a depth approximately half the thickness of said cellulose acetate layer. [Silver receptive layers prepared by the vacuum deposition of a silver precipitating agent onto a matrix material, dissolving the resulting mixture in a solvent for matrix material which solvent is not a solvent for the silver precipitating agent to form a dispersion of said silver precipitating agent in said matrix material and coating said dispersion on a support are disclosed and claimed in the copending application of Edwin H. Land, Ser. No. 675,472 filed Oct. 16, 1967 as a continuation-in-part of Ser. No. 437,799 filed Mar. 8, 1965, now abandoned, as a continuation-in-part of Ser. No. 249,922 filed Jan. 7, 1963 now Pat. No. 3,295,972.]

EXAMPLE 26

A high speed panchromatic negative (average 138 mg. Ag/sq. ft.) was exposed at Shutter 8 and processed by spreading a layer of the processing fluid, approximately 0.0022 inch thick, between the exposed negative and an image-receiving element of the type used in Type 47 Polaroid Land Film. The processing fluid comprised:

Water	9.2 cc.
Sodium carboxymethyl cellulose	0.39 g.
Sodium sulfite	0.64 g.
Sodium hydroxide	0.49 g.
Toluhydroquinone	0.36 g.
Sodium thiosulfate	0.23 g.
5-nitroindazole	0.05 g.

After an imbibition period of 2 minutes, the image-receiving element was separated and contained a negative silver transfer image.

EXAMPLE 27

A negative having a low speed fine grain silver halide emulsion of the X-ray type, having an average silver coverage of 174 mg. of silver per square foot, was exposed, through a 1.0 neutral density filter, for 1 second to a 7½ watt bulb positioned four feet from the negative. The so-exposed negative was then processed as described in example 1, except that the layer of processing fluid was 0.0026 inch thick. After an imbibition period of 3 minutes, the solidified layer of processing fluid adhered to the hydrolyzed surface of the cellulose acetate sheet contained a silver transfer image which exhibited both a negative and a positive scale. When this procedure was repeated except that the same thickness of processing fluid was applied 0.2 second before exposure, a silver transfer image was obtained which was very similar to the first transfer image but a little slower in film speed, i.e., sensitivity.

EXAMPLE 28

A photosensitive element having a layer of a low speed fine grain X-ray type emulsion (average 174 mg. Ag/sq. ft.) was exposed at an exposure of approximately one twenty-fifth of a second at f/4.5 and processed by spreading a layer of the processing fluid, approximately 0.0018 inch thick, between the exposed negative and a surface hydrolyzed sheet of cellulose acetate. The processing fluid comprised:

Water	9.0 cc.
Sodium carboxymethyl	0.4 g.
Sodium sulfite	0.33 g.
Potassium thiosulfate	0.14 g.
Diethylamine	0.5 cc.
N,N-diethyl hydroxylamine	0.7 cc.
Sodium hydroxide	0.26 g.
Aqueous solution of sodium sulfide (156 mg. Na_2S/cc.)	0.012 cc.
Aqueous solution of lead acetate and cadmium acetate (100 cc. H_2O, 2.9 g. lead acetate; 2.1 g. cadmium acetate)	0.36 cc.
1-phenyl-5-mercaptotetrazole	0.025 g.

After an imbibition period of 3 minutes, the cellulose acetate sheet was separated from the exposed negative, and a negative silver transfer image was present in the solidified layer of processing fluid adhered to the hydrolyzed surface of the cellulose acetate sheet.

EXAMPLE 29

A photosensitive element having a layer of a low speed fine grain X-ray type emulsion (average 174 mg. Ag/sq. ft.) was exposed at Shutter 3 and processed by spreading a layer of processing fluid, approximately 0.0034 inch, thick, between the exposed negative and a surface hydrolyzed sheet of cellulose acetate. The processing fluid comprised:

Water	9.0 cc.
Sodium carboxymethyl cellulose	0.4 g.
Sodium sulfite	0.33 g.
Potassium thiosulfate	0.14 g.
2,6-dimethoxy-4-aminophenol hydrochloride	0.08 g.
Ascorbic Acid	0.6 g.
Diethylamine	0.42 cc.
Sodium hydroxide	0.26 g.
Aqueous solution of sodium sulfide (156 mg. Na_2S/cc.)	0.012 cc.
Aqueous solution of lead acetate and cadmium acetate (100 cc. H_2O, 2.9 g. lead acetate; 2.1 g. cadmium acetate)	0.36 cc.
2-thio-6-azauracil	0.05 g.

After an imbibition period of 3 minutes, the cellulose acetate sheet was separated from the exposed negative, and a negative silver transfer image was present in the solidified layer of processing fluid adhered to the hydrolyzed surface of the cellulose acetate sheet.

EXAMPLE 30

The procedure described in example 29 was repeated using baryta paper instead of a surface hydrolyzed cellulose acetate sheet. A negative transfer image was obtained in the solidified layer of processing fluid adhered to the baryta paper.

EXAMPLE 31

The procedure described in example 29 was repeated, using as the photosensitive element a sheet of Kodak Azo F/2 printing paper exposed 0.2 of a second on a light box. After an imbibition period of 5 minutes, a negative transfer image was obtained in the solidified layer of processing fluid adhered to the hydrolyzed surface of the cellulose acetate sheet.

EXAMPLE 32

The procedure described in example 31 was repeated, using as the photosensitive element a sheet of Kodak Kodabromide F/2 printing paper exposed one-tenth of a second at f/4.5. A negative silver transfer image was obtained.

EXAMPLE 33

A sheet of high speed panchromatic negative (average 139 mg. Ag/sq. ft. was exposed at Shutter 5 and processed by

spreading a layer of processing fluid 0.0018 inch thick between the exposed negative and a conventional image-receiving element of the type used in Type 47 Polaroid Land Film. The processing fluid comprised:

Water	9.0 cc.
Sodium carboxymethyl cellulose	0.4 g.
Potassium hydroxide	0.1 g.
Sodium sulfite	0.33 g.
Sodium hydroxide	0.26 g.
Diethylamine	0.5 cc.
Potassium thiosulfate	1.4 g.
2,4-diamino phenol dihydrochloride	0.6 g.

After an imbibition period of 4 minutes, the image-receiving element was separated and print-coated to remove surface silver and any residual processing fluid. The silver transfer image in the image-receiving element was a negative image with a D_{max} of 1.05 and a D_{min} of 0.05. It was found that by increasing the concentration of potassium thiosulfate, negative transfer images could be obtained in imbibition periods as short as 20 seconds, but with some loss of transfer density.

EXAMPLE 34

A medium to high speed orthochromatic paper base negative (average 176 mg. Ag/sq. ft.) was exposed at Shutter 3 and processed by spreading a layer of processing fluid, approximately 0.0026 inch thick, between the exposed negative and a surface hydrolyzed sheet of cellulose acetate. The processing fluid comprised:

Water	91.0 cc.
Hydroxyethyl cellulose	3.9 g.
Potassium thiosulfate	2.8 g.
Sodium sulfite	3.3 g.
Ascorbic Acid	6.0 g.
4,6-diamino-ortho-cresol	0.2 g.
Diethylamine	5.0 cc.
Sodium hydroxide	2.5 g.
Aqueous solution of sodium sulfide (156 mg. Na₂S/cc.)	0.118 cc.
Aqueous solution of lead acetate and cadmium acetate (100 cc. H₂O, 2.9 g. lead acetate; 2.1 g. cadmium acetate)	3.55 cc.
1-phenyl-5-mercaptotetrazole	0.22 g.

After an imbibition period of 10 minutes, the cellulose acetate sheet was separated from the exposed negative, and a negative silver transfer image was present in the solidified layer of processing fluid adhered to the hydrolyzed surface of the cellulose acetate sheet. The characteristic curve (in terms of transmission density) of this negative transfer image is reproduced in FIG. 2 as curve B. When this experiment was repeated omitting the 1-phenyl-5-mercaptotetrazole and employing an imbibition period of 1 minute, a positive silver transfer image was obtained; the characteristic curve (in terms of transmission density) of this positive silver transfer image is reproduced in FIG. 2 as curve A. The exposed and developed negatives in each of these experiments were stopped and fixed in the dark, and the characteristic curves of the negative images developed in exposed areas of these negatives are reproduced (in terms of reflection density) in FIG. 2 as curve D (10 minute imbibition, 1-phenyl-5-mercaptotetrazole present) and curve C (1 minute imbibition, no 1-phenyl-5-mercaptotetrazole present, reflection densities in curve C being corrected for 0.24 background density). When the experiment was repeated employing the processing fluid containing 1-phenyl-5-mercaptotetrazole but with an imbibition period of only 1 minute, a pale negative transfer image was obtained, and the fixed negative image developed in the exposed areas of the negative had the characteristic curve reproduced in FIG. 2 as curve E. It is believed significant to note the general similarities, including maximum densities, of the

characteristic curves of the three negative images developed in the exposed silver halide emulsion layers, particularly curves C and D, and also the general similarities, including maximum densities, of the characteristic curves of the silver transfer images, whether negative or positive, reproduced as curves B and A, respectively.

EXAMPLE 35

A photosensitive element having a layer of a low speed fine grain X-ray type emulsion (average 174 mg. Ag/sq. ft. was exposed at Shutter 4 and placed in a nonviscous developing bath of the following composition:

Water	180 cc.
Sodium hydroxide	5.2 g.
Potassium thiosulfate	7.0 g.
Sodium sulfite	6.6 g.
Ascorbic acid	12 g.
2,4-diamino-ortho-cresol	0.4 g.
Diethylamine	10 cc.
1-phenyl-5-mercaptotetrazole	0.4 g.

After 3 minutes, the photosensitive element was removed from the developing bath and washed. The lights are turned on and the developed and washed photosensitive element was placed in a tray of Kodak Dektol developer (undiluted) for 2 to 3 minutes. A weak positive image was obtained in the silver halide emulsion.

EXAMPLE 36

The procedure described in example 35 was repeated except that the lights were turned on 3 minutes after the exposed photosensitive element was placed in the nonviscous developing bath. The thus re-exposed photosensitive element was allowed to remain in the nonviscous developing bath for an additional 2 to 3 minutes. When removed from the nonviscous developing bath, the photosensitive element obtained a good positive image.

EXAMPLE 37

A sheet of high speed panchromatic negative (average 139 mg. Ag/sq. ft. was exposed at Shutter 7 and processed by spreading a layer of processing fluid 0.0022 inch thick between the exposed negative and a conventional image-receiving element of the type used in Type 47 Polaroid Land Film. The processing fluid comprised:

Water	100 cc.
Sodium carboxymethyl cellulose	5.0 g.
Sodium hydroxide	15.0 g.
Uracil	11.25 g.
29.4% aqueous ammonium hydroxide	3.5 cc.
N,N-diethylhydroxylamine	7.5 cc.
1-phenyl-5-mercaptotetrazole	0.2 g.

After an imbibition period of 4 minutes, the image-receiving element was separated and contained a negative transfer image. When this experiment was repeated with another frame of the negative exposed at Shutter 6 and imbibed for 3 minutes, a negative transfer image of somewhat lower density was obtained.

EXAMPLE 38

A film roll, similar to that described in U.S. Pat. No. 2,579,587, issued Dec. 25, 1951 to Edwin H. Land, was prepared using a high speed panchromatic negative (average 138 mg. Ag/sq. ft.), a conventional image-receiving element of the type used in Type 47 Polaroid Land Film, and pods containing the processing fluid described in example 22. This film roll was loaded in a Model 150 Polaroid Land Camera and an exposure was made at EV 10 (Shutter 1) in an office with the room lights off, the only illumination being window light. After an imbibition period of approximately 1 minute, the image-receiving element was separated from the negative and

contained a good quality negative silver transfer image. The room lights were then turned on and a second exposure made at the same EV number; after an imbibition period of 1 minute, the image-receiving element was found to contain a positive silver transfer image. For comparison, an exposure was made at EV 10 (Shutter 1) without the room lights using the same negative and image-receiving element and a pod containing a processing fluid of the type used in Type 47 Polaroid Land Film (Equivalent ASA Exposure Index 3200), and a positive silver transfer image was obtained after ten seconds imbibition. When this comparison was repeated with the room lights on, it was found that the proper exposure was EV 13 (Shutter 4). Thus the experimental film roll gave a positive transfer image when exposed at an Equivalent A.S.A. Exposure Index of 400 and a negative transfer image when exposed at an Equivalent A.S.A. Exposure Index of 3200.

EXAMPLE 39

A sheet of Kodak Azo F/2 printing paper was exposed 0.1 of a second on a light box and processed by spreading a layer 0.0035 inch thick of a processing fluid between the exposed printing paper and a sheet of baryta paper. The processing fluid comprised:

Water	9.1 cc.
Sodium carboxymethyl cellulose	0.4 g.
Ascorbic acid	0.6 g.
Sodium sulfite	0.6 g.
Sodium hydroxide	0.26 g.
Aqueous solution of sodium sulfide (156 mg. Na₄S/cc.)	0.011 cc.
Aqueous solution of lead acetate and cadmium acetate (100 cc. H₂O, 2.9 g. lead acetate; 2.1 g. cadmium acetate)	0.34 cc.

After an imbibition period of 3 minutes, the baryta paper was separated from the exposed printing paper, and a negative silver transfer image was present in the solidified layer of processing fluid adhered to the surface of the baryta paper. In this example, the only silver halide solvent was the sodium sulfite, and the only silver halide developing agent was ascorbic acid.

EXAMPLE 40

A monodisperse silver bromide emulsion was prepared, the cubic grains of which had an average particle size of 1.2 microns. Solid 1-phenyl-5-mercaptotetrazole was added to an aqueous gelatin solution and dispersed therein by high speed sonification, and the resulting dispersion was added to the monodisperse silver bromide emulsion. A coating of this emulsion was made on film base to provide a photosensitive silver bromide layer containing 61 mg. of silver per square foot (as determined by X-ray fluorescence) and 12 mg. of 1-phenyl-5-mercaptotetrazole per square foot; the gelatin to silver ratio being 5:1. This coating was cut into a plurality of sheets, individual sheets were exposed as noted in the table below, developed for 2 minutes with mild agitation in a tray of the following developer solution:

Water	600 cc.
Sodium carbonate	24.0 g.
Sodium sulfite	13.5 g.
Potassium thiosulfate	10.0 g.
Hydroquinone	3.6 g.
Metol	0.9 g.

The developed sheets were then placed in a stop bath for 10 seconds, washed, and the residual silver determined by X-ray fluorescence.

Exposure (meter-candle-seconds	Residual Silver (mg./ft.²)

0	53
20	36.8
40	11.5
112	8.7
200	15.9
500	15.8
1200	16.2
2200	17

The above results clearly demonstrate both the insolubility of unexposed silver halide and the high efficiency with which silver bromide can be dissolved by development solubilization.

The above examples have employed gelatino silver halide emulsions. Good results also have been obtained using binderless silver halide, e.g., a silver bromide stratum prepared by vacuum deposition of silver and bromination of the vacuum deposited silver. Such experiments clearly establish the fact that the presence of a silver halide binder is not essential to the practice of this invention.

As previously indicated, the quantity of silver halide transferred to the silver receptive stratum is proportional to the size of the grains rendered incipiently developable. Confirmation that the silver halide grains do "divide" their mass between the "donor" silver halide stratum and the "receptor" or image-receiving stratum was obtained by the experimental observation that the grains of a monodisperse silver bromide emulsion was essentially identical before and after exposure and development solubilization process.

In example 40 above, 1-phenyl-5-mercaptotetrazole was added to the silver halide emulsion in the form of a very fine solid dispersion. If it is desired, one may employ a soluble salt, e.g., the sodium salt of 1-phenyl-5-mercaptotetrazole.

This invention makes it possible to provide a convenient source of silver ions for use in various other image-forming processes. One such utilization involves the formation of an imagewise distribution of silver precipitating nuclei, e.g., by photoexposure of a photosensitive semiconductor pigment such as zinc oxide or titanium dioxide; the resulting "latent image" is "developed" by processing in diffusion transfer contact with a uniformly exposed silver halide stratum, the silver halide being dissolved and precipitated on said nuclei by the solubilization development process of this invention. The silver halide may be in the same stratum with the photosensitive semiconductor pigment or in a separate stratum.

It should also be noted that the latent image may be formed by means other than electromagnetic radiation, and that latent images thus formed are within the meaning of exposed silver halide emulsions which may be processed in accordance with this invention.

As noted above, mercapto development solubilization promoters may be employed in the form of the corresponding disulfides. If has been found that the use of such disulfides, e.g., the disulfides of 1-phenyl-5-mercaptotetrazole, 2-mercapto-5-furyl-1,3,4-oxadiazole and 2-mercapto-5-phenyl-1,3,4-oxadiazole, give increased transfer density and longer shelf life for processing compositions containing them as compared with the respective mercaptan. Particularly good results have been obtained using such disulfides with processing compositions containing N,N-bis-methoxyethyl-hydroxylamine and uracil and silver-receptive strata comprising nuclei dispersed in regenerated cellulose.

It is within the scope of this invention to provide the silver halide emulsion and the silver-receptive strata on a common support, and to mask the image developed in the "donor" or silver halide strata by use of a pigmented interlayer, e.g., a layer of titanium dioxide dispersed in gelatin.

In the preferred embodiments of this invention, the silver halide emulsion is predominantly silver bromide, e.g., a silver iodobromide emulsion, and has a film speed suitable for use in cameras. It will be recognized from the examples, however, that the invention is applicable to silver chloride and silver bromide emulsions which usually are of printing paper speed, such as Kodak Azo and Kodak Kodabromide printing papers.

The silver halide emulsion may be of any desired spectral sensitivity, e.g., panchromatic sensitized.

In general, it has been found that better results are obtained when the processing fluid is spread in very thin layers, i.e., processing is effected at smaller gaps. The presence of potassium ions appear to accelerate the transfer and thus their presence frequently is preferred. The concentration of the various reagents may be varied considerably, depending upon the particular silver halide emulsion and other variables. By way of illustration, concentrations of 1-phenyl-5-mercaptotetrazole of about 1 to 35 g./liter of processing fluid have been found to be useful. The concentration of the silver halide solvent will vary with the concentration of the development solubilization promoter; by way of illustration, concentrations of sodium thiosulfate of about 20 to 80 g./liter have been found to be useful when employed in combination with 1-phenyl-5-mercaptotetrazole.

It is believed that the transferred complex may be a complex of silver halide with both the silver halide solvent and the development solubilization promoter. The invisible transfer image formed in example 16 has been demonstrated to be capable of absorbing ultraviolet light. The ordinary complex of silver halide with an alkali metal thiosulfate does not absorb ultraviolet light, but 1-phenyl-5-mercaptotetrazole does absorb ultraviolet light. Although it is possible that the 1-phenyl-5-mercaptotetrazole in some manner also is transferred imagewise with the silver complex to the image-receiving layer, it is believed to be more likely that the 1-phenyl-5-mercaptotetrazole is part of a novel complex with the silver halide solvent and the silver halide.

The addition of an ethylenic thioether, such as the alkyl polyoxyethylene thioether sold under the trade name Cerfak 1300 by E. F. Houghton, has been found to increase film speed, in some instances by as much as three stops, with a gain in overall smoothness of the negative transfer and with no loss of steps. The use of ethylenic thioethers in silver diffusion transfer processes is described in U.S. Pat. No. 2,938,792 issued to Meroe M. Morse on May 31, 1960.

The above examples have illustrated the use of a large variety of negative materials, processing compositions and image-forming systems in this invention. It will be readily apparent that a number of modifications may be made without departing from the scope of this invention, e.g., an additive color image may be obtained by exposing the photosensitive silver halide emulsion through an additive color screen and transferring silver halide from the exposed areas to another stratum, after which the residual silver halide in the originally unexposed areas may be given an overall exposure and developed to provide a positive silver image in registration with the same additive color screen through which the original exposure was made. In another embodiment, the transferred silver halide may be reduced in the presence of a color developer and color coupler to provide a dye image; the thus precipitated silver may subsequently be bleached out to leave only a dye image in the original image-receiving layer. In such an embodiment, the color coupler may be of the nondiffusing type and initially positioned in the image-receiving layer, and the same developing agent employed to develop both images, the developer oxidation product formed by development of exposed silver halide in the silver halide emulsion layer being immobilized, i.e., prevented from transferring to the image-receiving layer, by reaction with a nondiffusing coupler positioned in the emulsion layer; alternatively, the coupler in the emulsion layer may be a coupler of the type which gives a substantially colorless coupling product. The silver transfer image formed in accordance with this invention also may be employed in the formation of a color image by silver dye bleach processes.

Because of the remarkably high sensitivity to light which is obtained in the practice of this invention, it will be apparent that this invention is particularly useful in recording information under such low light level conditions as found in X-ray photography, oscilloscope trace recording, night and other

"available light" photography, etc. Further since "overexposure" in processes of the instant invention simply reverses, fully or in part, the scale of the transfer image, one may thus photographically record information over such a wide range of exposure levels as to have, in effect, a continuous photometer.

In the development solubilization process, the smallest grains are the last to be exposed and the last to be developed, and the largest grains are the most likely to be exposed and hence the most likely to be developed and partially dissolved; in the conventional positive silver transfer process, the smallest grains are the first to be dissolved. Once a grain starts to develop in our process, it is completely involved, and the silver halide thereof is either reduced to silver in the emulsion layer or removed to another locus.

We have found that the development solubilization process is very effective over a wide range of temperatures, and in general gives more consistent sensitometric results over the temperature range of 32°–100° F. than the conventional positive silver transfer process. This very desirable property may be due to the fact that the relative rates of solubility and developability are initially more like each other, and thus can maintain this relationship more closely with variations in temperature. Our experiments indicate that the susceptibility of development solubilization processing to reciprocity failure is no greater than that of the conventional silver transfer process; indeed, there is some evidence that our process, under at least some conditions, may be less susceptible to reciprocity failure.

As noted above, the silver halide in the unexposed areas of the emulsion layer processed in accordance with this invention remains light-sensitive notwithstanding the fact that it has been subjected to the action of reagents which might be expected to form light-insensitive salts or complexes.

It therefore will be recognized that this invention does not involve the "fixing" or "stabilizing" of residual silver halide in the unexposed areas of the formation of a light-insensitive, relatively insoluble salt or complex, as the undeveloped and undissolved silver halide present in unexposed areas of silver halide emulsions processed in accordance with this invention remains light-sensitive.

This result clearly was unobvious in view of the prior art proposals to "fix" or "stabilize" developed silver halide emulsions by "inactivating" undeveloped silver halide in situ by treating a developed but unfixed negative with sodium thiosulfate, potassium thiosulfate, thiourea, etc. (Broughton et al. U.S. Pat. No. 2,614,927, issued Oct. 21, 1952) or by effecting development with a developer containing a developing agent and a compound such as 6-amino-4-hydroxy-2-mercapto-pyrimidine, 4-amino-6-hydroxy-2-mercapto-pyrimidine or 4-amino-6-hydroxy-2-mercapto-pyridine (Dreywood, S. Pat. No. 2,525,532, issued Oct. 10, 1950.

The herein described and claimed development solubilization process is readily distinguished from the "photosolubilization" process of Blake et al. U.S. Pat. Nos. 3,155,506–7 and 3,155,514–, Issued Nov. 3, 1964. In the photosolubilization process, the silver halide emulsion is treated with certain compounds, e.g., mercapto compounds, prior to exposure, and the thus treated and exposed silver halide emulsion is subjected, *in the absence of a silver halide developing agent, to the action of a silver halide solvent* to dissolve out the exposed silver halide. The residual undissolved, unexposed silver halide may be subsequently exposed and reduced to silver. The exposure employed to effect "photosolubilization" is many, many times greater than would be considered useful for camera exposures, and the "film speed" is extremely low. In contrast, our development solubilization process frequently results in increased light-sensitivity, and solubilizes silver halide only where incipient development occurs. It will also be noted that the development solubilization process is performed at the very alkaline pH levels associated with development, these pH levels being substantially more alkaline than the acidic aqueous hypo solutions employed in the photosolubilzation

process.

As previously stated, we employ reagents, such as 1-phenyl-5-mercaptotetrazole, in quantities substantially greater than if such compounds were being employed as image toners or as restrainers in the conventional manner. Thus, for example, Weyde, U.S. Pat. No. 2,699,393, issued Jan. 11, 1955, proposes to employ mercaptotetrazoles, and especially 1-phenyl-5-mercaptotetrazoles, as silver transfer toners by adding them to the processing solution in quantities of 0.01 to 1 g. per liter of developing solution.

Since certain changes may be made in the above products, processes and compositions without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The method which comprises exposing a photosensitive silver halide emulsion layer to form a latent image therein, applying to said exposed but undeveloped silver halide emulsion a single processing composition which provides in said silver halide emulsion in aqueous solution including an alkali, a silver halide developing agent, a first silver halide complexing agent which is a silver halide solvent and capable of forming a soluble silver complex, and a second silver halide complexing agent capable of forming a relatively insoluble silver complex with silver halide, each of said first and said second halide complexing agents being present in a quantity effective in combination with each other to form an imagewise distribution of a diffusible complex of silver halide substantially only from developing silver halide grains.

2. The method as defined in claim 1, wherein said processing composition includes a film-forming material.

3. The method as defined in claim 2, wherein said diffusible complex of silver halide is transferred by diffusion from said exposed and developing areas of said silver halide emulsion layer to a superposed stratum containing said film-forming material.

4. The method as defined in claim 3, wherein said stratum of film-forming material is separated from said exposed silver halide emulsion layer after an image-forming quantity of said diffusible complex of silver halide has been transferred to said stratum.

5. The method as defined in claim 4, wherein the image formed by said transfer of said diffusible complex of silver halide is capable of absorbing ultraviolet light, and including the steps of positioning a second photosensitive layer in photoexposure relationship with said separated stratum containing said ultraviolet light absorbing image while said stratum is still wet and without reduction of said transferred complex to silver, said second photosensitive layer being exposable by ultraviolet light, and passing ultraviolet light through said still wet stratum containing said transferred complex of silver halide, thereby forming a developable image on said second photosensitive layer, said developable image being negative with respect to said imagewise distribution of silver halide complex and to said latent image.

6. The method as defined in claim 1, wherein said diffusible complex of silver halide is transferred by diffusion to a silver receptive stratum in superposed relationship with said exposed silver halide emulsion layer, and said silver receptive stratum containing a silver precipitating agent, thereby forming a visible silver image on said silver receptive stratum.

7. The method as defined in claim 4, including the step of drying said separated stratum, whereby said transferred complex of silver halide is precipitated out of solution without being reduced to silver, thereby forming a visible image in said stratum, said image being visible by reflected or transmitted light.

8. The method as defined in claim 4, including the step of pressing said separated stratum containing said transferred silver complex, while said stratum is still wet, into contact with a silver receptive stratum, said silver receptive stratum containing a silver precipitating agent, and maintaining said

separated stratum and said silver receptive stratum in contact until a silver image is formed on said silver receptive stratum, said silver image being positive with respect to said imagewise distribution of transferred silver complex.

9. The method as defined in claim 1, wherein said first silver halide complexing agent is sodium thiosulfate.

10. The method as defined in claim 1, wherein said first silver halide complexing agent is potassium thiosulfate.

11. The method as defined in claim 1, wherein said second silver halide complexing agent is 1-phenyl-5-mercaptotetrazole.

12. The method as defined in claim 1, wherein said second silver halide complexing agent is 4-ethyl-2-thio-oxazoline.

13. The method as defined in claim 1, wherein said solution contains at least one silver halide developing agent selected from the group consisting of hydroquinone, 4-N-methylamino-phenol, ascorbic acid, isoascorbic acid, 2,6-dimethyl-4-amino-phenol, toluhydroquinone, 2,6-dimethyl-hydroquinone, 2-methyl-4-amino-6-methoxy-phenol, 2,6-dimethoxy-4-amino-phenol, 2,5-dimethyl-hydroquinone, 2,4,6-triamino-phenol, 2,4-diamino-phenol, N,N-diethyl-hydroxylamine, N,N-dimethoxyethyl-hydroxylamine, and 4,6-diamino-ortho-cresol.

14. The method as defined in claim 2, wherein said processing solution includes a silver-precipitating agent, and said silver receptive stratum comprises a stratum formed by solidification of a layer of said film-forming material containing said silver precipitating agent.

15. A silver diffusion transfer process comprising the steps of photoexposing a silver halide emulsion to form a latent image therein; applying a processing composition to said photoexposed silver halide emulsion, said processing composition containing a film-forming, viscosity-increasing polymeric material, and providing a silver halide developing agent, an alkali and a silver halide solvent, said processing composition containing, when applied to said photoexposed silver halide emulsion, a substantial concentration of a mercapto compound capable of forming a relatively insoluble silver complex with silver halide, said concentration of said mercapto compound being an amount which in combination with said silver halide solvent is effective to prevent the formation of a soluble silver complex from unexposed silver halide grains but is effective to dissolve silver halide where incipient development occurs; initiating development of exposed silver halide and forming in said developing exposed areas a soluble, diffusible silver complex, and transferring an imagewise distribution of said diffusible silver complex to a silver receptive stratum containing a silver precipitating agent and positioned in superposed relationship with said photoexposed silver handle emulsion; the silver transfer image formed on said silver receptive stratum being a positive image with respect to the latent image formed by said photoexposure and a negative image with respect to the photographed subject matter; and maintaining said photoexposed silver halide emulsion and said silver receptive stratum in superposed relationship until said negative silver transfer image is formed.

16. A process as defined in claim 15, wherein said mercapto compound is 1-phenyl-5-mercaptotetrazole.

17. A process as defined in claim 16, wherein said 1-phenyl-5-mercaptotetrazole is present in a concentration of at least 1 gram per liter of said processing composition.

18. A process as defined in claim 17, wherein said photoexposed silver halide emulsion and said silver receptive stratum are maintained in said superposed relationship for at least 2 minutes.

19. A process as defined in claim 15, wherein said processing composition contains silver precipitating nuclei, and said silver receptive stratum is provided by solidification of a layer of said processing composition.

20. A process as defined in claim 15, wherein said processing composition is applied to said photoexposed silver halide emulsion by spreading said composition in a thin layer between said photoexposed silver halide emulsion and said silver receptive stratum as said layer and said stratum are

brought into said superposed relationship.

21. The process as defined in claim 1, wherein the layer containing said silver halide emulsion also contains, prior to exposure, a silver precipitating agent, and including the step of reducing said dissolved silver halide substantially in situ with the developed latent image, thereby forming in said silver halide emulsion layer a negative silver image of substantially greater density and contrast.

22. The process as defined in clam 1, wherein the dissolved silver halide is removed from said exposed silver halide emulsion layer, and, without prior fixing, the exposed and developed silver halide emulsion layer is thereafter exposed to light, whereby a positive silver image is formed in said exposed and developed emulsion layer by development of silver halide exposed by said second exposure.

23. The process as defined in claim 1, wherein the dissolved silver halide is removed from said exposed silver halide emulsion layer, and, without further exposure, said emulsion layer thereafter is fixed, thereby providing a negative silver image in said emulsion layer.

24. A photographic process comprising photoexposing a silver halide emulsion and applying to said exposed silver halide emulsion an aqueous processing composition to provide in said exposed silver halide emulsion an aqueous solution comprising a silver halide developing agent, an alkali, and a silver halide solvent, said processing solution containing a compound normally being capable of forming a complex with said silver halide, which complex is less soluble than said silver halide, said compound being present in a quantity sufficient to so adjust the relative rates of developability and solubility of a given silver halide grain that the rate at which silver halide is dissolved becomes much greater in exposed grains where incipient development occurs than in grains where development does not occur, initiating development of exposed silver halide grains and thereby dissolving exposed silver halide grains more rapidly than unexposed silver halide grains.

25. The process as defined in claim 24, wherein an imagewise distribution of dissolved silver halide is formed from exposed grains, and said imagewise distribution is transferred, by diffusion, to a stratum in superposed relationship with said silver halide emulsion.

26. A process as defined in claim 24 wherein said complexing compound is a mercaptan and is present in said silver halide emulsion prior to exposure.

27. A process as defined in claim 24 wherein said complexing compound is a mercaptan and is present in said processing composition when it is applied to said silver halide emulsion.

28. The process as defined in claim 25, wherein said superposed stratum contains a silver precipitating agent, whereby said transferred dissolved silver halide is reduced to provide a negative silver transfer image.

29. A process for forming an image by diffusion transfer, comprising applying to an exposed silver halide emulsion an aqueous processing composition comprising an alkali, a silver halide developing agent, a silver halide solvent and a compound capable of restraining development by forming a relatively insoluble silver salt, said compound being present in a concentration substantially greater than a development restraining quantity and effective to prevent solution of unexposed silver halide grains, initiating development of exposed grains of silver halide and thereby forming a diffusible complex with silver halide of developing silver halide grains, and transferring said diffusible complex to a stratum in superposed relationship with said silver halide emulsion to provide an image in said stratum.

30. A process as defined in claim 29, wherein said superposed stratum contains a silver precipitating agent, and said transferred silver halide complex is reduced to form an image in silver.

31. A process as defined in claim 30, wherein said transfer image has a negative scale.

32. A process as defined in claim 30, wherein said transfer image has a positive scale.

33. A process as defined in claim 30, wherein said transfer image has both a positive and a negative scale.

34. A diffusion transfer process comprising the steps of subjecting a silver halide emulsion to a predetermined exposure to form a latent image therein, developing exposed silver halide with processing composition comprising an alkali, a silver halide developing agent, a first silver halide complexing agent which is a silver halide solvent and capable of forming a soluble silver complex, and a second silver halide complexing agent capable of forming a relatively insoluble silver complex with silver halide, each of said first and second silver halide complexing agents being present in a quantity effective in combination with each other to form an imagewise distribution of a transferable diffusible complex of silver halide substantially only with silver halide of incipiently developing grains of exposed silver halide, the quantity of transferable diffusible silver halide complex formed from a given exposed and developing grain being proportional to the mass of said grain and to the exposure received by said grain, transferring at least a portion of said imagewise distribution of diffusible silver complex to a superposed silver-receptive stratum containing a silver precipitating agent, and reducing said transferred silver complex to silver to provide a visible image in said silver-receptive stratum.

35. A process as defined in claim 34, wherein said silver halide emulsion includes a plurality of sets of silver halide grains, the grains of each said set being of substantially like sensitivity whereby the grains of a given set are exposable within substantially the same exposure range, each said set being exposable by a different exposure range.

36. A process as defined in claim 35, wherein said silver halide emulsion contains at least three of said sets of silver halide grains, and said predetermined exposure is effective to expose less than all of said sets of silver halide grains.

37. A process as defined in claim 35, wherein said predetermined exposure is at an exposure range whose minimum will render at least some grains developable and whose maximum is the exposure at which the maximum number of grains are rendered developable, whereby said silver transfer image has a negative scale.
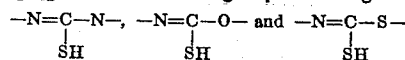
38. A process as defined in claim 35, wherein said predetermined exposure is at a range whose minimum is the exposure at which the maximum number of grains are rendered developable, whereby said silver transfer image has a positive scale.

39. A process as defined in claim 35, wherein the grain sensitivity distribution curve of said silver halide emulsion is bell-shaped.

40. A process as defined in claim 37, including the step of extending the length of the negative scale of said silver transfer image by including in said silver halide emulsion at least one additional set of lower sensitivity grains.

41. A photographic process comprising the steps of exposing a photosensitive silver halide emulsion layer to form a latent image therein, developing said latent image with a processing composition comprising a silver halide developing agent, an alkali, a silver halide solvent and a development solubilization promoter, said silver halide solvent and said development solubilization promoter each being present in a concentration effective in combination with each other to cause incipiently developing exposed silver halide grains to be preferentially dissolved in said processing composition to provide only in exposed and developing areas of said silver halide emulsion an imagewise distribution of a diffusible complex of silver halide, and transferring said diffusible complex by diffusion to a different locus to provide a photographic image.

42. A process as defined in claim 41, wherein said development solubilization promoter is a compound containing a mercapto grouping selected from the group consisting of

$$-N=C-N-, \quad -N=C-O- \text{ and } -N=C-S-$$
$$\quad\quad | \quad\quad\quad\quad | \quad\quad\quad\quad\quad |$$
$$\quad\quad SH \quad\quad\quad\quad SH \quad\quad\quad\quad SH$$

said compound being present in an amount effective, in combination with said silver halide solvent, to more rapidly dissolve developing silver halide grains than nondeveloping silver halide grains.

43. A process as defined in claim 42, wherein said silver halide solvent is potassium thiosulfate.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. _____3,615,438_____ Dated__ October 26, 1971 __

Inventor(s)__Edwin H. Land, Meroe M. Morse and Leonard C. Farney

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

IN THE SPECIFICATION

Column 24, line 37, delete "obtained" and insert --contained--.

Column 28, line 53, "S. Pat. No." should read --U.S. Pat. No.--

Column 28, line 58, "3,155,514" should read --3,155,514-9,--.

IN THE CLAIMS

Claim 15, line 50, delete "handle" and insert --halide--.

Claim 22, line 9, delete "clam" and insert --claim--.

Claim 34, line 4, after "with" insert --a--.

Signed and sealed this 14th day of November 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents