

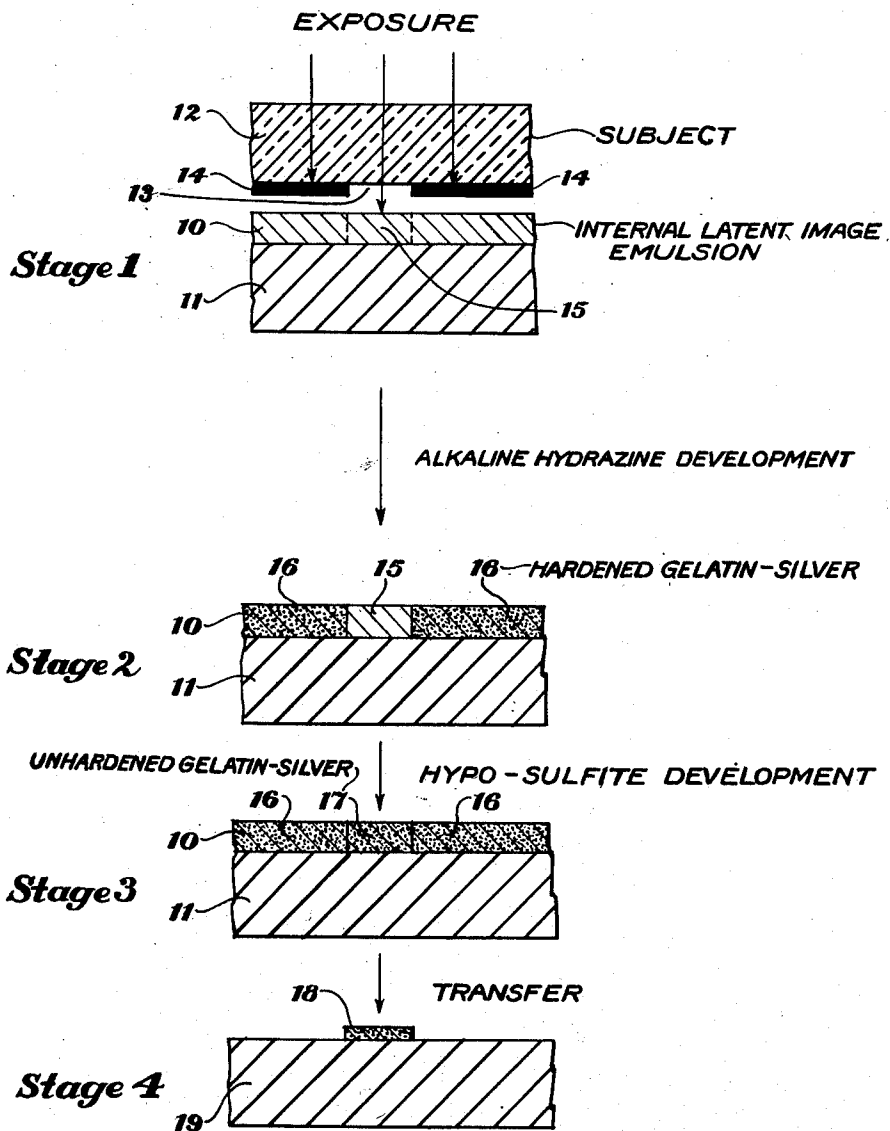
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H. B. COWDEN ET AL

2,835,575

PHOTOGRAPHIC REPRODUCTION PROCESS

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2,835,575

PHOTOGRAPHIC REPRODUCTION PROCESS

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8 Claims. (Cl. 96—28)

This invention relates to photography and more particularly, to a photographic copy method especially adapted to office copy work.

The Yackel and Yutzy U. S. Patent 2,596,756, granted May 13, 1952, and the Yutzy and Yackel patent application Serial No. 267,447, filed January 21, 1952, now U. S. Patent 2,716,059, granted August 23, 1955, describe photographic copying methods particularly adapted to office copy work wherein an unhardened gelatin-silver halide emulsion layer, preferably containing a gelatin tanning silver halide developing agent, is exposed to a two-tone subject (line or halftone subject) followed by treatment with an alkaline solution to obtain a hardened gelatin and silver image in the exposed portion of the emulsion layer. The emulsion layer, while moist, is then pressed into contact with an absorbent receiving sheet to cause only the unhardened portion of the emulsion layer to adhere to the receiving sheet with the result that when the sheet is removed from the emulsion layer, a thin stratum of the unhardened portions of the emulsion is found to be adhered to the sheet.

The mentioned processes are particularly adapted to the reproduction of positive originals such as printed subject matter which contain small dark images on a comparatively large light-colored background. In the case where it is desired to reproduce negative subject matter, such as paper or film negative which have a light-colored image on a comparatively large dark background, the mentioned processes are less useful since in the final transfer step, it is necessary to transfer large areas of the unexposed portions of the emulsion layer to the receiving sheet with the result that the copies, when first made, tend to curl and may be somewhat sticky. Also, the large areas which are transferred are fragile and easily damaged during the mechanical steps of the process with the concomitant loss of definition in the copy. Also, such large areas may transfer as rather thick strata, leaving on the printing element insufficient unhardened portions of emulsion for the preparation of additional copies.

We have discovered that if a certain type of direct positive emulsion is used in the processes mentioned, the procedures can be adapted to the reproduction of both negative and positive subject matter as either negative or positive copy and the mentioned disadvantages overcome.

One object of our invention is to provide the direct positive element useful in the processes of our invention. Other objects reside in providing the procedures for use of the direct positive emulsions in the mentioned colloid image transfer processes.

The processes of our invention include exposing an unhardened direct positive emulsion of the nature indicated hereinafter to a line or halftone subject, followed by developing either the exposed or unexposed portions with an alkaline solution in the presence of a gelatin tanning silver halide developing agent which may or may

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not be present in the original emulsion layer, under conditions of gelatin tanning silver halide development, so as to obtain a hardened gelatin and silver image in the emulsion layer. Thereafter, the emulsion is developed with another alkaline solution in the presence of a silver halide developing agent and a compound inhibiting gelatin tanning so as to develop an unhardened gelatin and silver image in the remaining region of the emulsion layer. In addition, either one of the alkaline solutions contains a silver halide solvent such as sodium thiosulfate when the other alkaline solution contains a hydrazine compound except that the first alkaline solution should not contain an amount of sulfite sufficient to inhibit gelatin tanning silver halide development. Thus, in a negative-positive process the first alkaline solution may contain the hydrazine compound but is substantially free of sulfite or other compound inhibiting gelatin tanning and the other alkaline solution contains a silver halide solvent and a gelatin tanning inhibitor. Conversely, in a positive process the first alkaline solution contains the silver halide solvent except no substantial amount of sulfite, and the second alkaline solution contains the hydrazine compound and gelatin tanning inhibitor. Following this, the emulsion layer is squeezed or pressed against a receiving sheet to transfer a thin stratum of the unhardened gelatin and silver image to the receiving sheet. The particular alkaline solutions in which the hydrazine compound and the silver halide solvent are incorporated determine whether a negative or positive reproduction is obtained. In the specific Example III provided hereinafter, a negative-positive process is illustrated since the hydrazine compound is present in the first alkaline developer solution and the silver halide solvent is present in the second non-tanning alkaline developer solution, the first alkaline solution causing tanning development in the unexposed portions of the direct positive emulsion layer and the other alkaline solution causing non-tanning development in the exposed portions of the emulsion layer.

The direct positive types of emulsion used in our invention are those known as internal latent image emulsions—that is, emulsions which form latent images mostly inside the silver halide grains. To the internal latent image emulsions may be added one or more gelatin tanning silver halide developing agents. An internal latent image emulsion, that is, one which forms the latent image mostly inside the silver halide grains, as described on pages 296 and 297 of Mees' "The Theory of the Photographic Process," 1942, is especially useful for the process of my invention. Most of the internal latent image emulsions to which the gelatin tanning silver halide developing agents may be added are silver bromide emulsions of high iodide content, preferably containing at least 10%-20% of iodide. Burton's emulsion is an emulsion of this type, having a silver iodide content of approximately 40% of the content of silver halide. It is not absolutely essential, however, for the emulsion to contain silver iodide.

Burton's emulsion described in Wall's "Photographic Emulsions," 1929, pages 52 and 53, is an emulsion of this type prepared as follows:

A

Silver nitrate -----grams-- 100
Water -----cc-- 500
Ammonia, to form clear solution.

B

Potassium bromide -----grams-- 80
Potassium iodide -----do-- 50
Soft gelatin -----do-- 30
Water -----cc-- 1000

Dry gelatin -----grams-- 250

(B is heated to 70° C., and A, cold, added to B with constant shaking, digested for 20 minutes at 50° C., and allowed to cool slowly. C is added after being allowed to swell for 20 minutes in water, drained and melted. The emulsion is then set and washed.)

A gelatin tanning silver halide developing agent can then be added to the emulsion in the manner described in the examples hereinafter.

An internal latent image emulsion made as described in the Davey and Knott U. S. Patent 2,592,250 is particularly useful in the processes of our invention. This emulsion is prepared by first forming in the absence of ammonia and in one or more stages silver salt grains consisting at least partly of a silver salt which is more soluble in water than silver bromide, subsequently converting the grains to silver bromide or silver bromiodide and if the silver iodide content of the emulsion is less than 6% calculated on the total silver halide, preferably treating such grains with an iodine compound to bring the silver iodide up to at least 6%, ripening preferably in the absence of ammonia and then either washing out some of the soluble salts or washing out the whole of the soluble salts, followed by the addition of soluble salts such as soluble chloride or bromide. An example of an emulsion made in this way is as follows:

Solution No. 1:

Inert gelatin-----	20 grams	} at 40° C.
KCl -----	20 grams	
Water -----	560 cc.	

Solution No. 2:

KCl -----	100 grams	} at 45° C.
Water -----	520 cc.	

Solution No. 3:

AgNO ₃ -----	195 grams	} at 45° C.
Water -----	520 cc.	

Solution No. 4:

KBr -----	160 grams	} at 45° C.
KI -----	40 grams	
Water -----	500 cc.	

Run solutions Nos. 2 and 3 simultaneously into solution No. 1 in a vessel, taking 90 seconds to do this. Then ripen for 1 minute at 45° C. Next add solution No. 4, then ripen for 20 minutes at 45° C. Next add 235 grams of inert gelatin (dry). Then ripen at 45° C. for 15 minutes during which time the gelatin dissolves. Set and shred the emulsion and then wash until free from all soluble bromide and then add about 150 cc. of 10% solution of KCl (by weight), and then add water to make 3½ liters. The tanning developing agents such as described hereinafter may then be added to the melted emulsion.

An internal latent image type of silver halide emulsion may be defined as one which, when a test portion is exposed to a light intensity scale for a fixed time between 1/100 and 1 second, and developed for 4 minutes at 20° F. in the ordinary, "surface" developer (Example I), exhibits a maximum density not greater than 1/3 the maximum density obtained when the same emulsion is equally exposed and developed for 3 minutes at 20° C. in an internal type developer (Example II). Preferably the maximum density obtained with the surface developer is not greater than 1/10 the maximum density obtained when the same emulsion is developed in the internal type developer. Stated conversely, an internal latent image emulsion, when developed in an internal type developer (Example II) exhibits a maximum density at least 5, and preferably at least 10, times the maximum density obtained when the same emulsion is exposed

in the same way and developed in a surface developer (Example I).

An ordinary, surface-type developer, that is, one which develops an image only on the surface of the grains of an internal latent image emulsion, is the following:

Example I

	Grams
p-Hydroxyphenylglycine -----	10
Sodium carbonate (crystals) -----	100
Water to 1 liter.	

(Development time, 4 min. at 20° C.)

An internal type developer, that is, one which develops an image inside the grains of an internal latent image emulsion, is the following:

Example II

	Grams
Hydroquinone -----	15
Monomethyl-p-aminophenol sulfate -----	15
Sodium sulfite (anhydrous) -----	50
Potassium bromide -----	10
Sodium hydroxide -----	25
Sodium thiosulfate (crystals) -----	20
Water to 1 liter.	

(Development time, 3 min. at 20° C.)

The internal latent image emulsions useful in our invention, such as described above, are separate and distinct from direct positive emulsions, such as described in the Kendall U. S. Patent 2,541,472, which are fogged before image-forming exposure. Such emulsions have not been found to be useful in our processes.

Our invention will now be described with particular reference to the accompanying drawing and the following specific example:

Example III

An internal latent image emulsion prepared as described by the method of the Davey and Knott patent above and containing one mol of silver halide, 476 grams of gelatin and 4000 cc. of water, was melted at 40° C. and the following additions made: 100 grams of 8% aqueous saponin solution and 600 grams of a developer dispersion prepared by dissolving 44.5 grams of 4-phenyl catechol (3,4-dihydroxydiphenyl) in 67.5 grams of dibutyl phthalate at 80° C. and pouring slowly into a rapidly stirred solution of 44.5 grams of gelatin and 44.5 cc. of 8% aqueous saponin solution in 475 cc. of water at 50° C. The mixture was then coated over 400 square feet of paper which had been made without addition of a gelatin hardening agent. The accompanying drawing illustrates in greatly enlarged cross-sectional view the manner of use of the resulting element having an unhardened internal latent image gelatino-silver halide emulsion 10 containing the gelatin tanning silver halide developing agent 4-phenyl catechol on support 11. As shown, the emulsion layer 10 is exposed to a subject 12 which may be either a negative or positive line or halftone subject having the image 13 on the dark background 14 until area 15 of the emulsion layer has been adequately exposed.

The exposed emulsion is then treated in the manner described in the Ives U. S. Patents 2,563,785 and 2,588,982 for 20 seconds with an alkaline solution preferably containing an aromatic hydrazine (if the hydrazine has not already been incorporated into the emulsion layer) such as the following:

	Grams
Na ₂ SO ₃ -----	2
p(β-Methylsulfonamidoethyl) phenyl hydrazine-----	2
Na ₂ CO ₃ ·H ₂ O -----	40
NaOH -----	1.4
Water to 1 liter.	

This treatment brings about tanning development of the emulsion layer 10 only in the unexposed areas 16, a hardened gelatin and silver image being obtained there-

in, whereas development does not take place in the exposed areas 15 of the emulsion layer as shown in stage 2 of the drawing.

Thereafter, the developed emulsion layer is directly treated with an alkaline solution containing a silver halide solvent such as sodium thiosulfate which dissolves the surface of the exposed silver halide grains and uncovers the underlying internal latent image. The alkaline solution also contains a compound such as sodium sulfite which inhibits tanning of the gelatin in the presence of the fogged silver halide and the gelatin tanning silver halide developing agent, such as the following solution:

	Grams
Na ₂ SO ₃ -----	20
Na ₂ CO ₃ ·H ₂ O -----	40
Sodium thiosulfate -----	10
Water, 1 liter.	

If desired, urea or another gelatin softening agent may be added to the above solution to facilitate the subsequent transfer operation. As a result of this treatment, the internal latent image in the exposed silver halide in area 15 of the emulsion layer is uncovered and developed to silver; thus an unhardened gelatin and silver image is obtained in that area 17 as shown in stage 3 of the drawings.

In order to now obtain a print from the resulting element containing the unhardened gelatin and silver image, the emulsion layer is squeegeed to free it of excess moisture and while it is still moist the emulsion layer is pressed into contact with a fairly dry absorbent surface or receiving sheet such as paper, to cause only the unhardened emulsion areas to adhere to the paper. Thereafter the receiving paper is peeled off of the emulsion layer to obtain a thin stratum 18 of the unhardened gelatin and silver image 17 on the paper 19, as shown in stage 4 of the drawing. Image 18 is therefore a negative with respect to the original subject 12.

In a similar manner, other copies can be obtained by merely rewetting the emulsion of the element used for making the first print with the solution containing sodium thiosulfate, squeegeeing the element momentarily and pressing it against a blank sheet of paper and peeling off the print from the emulsion layer.

While in the described process it is preferred that the gelatin tanning silver halide developing agent be incorporated into the emulsion layer, the more soluble tanning developing agents, such as hydroquinone and pyrogallol can be incorporated into the first-mentioned alkaline developer solution, in which case it may be necessary also to incorporate a quantity of the same developing agent or even a non-tanning silver halide developing agent, such as p-methyl-aminophenol sulfate, in the second developer solution to insure that a print containing adequate density is obtained in the subsequent transfer step. It may also be necessary to incorporate additional developing agent into the second alkaline processing solution in case the more soluble tanning developing agents have been present originally only in the emulsion layer and are found to unduly diffuse out in the first developing step so that an insufficient amount of developing agent is present for the second developing step.

In a less preferred variation of the process just described in reference to the drawing, it is possible to shorten the process materially as follows: After exposure of the emulsion containing the tanning developing agent as shown in stage 1 of the drawing, followed directly by treatment with the alkaline hydrazine solution, the resulting emulsion layer containing unhardened emulsion only in the exposed region, while moist, may be pressed into contact with a fairly dry receiving sheet in the presence of a compound such as a sulfur compound which reacts with the silver halide to form a dark image. For this purpose thiourea is a suitable compound which can be present on the surface of the receiving sheet. After pressing

the emulsion and receiving sheet together they are stripped apart leaving a stratum of dark colored gelatin image on the receiving sheet which is a negative with respect to the original subject. In place of thiourea may be used other compounds which react with the gelatino-silver halide image transferred to the receiving sheet to form an image of appreciable optical density, or cause the silver halide to become developable, e. g., sodium sulfide, sodium stannite, stannous chloride, mercaptans or zinc sulfide.

The gelatin tanning silver halide developing agents which can be used in the invention in the manner described include, for example, hydroquinone, catechol, and pyrogallol, although these gelatin tanning silver halide developing agents are less preferred because of their water-solubility and wandering characteristics in gelatin emulsion layers as mentioned. The most preferred gelatin tanning silver halide developing agents are those which are substantially insoluble in water, for example,

- 3,4-dihydroxy diphenyl
- 2,5-dihydroxy diphenyl
- 2,3-dihydroxy diphenyl
- 4-phenoxy catechol
- 4-(2-cyclopentenyl) catechol
- 1,2-diethoxallyl-4-phenyl catechol
- 1,2,3-triethoxallyl pyrogallol

3,4-dihydroxydiphenyl is especially useful as well as 4-phenoxy catechol because these compounds have high gelatin tanning silver halide development activity and are non-wandering in emulsion layers. The above two ethoxallyl derivatives of catechol and pyrogallol are unique since they are very stable in the emulsion layers under adverse conditions of temperature and humidity, yet these compounds readily hydrolyze in the alkaline processing solutions of the invention to yield the corresponding tanning developing agents 4-phenyl catechol and pyrogallol.

The preparation of the three latter compounds tabulated above is described in the Salminen et al. U. S. Patent 2,751,295, granted June 19, 1956.

The hydrazine compounds which can be used in the alkaline solutions employed in the process of the invention as described above, have the general formula



in which at least two R's are hydrogen atoms and when less than four R's are hydrogen atoms, the remaining R's are aryl, aralkyl, acyl, or carboxylic acid amide groups. Preferably, the hydrazine compound does not contain more than one aralkyl, acyl, or carboxylic acid amide group, although it may contain either one or two aryl groups. The hydrazine compound may be present either in the developing solution itself or in the emulsion. In the latter case, of course, the development of the exposed emulsion layer (stage 1 of the drawing) can be carried out with a simple alkaline solution containing little or no sulfite which would inhibit tanning development.

Representative hydrazine compounds having the above formula and whose structures may be better understood from consideration of Ives U. S. Patent 2,588,982, granted March 11, 1952, are as follows:

- Hydrazine dihydrochloride
- Phenylhydrazine hydrochloride
- p-Bromophenylhydrazine hydrochloride
- p-Chlorophenylhydrazine hydrochloride
- 2,5-dichlorophenyl hydrazine
- p-Tolyl hydrazine hydrochloride
- p-Toluene sulfonyl hydrazine
- α-Naphthylhydrazine
- p-Acetylphenylhydrazine
- α-Benzyl-α-phenylhydrazine hydrochloride
- n-Amyl succinyl dihydrazide

Sodium sulfosuccinyl dihydrazide
 Hydrazine dicarbonic dihydrazide
 Hydrazobenzene
 p-Hydrazinobenzoic acid
 p-Hydrazinobenzene sulfonic acid (sodium salt)
 Phenylhydrazine-m-sulfonic acid (sodium salt)
 Triphenyl phosphonium chloride acetohydrazide
 β -Phenyl acetohydrazido pyridinium chloride
 Addition product of phenyl hydrazine and 1-phenyl-3-hydroxy-5-pyrazolone
 p,p'-Dihydrazino-diphenyl-dihydrochloride
 4-p-phenylene disemicarbazide

The hydrazines disclosed in U. S. Patents 2,663,732 and 2,618,565 are preferred for use in the alkaline processing solutions of the invention or in the emulsion layers. These hydrazines have the general formula



in which D represents a divalent mononuclear arylene group of the benzene series, n represents a positive integer of from 1 to 5 and R represents an alkyl group of from 1 to 4 carbon atoms. Representative hydrazines having this general formula are as follows:

p-(Methylsulfonamidomethyl)-phenylhydrazine
 m-(Methylsulfonamidomethyl)-phenylhydrazine
 o-(Methylsulfonamidomethyl)-phenylhydrazine
 p-(β -Methylsulfonamidoethyl)-phenylhydrazine
 m-(β -Methylsulfonamidoethyl)-phenylhydrazine
 o-(β -Methylsulfonamidoethyl)-phenylhydrazine
 m-(Methylsulfonamido)-phenylhydrazine
 p-(Methylsulfonamido)-phenylhydrazine
 m-(Ethylsulfonamido)-phenylhydrazine
 p-(Ethylsulfonamido)-phenylhydrazine
 o-(Methylsulfonamido)-phenylhydrazine

The silver halide solvents which can be used in the alkaline processing solutions of the invention as described above to dissolve the surface of the silver halide grains of the emulsion layer and to uncover the internal latent image, include those silver halide solvents well known in the art such as alkali metal and ammonium thiosulfates and sulfites, ammonium salts, ammonium hydroxide, alkali metal thiocyanates, sodium bisulfite, potassium metabisulfite, etc.

The compounds used in the alkaline processing solutions of the invention to inhibit the tanning of the emulsion layer in the desired region include those compounds well known in the art to inhibit gelatin tanning silver halide development, for example, alkali metal sulfites, borax and alkali metal formaldehyde bisulfites.

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 of 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 "unhardened" or "substantially unhardened" as used here and in the appended claims, it is to be understood that this means the hardness of the order obtained with gelatin treated with formaldehyde under the conditions above. The emulsion can, of course, contain no formaldehyde whatsoever. Emulsion layers appreciably harder will not transfer satisfactorily. Similarly, if, after the final development step of the processes it is found that the layer is too hard and to accommodate variations in hardness and tanning sometimes encountered, we can use variations of temperature or pressure when making the transfer print. To this end we ordinarily apply pressure or temperature or both when rolling the developed emulsion down onto the receiving support. With an emulsion which transfers slowly with heat or pressure applied, we can, without use of increased heat or pressure during the transfer operation, make the transfer by treatment of the developed emulsion with solutions having a softening effect upon the colloid vehicle. Thus,

there may be incorporated into the alkaline solution used in the final development step a suitable quantity of a compound having a softening effect upon gelatin such as urea, sodium nitrate, glycerol, formamide or ethylene chlorohydrin.

In the above example, as illustrated in the drawings, the emulsion was exposed by contact printing. If desired, the exposure can be made by well known projection or reflex exposure methods. In some instances, as when the original subject contains both heavy black characters such as typewritten matter, and fine light gray lines such as pencil marks, it may be desirable to insert a separate exposure step either before or just after the image exposure step illustrated in stage 1 of the drawing. This exposure may be made with a halftone screen having about 120 or 133 lines per inch in contact with the emulsion layer before or after the image exposure. Otherwise the emulsion is processed as described in the above specific example with the result that the final copy obtained on the receiving sheet is composed of a series of dots and the dark and light images of the original are reproduced with adequate legibility. This procedure is particularly applicable to the direct positive processes of U. S. Patent 2,596,756 and that variation of our invention described hereinafter where the original subject is a positive and is reproduced as a positive. It is thus possible to use minimum subject exposure required to reproduce low-density pencil lines without causing the wide high-density lines to become indistinct and blurred in the final copy.

In the mentioned variation of our process in which the silver halide solvent is present in the first developing solution and the hydrazine compound in the second, the internal latent image emulsion, such as provided in Example III above, containing a gelatin tanning silver halide developing agent, after exposure is treated with an alkaline developing solution such as a sodium carbonate solution containing a silver halide solvent, such as sodium thiosulfate, under conditions of tanning development, that is, the solution should be substantially free of sulfite, to uncover the internal latent image in the exposed emulsion region and develop a hardened gelatin and silver image only in the exposed area of the emulsion layer. Thereafter the emulsion is developed with an alkaline solution such as provided in the above specific example and containing the hydrazine compound and sodium sulfite to obtain an unhardened gelatin and silver image in the unexposed portion of the emulsion layer. A direct-positive print is then obtained by merely pressing the emulsion layer against an absorbent receiving surface to transfer a thin stratum of the unhardened image area to the receiving surface. In this process, the tanning developing agent may also be present only in the first alkaline developing solution rather than in the emulsion layer and then it may be necessary to add silver halide developing agent of either the tanning or non-tanning variety to the second alkaline developing solution to insure adequate density in the final print.

We claim:

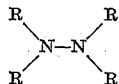
1. A photographic reproduction process which comprises exposing to a two-tone subject an unhardened gelatino-silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $\frac{1}{400}$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer (II):

	Grams
Hydroquinone	15
Monomethyl-p-aminophenol sulfate	15
Anhydrous sodium sulfite	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate	20
Water to 1 liter.	

gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C. in the following surface developer (I):

	Grams
p-Hydroxyphenylglycine -----	10
Sodium carbonate -----	100
Water to 1 liter.	

developing said exposed emulsion layer with an alkaline solution in the presence of a gelatin tanning silver halide developing agent under conditions of gelatin-tanning silver halide development until a hardened gelatin and silver image is obtained in the emulsion layer, thereafter developing said emulsion layer with an alkaline solution in the presence of a silver halide developing agent and a compound inhibiting gelatin tanning, until an unhardened gelatin and silver image is obtained in the remaining regions of the emulsion layer, pressing an absorbent sheet against said emulsion layer while the emulsion layer is moist to cause the unhardened gelatin and silver image to adhere to said sheet, and separating said sheet and emulsion layer to transfer only a stratum of said unhardened gelatin and silver image to said sheet, only one of said alkaline solutions containing a silver halide solvent when the other contains a hydrazine compound having the general formula



in which at least 2 R's are hydrogen atoms and when less than 4 R's are hydrogen atoms, the remaining R's are selected from the class consisting of aryl, aralkyl, acyl and carboxylic acid amide groups, but not more than one R is any one of said aralkyl, acyl and carboxylic acid amide groups.

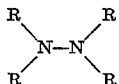
2. A photographic reproduction process which comprises exposing to a two-tone subject an unhardened gelatino-silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $\frac{1}{100}$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer (II):

	Grams
Hydroquinone -----	15
Monomethyl-p-aminophenol sulfate -----	15
Anhydrous sodium sulfite -----	50
Potassium bromide -----	10
Sodium hydroxide -----	25
Sodium thiosulfate -----	20
Water to 1 liter.	

gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C. in the following surface developer (I):

	Grams
p-Hydroxyphenylglycine -----	10
Sodium carbonate -----	100
Water to 1 liter.	

said emulsion containing a gelatin tanning silver halide developing agent, treating the exposed emulsion layer with an alkaline solution containing a hydrazine compound having the general formula



in which at least 2 R's are hydrogen atoms and when less than 4 R's are hydrogen atoms, the remaining R's are selected from the class consisting of aryl, aralkyl, acyl and carboxylic acid amide groups, but not more than one R is any one of said aralkyl, acyl and carboxylic acid amide groups, said treatment being carried out under

conditions of gelatin tanning silver halide development until a hardened gelatin and silver image is obtained only in the unexposed portion of the emulsion layer, treating the resulting developed emulsion layer with an alkaline solution containing a silver halide solvent and a compound inhibiting gelatin tanning, until an unhardened gelatin and silver image is obtained in the exposed portion of the emulsion layer, pressing an absorbent sheet against said emulsion layer while the emulsion layer is moist to cause the unhardened gelatin and silver image to adhere to said sheet, and separating said sheet and emulsion layer to transfer only a stratum of said unhardened gelatin and silver image to said sheet.

3. The process of claim 1 wherein said first mentioned alkaline developing solution contains a silver halide solvent and said other alkaline solution contains the designated hydrazine compound and a compound inhibiting gelatin tanning.

4. The process of claim 1 wherein the silver halide solvent is an alkali metal thiosulfate and the compound inhibiting gelatin tanning is an alkali metal sulfite.

5. A photographic reproduction process which comprises exposing to a two-tone subject an unhardened gelatino-silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $\frac{1}{100}$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer (II):

	Grams
Hydroquinone -----	15
Monomethyl-p-aminophenol sulfate -----	15
Anhydrous sodium sulfite -----	50
Potassium bromide -----	10
Sodium hydroxide -----	25
Sodium thiosulfate -----	20
Water to 1 liter.	

gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C. in the following surface developer (I):

	Grams
p-Hydroxyphenylglycine -----	10
Sodium carbonate -----	100
Water to 1 liter.	

said emulsion layer containing a compound of the class consisting of

- 3,4-dihydroxy diphenyl
- 2,5-dihydroxy diphenyl
- 2,3-dihydroxy diphenyl
- 4-phenoxy catechol
- 4-(2-cyclopentenyl) catechol
- 1,2-diethoxallyl-4-phenyl catechol
- 1,2,3-triethoxallyl pyrogallol

developing the exposed emulsion layer with an alkaline solution containing a compound of the class consisting of

- p-(Methylsulfonamidomethyl)-phenylhydrazine
- m-(Methylsulfoamidomethyl)-phenylhydrazine
- o-(Methylsulfonamidomethyl)-phenylhydrazine
- p-(β -Methylsulfonamidoethyl)-phenylhydrazine
- m-(β -Methylsulfonamidoethyl)-phenylhydrazine
- o-(β -Methylsulfonamidoethyl)-phenylhydrazine
- m-(Methylsulfonamido)-phenylhydrazine
- p-(Methylsulfonamido)-phenylhydrazine
- m-(Ethylsulfonamido)-phenylhydrazine
- p-(Ethylsulfonamido)-phenylhydrazine
- o-(Methylsulfonamido)-phenylhydrazine

until a hardened gelatin and silver image is obtained only in the unexposed portion of the emulsion layer, treating the resulting developed emulsion layer with an alkaline solution containing an alkali metal sulfite and an alkali metal thiosulfate until an unhardened gelatin and silver image is obtained in the exposed portion of the emul-

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sion layer, pressing an absorbent sheet against said emulsion layer while the emulsion layer is moist to cause the unhardened gelatin and silver image to adhere to said sheet, and separating said sheet and emulsion layer to transfer only a stratum of said unhardened gelatin and silver image to said sheet.

6. A photographic reproduction process which comprises exposing to a two-tone subject an unhardened gelatino-silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $\frac{1}{100}$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer (II):

	Grams
Hydroquinone	15
Monomethyl-p-aminophenol sulfate.....	15
Anhydrous sodium sulfite.....	50
Potassium bromide.....	10
Sodium hydroxide.....	25
Sodium thiosulfate.....	20
Water to 1 liter.	

gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C. in the following surface developer (I):

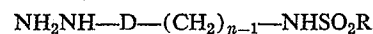
	Grams
p-Hydroxyphenylglycine	10
Sodium carbonate.....	100
Water to 1 liter.	

said emulsion layer containing 3,4-dihydroxy diphenyl as a gelatin tanning silver halide developing agent, developing the exposed emulsion layer with an alkaline solution containing p-(β -methylsulfonamidoethyl)phenyl hydrazine,

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until a hardened gelatin and silver image is obtained only in the unexposed portion of the emulsion layer, treating the resulting developed emulsion layer with an alkaline solution containing sodium thiosulfate and sodium sulfite so as to obtain an unhardened gelatin and silver image in the exposed portion of the emulsion layer, pressing an absorbent sheet against said emulsion layer while the emulsion layer is moist to cause the unhardened gelatin and silver image to adhere to said sheet, and separating said sheet and emulsion layer to transfer only a stratum of said unhardened gelatin and silver image to said sheet.

7. The process of claim 1 wherein the hydrazine compound used has the general formula



wherein D represents a divalent mononuclear arylene group of the benzene series, n represents a positive integer of from 1 to 5, and R represents an alkyl group of from 1 to 4 carbon atoms.

8. The process of claim 2 wherein the hydrazine compound used has the general formula



wherein D represents a divalent mononuclear aryl group of the benzene series, n represents a positive integer of from 1 to 5 and R represents an alkyl group of from 1 to 4 carbon atoms.

References Cited in the file of this patent

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