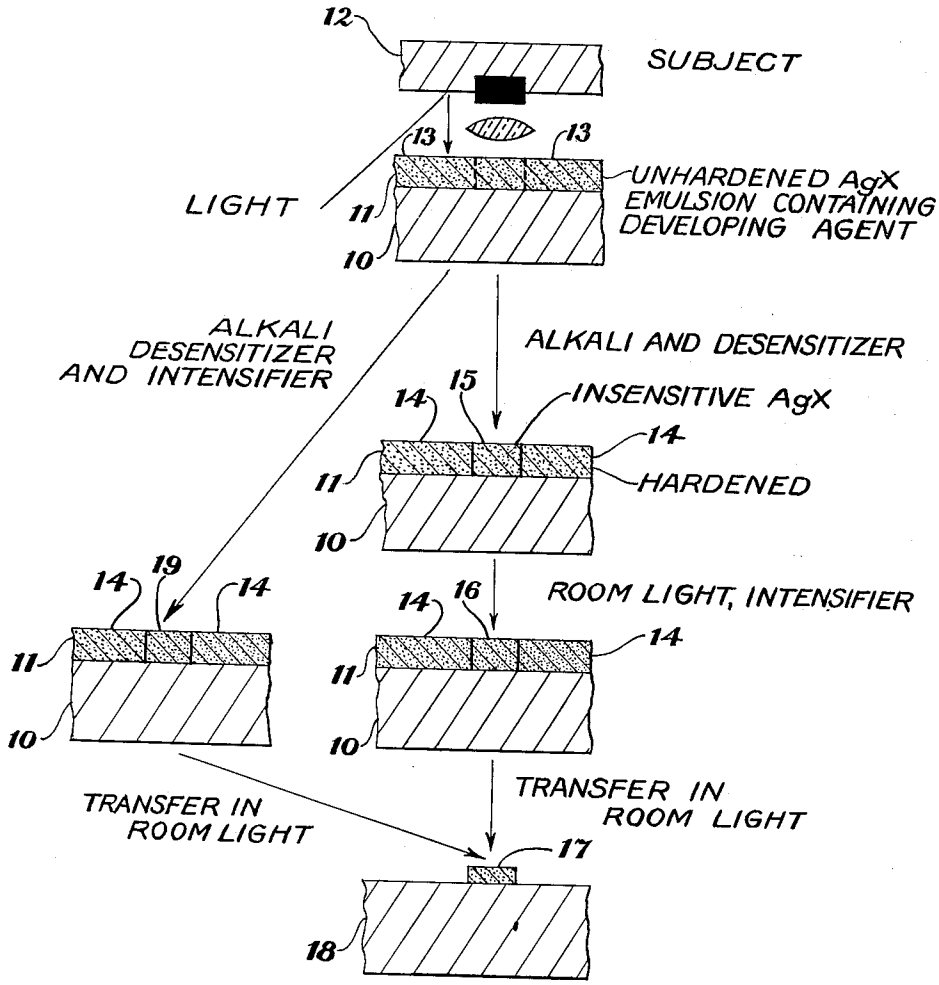
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PHOTOGRAPHIC REPRODUCTION PROCESS

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PHOTOGRAPHIC REPRODUCTION PROCESS

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6 Claims. (Cl. 95—5.6)

This application is a division of our U. S. patent application Serial No. 267,446, filed January 21, 1952, now U. S. Patent 2,675,313, granted April 13, 1954, which is a continuation-in-part of our U. S. patent application Serial No. 783,914, filed November 4, 1947, now U. S. Patent 2,596,756.

This invention relates to photography and particularly to a photographic copy method for use in the reproduction of printed matter.

There are a number of well-known photographic methods of reproducing designs such as printed matter on paper or other supports. For instance, by the so-called reflex copy method an emulsion layer is exposed through its support and the printed matter is reproduced as a negative, or one may print a negative and a positive therefrom by conventional methods. In the photomechanical art a common practice is to expose a suitable photographic element such as a tissue and to transfer the exposed element to a metal plate after which the unexposed emulsion is washed off the plate or the washing off may occur before transfer of the resist to the plate. Similarly, in the Pinatype process after forming a hardened image, colored matter is printed from the unhardened area of the element but the colloid vehicle is not transferred from that area to the printing surface. A limited amount of endeavor which apparently has not been successful has been directed to a process wherein after exposing a dichromated albumen element, the unexposed and unhardened portion of the element is transferred to a second support.

In the Yutzy et al. U. S. patent application Serial No. 783,914, filed November 4, 1947, now U. S. Patent 2,596,756, granted May 13, 1952, is described a simple photographic method including differentially hardening silver salt emulsion layers and transferring unhardened strata of such layers to a support to obtain useful images. In that process, a substantially unhardened colloid-silver halide emulsion layer, preferably containing a colloid tanning silver halide developing agent, is exposed to a two-tone subject (line or half-tone subject) and after development in the presence of alkali, a stratum of the unexposed region of the emulsion layer is transferred to a receiving sheet by merely pressing the sheet into contact with the developed emulsion layer and peeling off the sheet carrying a stratum of the unexposed region of the emulsion adhered thereto. The simplicity of the process is apparent when the comparison is made with well-known reproduction methods such as those employing metal printing plates and which involve tedious etching steps for the preparation of the printing form. Other advantages reside in the fact that the silver halide sensitized materials are employed, the superior properties of which are well known compared to elements sensitized by other means such as bichromated colloid layers.

In the mentioned process, it is desirable that the stratum of emulsion obtained on the receiving sheet have sufficient optical density that it is readily visible. To that end, colored matter was either initially incorporated into the emulsion layer before exposure or subsequently was formed in the emulsion layer; for example, by exposure

of the transferred stratum of emulsion to light followed by heating, if desired, to accelerate development of the silver halide in the stratum. Also, the invention described incorporating the components of color-forming development or of the diazo process into the emulsion layer to form a dye image therein for purpose of intensifying the transferred stratum. In addition, the mentioned process was essentially a darkroom process inasmuch as the developed emulsion layer possessed unhardened emulsion regions containing developing agent and alkali associated with the unexposed silver halide and since premature exposure of that region of the emulsion would cause tanning development to proceed and thus prevent transfer of an emulsion stratum from the desired regions. Accordingly, the amount of room light which could be tolerated in the process was a function of the speed of the emulsion and unless the process was carried out in lighttight processing equipment, the operations had to be carried out under safelights. In office copy work, for which the process finds great commercial application, some economical method had to be provided to enable the use of high speed silver halide emulsions in relatively simple processing equipment with a maximum amount of the processing being carried out under room lights.

The objects of our invention are to provide improvements in the mentioned photomechanical copy method which satisfy the mentioned need for an efficacious process of obtaining copy having good optical density and preferably by means of a process, the greater part of which can be carried out under ordinary conditions of illumination.

In general, the objects of our invention are accomplished by carrying out the mentioned exposure, development and transfer steps but at some stage between the exposure and transfer steps treating the exposed emulsion layer to increase the optical density of the unexposed portions corresponding to the shadows of the original subject. This treatment preferably includes treating the emulsion layer some time following exposure with a compound which reacts with the silver halide in the unexposed region of the emulsion layer to form a substance having the desired optical density. Our objects are also accomplished by treating the exposed emulsion layer during or following development with a desensitizing agent for silver halide to materially reduce the light sensitivity of the silver halide in the unexposed regions of the emulsion layer. If desired, the desensitization and optical density increasing treatments may be carried out during the alkaline development step.

In the preferred process of the invention, it is desirable but not necessary to incorporate a desensitizing agent for silver halide in the alkaline solution used for development and after development and prior to the transfer step, to treat the developed emulsion layer with a material such as a compound containing a sulfur atom reactive with silver halide in the unexposed regions of the emulsion; for example, thiourea, to form silver sulfide in that region. As a consequence of the use of the desensitizer, devopment and any subsequent steps in the process can be carried out under room lights and the silver sulfide image formed in the unexposed regions transfers along with the emulsion stratum during the transfer step to provide copy having good optical density. The objects of the invention can be accomplished in other ways as will be apparent from consideration of the following detailed description of our invention and the drawings:

In the accompanying drawings are shown in greatly enlarged cross-sectional view, the appearance of a typical photographic element at various stages in the process of copying a two-tone subject.

The following detailed example is given to illustrate the preferred embodiments of our invention:

Example

A projection speed emulsion is prepared as described in detail in Example 1 of the mentioned Yutzy et al. application containing 3,4-dihydroxy diphenyl as the tanning developing agent and preferably being pigmented with a material such as metallic silver, carbon black, or a dye such as Monastral Fast Blue BWD (copper phthalocyanine dye) or other insoluble pigments imparting some optical density to the emulsion layer but generally providing an insufficient amount of optical density to interfere with exposure to any great extent. When the dye is employed, a suitable quantity is 15 grams per mol of silver in the emulsion. The light-sensitive element thus prepared is shown in the first stage of the accompanying drawings wherein layer **10** is the support for the emulsion such as cellulose ester film base or preferably paper containing no agent tending to harden the emulsion. Layer **11** represents the emulsion layer containing the tanning development agent. The emulsion layer **11** is exposed to a suitable subject **12** as shown in the drawings by any suitable projection means with the result that a latent image is obtained only in the silver halide in areas **13** of emulsion layer **11**. To obtain the optimum results, the exposure should be adjusted so that little or no latent image is obtained in regions other than **13**. Exposure may be carried out by well-known reflex copy methods but is obviously not very satisfactory if the emulsion contains colored pigment. Exposure by the reflex copy method is preferably carried out by use of materials and methods which will be described in more detail hereinafter in connection with the methods of the Yutzy and Yackel patent application Serial No. 267,447, filed January 21, 1952.

After exposure of the emulsion layer, as described, development is carried out in absence of light or under suitable safelights in an alkaline solution preferably containing a desensitizing agent for silver halide and which may contain a tanning developing agent if none has been incorporated in the emulsion layer. A suitable aqueous solution is as follows:

	Percent
Sodium carbonate	4
Urea	10
Potassium bromide	0.1

Development can be carried out at a temperature of from 80 to 85° F. for from 15 to 30 seconds to obtain satisfactory results. Potassium bromide is used as the desensitizer in this example and should be used in the quantity required to reduce the light sensitivity of the silver halide in the unexposed regions of the emulsion layer to the requisite level. The use of 0.05 to 1.0 percent of potassium bromide in the solution will allow use of ordinary room illumination in carrying out the remaining steps of the process. Other desensitizers, such as desensitizing dyes, when used in the alkaline solution are employed in amounts in proportion to their activity as desensitizers. Typical desensitizing compounds are:

Pinakryptol Green
Pinakryptol Yellow
2-(p-diethylaminophenyliminomethyl)-6-methyl quinoline methochloride
4-nitro-6-chlorobenzotriazole
6-ethoxy - 2 - p-nitrostyryl-quinoline metho-p-toluenesulfonate

Desensitizing dyes are adequately effective in the alkaline solution in concentrations of the order of 0.025 gram to 5 grams per liter of solution. Urea or other gelatin softeners can be used as shown in the solution to facilitate subsequent transfer of the stratum of undeveloped emulsion. The quantity used, of course, depends upon the hardness of the emulsion at this stage of the process and, of course, the activity of the material as a gelatin softener.

Urea and other gelatin softeners such as formamide, ethylene chlorohydrin, and sodium nitrate can be used in the alkaline solution or in a separate solution following development in concentrations of the order of from about 2 to 20 percent to accommodate variations which may be encountered with different emulsions and conditions of development.

At this stage in the process the developed element appears substantially as shown in the second stage of the drawings wherein the emulsion layer **11** is shown as containing a tanned gelatin and silver image in regions **14** and the substantially unhardened emulsion and desensitized silver halide in the unexposed region **15**.

The balance of the process may now be carried out under room lights. To this end, excess solution can be drained or squeegeed from the surface of the emulsion and the element then treated in an intensifying bath preferably containing a compound which reacts with the silver halide in the unexposed regions of the emulsion layer to form a substance having appreciable optical density. A satisfactory and preferred bath contains a compound having a sulfur atom reactive with the silver halide in the unexposed region **15** of layer **11** to form silver sulfide therein such as the following aqueous solution:

	Percent
Sodium carbonate	4
Thiourea	2

The quantity of thiourea in the bath is not especially critical and alkaline baths containing from about 0.5 to 5 percent thiourea give useful results. Other compounds of a similar nature, such as thiosemicarbazide and sodium sulfide may be used for the same purpose in similar quantity. In place of using a sulfur compound for increasing the optical density of the unexposed regions, solutions of compounds capable of reducing the desensitized silver halide to silver in the absence of a latent image may be used, such as 0.5 to 2 percent solutions of hydrazine hydrate, aminoguanidine sulfate, sodium arsenite, ferrous oxalate and stannite solutions.

The intensified element now appears as shown in the third stage of the drawings wherein layer **11** is shown as containing the intensified image in area **16** which area is still unhardened.

After removing excess moisture from the emulsion surface of the intensified element as by squeegeeing, it is then pressed with the emulsion side next to an absorbent sheet or other surface such as paper **18** with the result that only the intensified and unhardened region **16** adheres to the sheet. When the sheets are separated only a thin stratum **17** of region **16** adheres to the sheet **18** as shown in the last stage of the drawings. Additional copies of the subject **12** can be made by merely remoistening the emulsion layer **11** with alkaline solution and transferring to sheets until the intensified and unhardened region **16** of layer **11** has been exhausted. It is not necessary to further treat the copies obtained inasmuch as they are comparatively dry and the image thereon is stable.

In an alternate procedure after exposure of the sensitive element as shown in the first stage of the drawings, it may be treated directly with an alkaline solution containing both the silver halide desensitizer and the intensifying agent for the unexposed region of the emulsion layer. The result is to obtain an element appearing substantially as shown in enlarged cross-sectional view at the left of the drawings wherein region **19** of layer **11** comprises the unhardened emulsion region which has been intensified and region **14** desensitized. For this purpose the alkaline solution may contain the indicated quantity and types of desensitizing agents, particularly a desensitizing dye, together with the compound reacting with silver halide in the unexposed region to increase the optical density. The following concentrations of the intensifying compounds may be used in the alkaline solution:

	Mg. per liter of solution
Sodium sulfide	250
Thiourea	50
Thiosemicarbazide	250
Hydrazine hydrate (85% in water)	25
Aminoguanidine sulfate	500

The concentration of these ingredients can be varied as much as about 50 percent to obtain useful results. Other agents which may be used in the alkaline developing solution in similar concentration to reduce the silver halide in the unexposed regions of the element are arsenite, stannite and ferrous oxalate compounds.

When the intensifying agents are used in the alkaline solution as described and the emulsion contains a tanning silver halide developing agent, an unusual mechanism becomes patent. That is, it would be supposed that the reagent, such as thiourea, would react with all of the silver halide in the emulsion layer, whether it has been exposed or not, and prevent differential tanning of the emulsion layer. However, it appears that the diffusion rate of alkali into the emulsion layer is greater than the diffusion rate of the sulfur compound; consequently, development precedes intensification as attested by the results. Otherwise, it appears that the results could possibly be explained by development proceeding at a rate greater than intensification. When emulsion layers free of developing agents are treated similarly, this is not observed.

The process of our invention is subject to numerous variations. The use of the desensitizing agent in the developing solution is preferred; however, it may be employed in a step following development alone or in conjunction with the intensifying compound. Also the alkaline solution may contain the intensifier and desensitizing can be effected in a step following development. Similarly, as mentioned in our U. S. application Serial No. 783,914, now U. S. Patent 2,596,756, granted May 13, 1952, the intensifying agent, such as thiourea, may be incorporated in the receiving sheet or if desired may be used for treating the transferred stratum of silver halide emulsion.

The concentration of developing agent in the emulsion is dependent in part upon the result desired but can be of the order of 350 grams of developing agent per kg. of silver nitrate converted to silver halide used in making the emulsion to obtain good density, or about 250 grams per kg. of silver nitrate to obtain adequate density and an emulsion having optimum keeping properties.

It is necessary for the successful operation of the invention that the emulsion layer be not harder than would be the case with gelatin containing 0.25 oz. of formaldehyde (40% diluted 1 to 3 with water) or 0.7 gram dry formaldehyde per pound when freshly coated, or 0.1 oz. of the solution per pound for a sample aged three to six months. By "substantially unhardened" as used here, and in the appended claims, it is to be understood that this means a hardness of the order obtained with gelatin treated with formaldehyde under the conditions above. Emulsion layers appreciably harder will not transfer satisfactorily. Similarly, if after development of the tanned image it is found that the layer is too hard, and to accommodate variations in hardness and tanning encountered, we can use variations of temperature or pressure when making a transfer. To this end we ordinarily apply pressure or temperature or both when rolling the developed emulsion down onto the receiving support.

Examples of tanning developing agents especially useful because of nonwandering characteristics in emulsion layers are those having a solubility at 20° C. of from about .005 to 1.0 gram per 100 cc. of a phosphate-citric acid buffer solution of pH 5.0 prepared from a 1.5 percent solution of sodium dihydrogen phosphate and sufficient citric acid to bring the pH to 5.0. The preferred developing agents have a solubility of from about .01 to .2 gram per 100 cc. of buffer solution. Developing agents falling within the above classification are, for example, 3,4-dihydroxy diphenyl, 2,5-dihydroxy diphenyl, 5,6,7,8 - tetrahydronaphthohydroquinone, and 2,3 - dihydroxy diphenyl. The mentioned diphenyl compounds are preferred because they possess the combination of the common properties, high rate of development, high tanning efficiency, and solubility in the preferred range. Here, and in the appended claims, where the tanning developing agents are mentioned as incorporated in the emulsion, the desired compounds are, for example, those mentioned and having the mentioned characteristics. Otherwise, where tanning developing agents as hydroquinone and pyrocatechol, in absence of sulfite, are used, they are less desirable but useful results may be obtained. Compounds like 2-hydroxy-5-amino diphenyl or 3,4-diamino diphenyl are not especially useful because of their poor stability or failure to tan. It is, therefore, apparent that after exposure to a subject the differential hardening of the exposed emulsion can take place in the presence of a tanning developing agent and that this includes whether or not the agent is in the emulsion before exposure.

When the tanning developing agent is employed in the alkaline developing solution rather than in the emulsion layer, this solution may also contain the desensitizing compound but it is preferred to utilize an intensifier in a subsequent operation rather than employing it together with the tanning developing agent in the alkaline developing solution.

As mentioned, the emulsion layers of our invention preferably contain a tanning developing agent but very desirable results are obtained by the use of a mixture of tanning and feebly tanning or nontanning developing agents such as described in the Yutzy and Yackel application Serial No. 267,447, filed January 21, 1952. Such emulsion layers are employed advantageously when exposures are to be made by the reflex copy method. Substantially nontanning silver halide developing agents satisfactory for this purpose are: N-methyl-p-aminophenol-x-sulfonic acid, p-hydroxy-anilino-methane sulfonic acid, pyrogallol dimethyl ether, 1,8-dihydroxy naphthalene and 4-methoxy-1-naphthol. These developing agents are preferably employed in emulsions along with about 60 to 65 percent of the tanning developing agents. The latter two developing agents are self-coupling in alkaline solution and thus yield colored images during development.

The following nontanning colloid silver halide developing agents are preferably used in the alkaline developing solution, the emulsion containing a tanning developing agent, at not greater than the indicated concentrations to insure that the nontanning developing agent does not unduly compete with the tanning developing agent.

	G./liter
2,4-diamino phenol	1.6
5-amino-2-hydroxy toluene sulfate	1.6
2,5-diamino toluene sulfate	1.6
p-Phenylenediamine	0.8
p-Aminophenol	1.6
p-Methylamino phenol sulfate	3.2
Isoascorbic acid	3.2

Emulsions containing mixtures of the two types of developing agents are utilized in our process, for example, as set forth in detail in the example above. The desensitizing and intensifying operations are likewise employed to facilitate handling under room-lights and to yield intensified copy of the original subject.

The colloid vehicle of the silver halide emulsion layers used in our invention is preferably gelatin although other materials capable of being differentially tanned with silver halide developing agents can be used, for example, polyvinyl alcohol, polyacrylamide and partially hydrolyzed polyvinyl esters.

A particularly valuable modification of our invention includes exposing the substantially unhardened emulsion

layer preferably containing a tanning developing agent, followed by development with an alkaline solution preferably containing one of the mentioned silver halide desensitizing agents, such as one containing 4% sodium carbonate and 0.1% potassium bromide. The developed emulsion is then treated with an alkali metal sulfite solution containing an intensifying agent such as an aqueous solution containing 4% sodium carbonate, 2% sodium sulfite, 10% urea and about 0.1% thiourea or other intensifying agent mentioned above such as thiosemicarbazide, arsensite, stannite, etc. The result is to develop a black silver image in the unexposed region of the emulsion layer and at the same time some silver sulfide may be obtained in that region, yet hardening of the gelatin in the region is retarded or suppressed by the sulfite in the solution. In this procedure it is not necessary to uniformly expose the emulsion prior to use of the sulfite solution since the intensifying compounds chemically fog and initiate development of the silver halide.

In a similar manner, after initial exposure to a subject of the emulsion layer containing tanning developing agent, the latent image can be developed in alkaline solution such as 4% sodium carbonate containing 0.1% potassium bromide, followed by treatment in alkaline sulfite solution to retard hardening such as 4% sodium carbonate, 2% sodium sulfite and 10% urea. After treatment in this solution for a few seconds the emulsion is then uniformly exposed to light to render the newly exposed silver halide developable and non-tanning development of the emulsion proceeds with the formation of a black silver image in substantially unhardened gelatin in the shadow region of the emulsion. Of course, this and the process just above then entail transfer to an absorbent surface of a stratum of the shadow region of the emulsion the optical density of which has been increased.

What we claim is:

1. A method of photographic reproduction which comprises exposing to a two-tone subject a substantially unhardened gelatino-silver halide emulsion layer containing a gelatin tanning silver halide developing agent, said emulsion being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, developing the exposed emulsion layer with an alkaline solution to obtain a hardened gelatin and silver image in the region of exposure and substantially unhardened gelatin and silver halide in the unexposed region of the emulsion layer, treating the developed emulsion layer with a member of the class consisting of an alkaline solution of from about 0.5 to 5% of a compound having a sulfur atom reacting with silver halide to form silver sulfide, and an alkaline solution of from about 0.5 to 2% of a compound reducing silver halide to silver in the absence of a latent image, pressing a sheet having an absorbent surface against said emulsion layer while said emulsion layer is moist, to cause only said unexposed region to adhere to said sheet and separating said sheet and emulsion layer to transfer only a stratum of the unexposed region of the emulsion layer to said sheet.

2. A method of photographic reproduction which comprises exposing to a two-tone subject a substantially unhardened gelatino-silver halide emulsion layer containing a gelatin tanning silver halide developing agent, said emulsion being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, developing the exposed emulsion layer with an alkaline solution to obtain a hardened gelatin and silver image in the region of exposure and substantially unhardened gelatin and silver halide in the unexposed region of the emulsion layer, treating the developed emulsion layer with an alkaline solution of from about 0.5 to 5% of a sulfur compound of the class consisting of thiourea, thiosemicarbazide and sodium sulfide until said unexposed silver halide has been converted to silver sulfide, pressing a sheet having an absorbent surface against said emulsion layer while said emulsion layer is moist, to cause only said unexposed region to adhere to said sheet and separating said sheet and emulsion layer to transfer only a stratum of the unexposed region of the emulsion layer containing silver sulfide to said sheet.

3. A method of photographic reproduction which comprises exposing to a two-tone subject a substantially unhardened gelatino-silver halide emulsion layer containing a gelatin tanning silver halide developing agent, said emulsion being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, developing the exposed emulsion layer with an alkaline solution to obtain a hardened gelatin and silver image in the region of exposure and substantially unhardened gelatin and silver halide in the unexposed region of the emulsion layer, treating the developed emulsion layer with an alkaline solution of from about 0.5 to 2% of a compound reducing said silver halide to silver in the absence of a latent image, pressing a sheet having an absorbent surface against said emulsion layer while said emulsion layer is moist, to cause only said unexposed region to adhere to said sheet and separating said sheet and emulsion layer to transfer only a stratum of the unexposed region of the emulsion layer containing silver to said sheet.

4. A method of photographic reproduction which comprises exposing to a two-tone subject a substantially unhardened gelatino-silver halide emulsion layer containing a gelatin tanning silver halide developing agent, said emulsion being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, developing the exposed emulsion layer with an alkaline solution to obtain a hardened gelatin and silver image in the region of exposure and substantially unhardened gelatin and silver halide in the unexposed region of the emulsion layer, treating the developed emulsion layer with an alkaline solution of from about 0.5 to 5% of a compound having a sulfur atom reacting with said silver halide to form silver sulfide, pressing a sheet having an absorbent surface against said emulsion layer while said emulsion layer is moist, to cause only said unexposed region to adhere to said sheet and separating said sheet and emulsion layer to transfer only a stratum of the unexposed region of the emulsion layer containing silver sulfide to said sheet.

5. A method of photographic reproduction which comprises exposing to a two-tone subject a substantially unhardened gelatino-silver halide emulsion layer containing a gelatin tanning silver halide developing agent, said emulsion being not harder than a gelatin layer containing 0.7 gram of formaldehyde per pound of gelatin freshly coated, developing the exposed emulsion layer with an alkaline solution to obtain a hardened gelatin and silver image in the region of exposure and substantially unhardened gelatin and silver halide in the unexposed region of the emulsion layer, treating the developed emulsion layer with an alkaline solution of from about 0.5 to 5% of a member of the class consisting of hydrazine hydrate, aminoguanidine sulfate, sodium arsenite, ferrous oxalate and stannite until said unexposed silver halide has been reduced to silver, pressing a sheet having an absorbent surface against said emulsion layer while said emulsion layer is moist, to cause only said unexposed region to adhere to said sheet and separating said sheet and emulsion layer to transfer only a stratum of the unexposed region of the emulsion layer containing silver to said sheet.

6. The process of claim 2 wherein the sulfur compound used is thiourea.

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