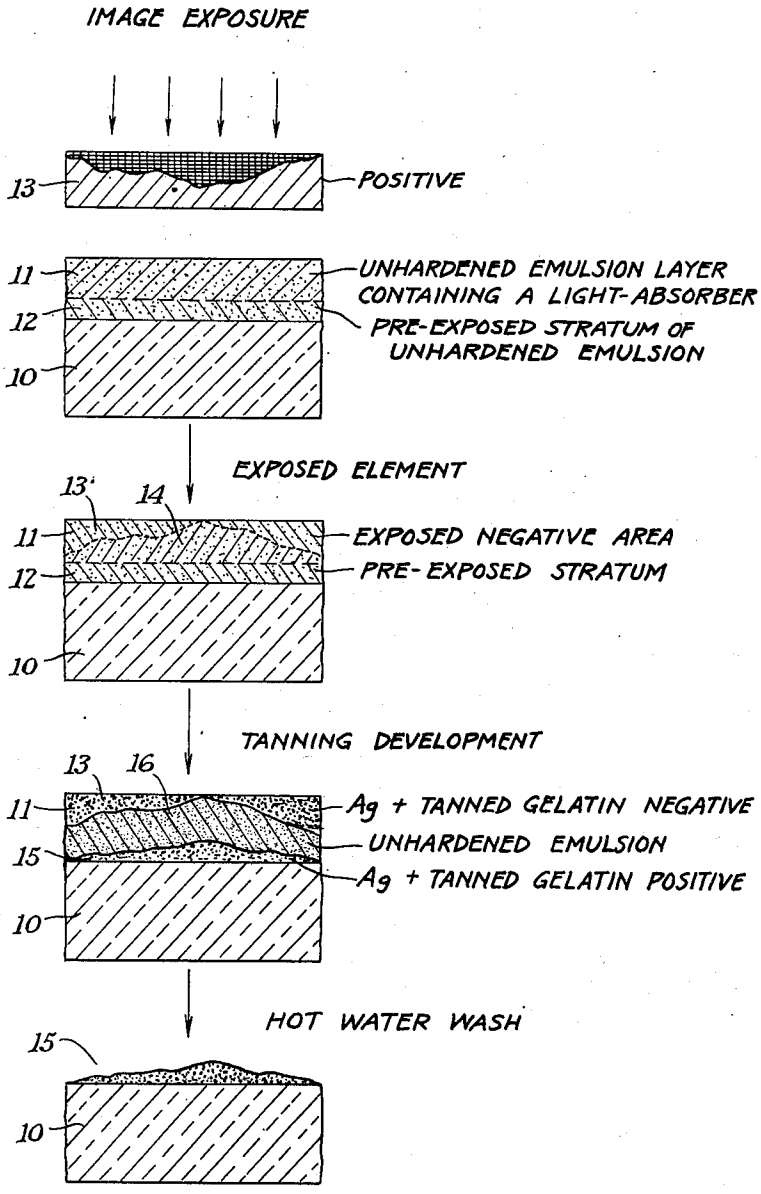
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DIRECT-POSITIVE PHOTOGRAPHIC PROCESS

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DIRECT-POSITIVE PHOTOGRAPHIC PROCESS

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This invention relates to the production of photographic images by a direct-positive process which images are particularly useful in color photography as imbibition dye transfer matrices.

The conventional method of producing dye-transfer matrices involves the production of three color-separation negatives and forming three matrices therefrom which are subsequently used in the transfer of three subtractively colored dyes to a single imbibition blank. In this process it is desirable to prepare the matrices by a direct positive process thereby eliminating the step of preparing the intermediate negatives. Several processes have been suggested for this purpose, for example, a gelatino-silver halide emulsion may be exposed to an aspect of a colored subject and after development of the exposed element, the exposed emulsion area is removed by means of a peroxide bleach bath which solubilizes the emulsion in the region of the silver image. One difficulty of this process, among others, lies in the fact that the process requires the use of a heavily dyed emulsion layer in order to restrict the color separation exposure to the outer surface of the emulsion layer. Since it is necessary to expose through to the base in the light region and since the dyed emulsion resists such exposure, the element has such low speed that the printing time is objectionably long.

Similarly, in cases where it is desirable to reproduce or duplicate black-and-white images, for example, in preparing duplicate negatives, an appreciable saving in time and materials as well as an improvement in quality can be effected if the intermediate step of producing a positive can be dispensed with.

One object of our process is to provide a simplified direct-positive process of producing dye-transfer matrices as well as silver images. Another object is to provide various methods and materials useful for carrying out our process. Another object is to provide a variation of our process by which matrices may be corrected to compensate for the deficiencies of the dyes of the process. Other objects will become apparent from consideration of the following description of our invention.

The objects of our invention are in general accomplished by image-wise exposure of an

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outer stratum of emulsion of a photographic element having a support usually a transparent film carrying two strata of gelatino-silver halide emulsion separated by a water-soluble colloid stratum, the stratum adjacent the support containing uniformly exposed silver halide, and after exposure, simultaneously developing a negative silver image in the outer stratum and a positive silver image in the stratum adjacent the support leaving soluble colloid separating the silver images, and then treating with warm water to remove the outer stratum and colloid stratum thereunder to leave a direct-positive image on the support. More particularly, when our process is applied to the production of direct-positive relief images, the objects of our invention in general are accomplished by image-wise exposing the outer stratum of a sensitive element having a support carrying a fogged and substantially unhardened gelatino-silver halide emulsion stratum adjacent the support and an unexposed substantially unhardened gelatino-silver halide emulsion stratum outermost, leaving a stratum of unexposed soluble emulsion separating the two exposed strata, then developing the element in a tanning developer composition to simultaneously form positive and negative tanned images separated by soluble emulsion and then removing the outer tanned negative stratum and soluble emulsion by treating with water to leave a direct-positive relief image on the support.

The accompanying drawings show in flow-chart form, in greatly enlarged cross-sectional view, the appearance of a typical sensitive material useful in our process, at various stages of forming a direct-positive matrix.

Our invention will be understood by consideration of the following examples together with the drawings which examples are merely illustrative of our invention.

EXAMPLE 1

A sensitive photographic film including a substantially unhardened panchromatic gelatino-silver halide emulsion layer on a cellulose ester support is provided. The emulsion layer should contain a light absorber such as a dye or carbon black. The emulsion layer is preferably first uniformly exposed from the base side so as to

obtain a pre-exposed stratum of emulsion adjacent to the support or this exposure can be made subsequent to the image exposure. It is within this region that the direct positive matrix will be formed. The film appears at this point as shown in the first stage of the drawings wherein layer 10 is a transparent support of a cellulose ester, for example, cellulose acetate carrying the unhardened emulsion layer 11, the stratum 12 of which has been exposed. The element is then exposed to the positive 13 which may be a positive subtractively colored transparency although negative color films as well as black-and-white transparencies, both positive and negative may be used. Since color-separation matrices are desired when the positive 13 is a color transparency, the exposure light is suitably filtered, for example, using a blue, green or red filter. The duration and intensity of exposure are so adjusted that a stratum of unexposed emulsion remains separating the exposed areas as represented in the second stage of the drawings wherein the emulsion layer 11 is shown as now containing the exposed stratum 12, the exposed negative area 13 and a stratum 14 of unexposed emulsion separating the exposed areas 12 and 13.

The element is then developed for 2 minutes at 68° F., or longer depending on whether lower contrast is desired in the final positive relief image, in a tanning developer of the following composition:

Solution A

	Grams
Pyrocatechol	2.5
Pyrogallol	2.5
Potassium metabisulfite	3
Potassium bromide	1

Water to make 1 liter.

Solution B

	Grams
Sodium hydroxide	5

Water to make 1 liter.

Mix 1 part of Solution A, 1 part of Solution B, 2 parts water and use immediately after mixing.

The result is to obtain simultaneously silver and tanned gelatin images of the character represented in the third stage of the drawings wherein emulsion layer 11 is shown as containing a silver and tanned gelatin negative image in area 13 and a silver and tanned gelatin positive image in area 15. Area 16, comprising unhardened emulsion, separates the images in areas 13 and 15. Subsequently, the element of the third stage of the drawings, is treated with a dilute acetic acid stop bath, 0.5% acetic acid is satisfactory, and then immersed in or treated with hot water at about 130° F. which causes the emulsion area 16 to melt and dissolve, thereby allowing the tanned image 13 to be removed. The appearance of the resultant direct positive matrix film is shown in the last stage of the drawings according to which the support 10 now carries the direct-positive relief image 15. The element may be further washed with hot water to remove the last traces of unhardened emulsion, then hardened in a hardening bath such as the usual acid hardening fixing bath, and if desired, the silver image in the colloid relief may be removed by conventional methods involving bleaching the silver and fixing out.

It is desirable to incorporate an absorber such as carbon black in the initial emulsion in order to prevent joining of the image and flash exposed regions. However, in this case a considerable speed advantage is obtained over other reversal processes, such as the mentioned peroxide-etch process, because it is unnecessary in our process to expose completely through the emulsion layer in the high-light regions.

EXAMPLE 2

In a variation of our process a film having two layers of gelatino-silver halide emulsion is used. The emulsion adjacent the support is a substantially unhardened slow panchromatic emulsion to which has been added a light absorber such as finely divided carbon or a colored pigment or dye. The purpose of the absorber is to prevent unwanted exposure of this layer. The other emulsion layer is a relatively fast substantially unhardened panchromatic emulsion of a well-known negative type containing no absorber. The film is given a uniform flash exposure from the base side so as to expose a stratum but not necessarily all of the emulsion adjacent to the support, or the lower emulsion may previously have been made developable by chemical or exposure methods. An exposure of approximately 10 seconds at 8 feet from a 60-watt lamp through a red color-separation filter is generally satisfactory. The film is then exposed by contact or projection from the side opposite the support through a suitable color transparency using the appropriate color separation filter. With conventional tri-color filters, for example, Nos. 29, 61 and 47, approximately 10, 40 and 120 seconds exposure at 8 ft. from a 60-watt lamp are sufficient for the red, green and blue color-separation exposures, respectively. The filter numbers given refer to filters having the characteristics shown on pages 36, 50 and 42, respectively, of the publication "Wratten Light Filters," 14th edition, 1936, published by Eastman Kodak Company. The exposed film is then developed as in Example 1 in the tanning developer solution. Following a short rinse in the acetic acid stop bath, the film is washed in hot water to dissolve the unexposed emulsion stratum and remove the tanned negative image. The resultant direct-positive color-separation matrix is then hardened and fixed, and if desired, the silver image is removed from the colloid relief in a well-known manner. The matrix is then ready for use in a dye-transfer process involving the usual steps of dyeing up the matrix in an acid dye solution and transferring the imbibed dye to the imbibition blank. In this process, instead of flashing or fogging the lower-most stratum of emulsion, a comparable effect is obtained if an unhardened pre-fogged emulsion is coated, or fogged after coating on a support and overcoated with an unhardened panchromatic emulsion. Also, the initial sensitive element may be devoid of the light absorber in which case we use a slow blue sensitive emulsion next to the support the outer emulsion being a fast panchromatic emulsion. Useful results are obtained by using ultraviolet light for uniformly flashing the slower layer and to limit penetration of the exposure into the emulsion.

In case it is desired to introduce a correction into the matrix to compensate for the deficiencies in light absorption of the subtractive dyes of the process, prior to tanning development, the film is given a filtered supplementary exposure from the base side through the color transparency in register with the latent image already impressed onto the surface of the film.

In this case a part of the uniform exposure from the base side is replaced by the exposure through the transparency and the filter selected for color correction. The following table provides typical exposure times for three matrices using conventional red, green filters as color-correction filters.

Cyan matrix

	Seconds
Support side—	
Uniform flash No. 29 filter	4
Through original 29 filter	18
Emulsion side—	
Through original 29 filter	10

Magenta matrix

	Seconds
Support side—	
Uniform flash No. 29 filter	4
Through original 29 filter	18
Emulsion side—	
Through original 61 filter	40

Yellow matrix

	Seconds
Support side—	
Uniform flash No. 61 filter	16
Through original 61 filter	72
Emulsion side—	
Through original No. 47+29	120

After the color correction exposure has been made, the element is processed as described in the above examples employing tanning development and hot water washing steps.

While the mechanism of our process is not thoroughly understood, the following tentative explanation is given. Referring to the figure of the second stage of the drawings, it will be seen that the film at this stage contains latent images in areas **12** and **13**. It might be expected, as happens to be the case, that in the subsequent tanning development step, a tanned image would be produced in area **13** distributed in the layer as shown. Also it might be expected that a uniformly tanned image would be obtained throughout area **12**. However, it appears that because of exhaustion effects produced by development of area **13**, in area **12** less tanning is produced in those parts adjacent to the more heavily exposed areas of image area **13**, while tanning is not impeded in the vicinity of those regions of area **13** having less exposure. Consequently, the tanned image produced in area **12** has the characteristics shown in area **15** of the third stage of the drawings. Since untanned emulsion separates areas **13** and **15**, the subsequent hot water wash solubilizes this emulsion and permits removal of the overlying tanned gelation negative. When the auxiliary color correction exposure through the support has been employed, the characteristics of the final relief image are of course determined both by the auxiliary exposure and the exhaustion effects produced by development of the negative image in area **13**.

The principal advantages of our process now become apparent. The fact that our process produces matrices in a direct-positive manner eliminates appreciable materials, and effects considerable savings in processing time. Quality of the matrices is improved partly because fewer steps are required. Compared to the direct-positive peroxide-bleach process, we obtain all of the advantages of a faster printing film.

EXAMPLE 3

When adapting our process to the production of duplicate silver images for example, duplicate negatives, we take a film having a support carrying two gelatino-silver halide emulsions of the customary hardness, the emulsion adjacent the support is an inherently blue-sensitive emulsion and the other is preferably a long-scale ortho or panchromatic emulsion. The two emulsions are separated by a thin soluble colloid interlayer, for example, of unhardened gelatin or other warm water soluble colloid. The emulsion adjacent the support may have been fogged prior or subsequent to coating. Image-wise exposure of the outer emulsion under a suitable silver negative (or positive) is effected, followed by development in an ordinary black-and-white developer. Exhaustion effects of development of the image in the outer layer control development of the direct-positive image in the layer adjacent the support, and after development, the outer emulsion and soluble colloid thereunder are removed with warm water leaving the duplicate silver image on the support. In case the uniform exposure of the stratum of the lower layer is carried out by a flash exposure through the base, ultraviolet light may be used for this purpose and for the image-wise exposure of the other layer, green or yellow light is used having no effect on any unexposed emulsion of the bottom layer.

Here and in the appended claims we mean the word "stratum" to include not only a discrete layer positioned among or adjacent to layers of other kinds but also a uniform area having some character different than the single layer of which it was originally an integral part.

It is to be understood that the disclosure herein is by way of example and that we consider as included in our invention all modifications and equivalents falling within the scope of the appended claims.

We claim:

1. The method of making a direct-positive photographic relief image in a photographic element having a support substantially impermeable to photographic developing solution carrying a fogged substantially unhardened gelatino-silver halide emulsion stratum and an unexposed substantially unhardened gelatino-silver halide emulsion stratum over said fogged stratum, which comprises image-wise exposing said unexposed emulsion leaving a stratum of unexposed soluble emulsion separating the fogged stratum and the image-wise exposed stratum, developing the exposed element in a tanning developer composition to simultaneously form a positive silver and tanned gelatin image adjacent the support, a negative silver and tanned gelatin image in the region of the image exposure, and a stratum of soluble emulsion separating said tanned images, thereafter, removing said tanned negative image and soluble emulsion by treatment with hot water leaving a positive relief image on said support.

2. The method of making a direct-positive photographic relief image which comprises uniformly exposing to light a stratum of substantially unhardened gelatino-silver halide emulsion coated on a transparent support substantially impermeable to photographic developing solution from the support-side, image-wise exposing another stratum of substantially unhardened gelatin-silver halide emulsion from the side opposite the support leaving unexposed soluble emulsion separating said exposed strata, developing the exposed element in a tanning developer composition to simultaneously form a positive silver and tanned gelatin image adjacent the support, a negative silver and tanned gelatin

image in the region of the image exposure, and a stratum of soluble emulsion separating said tanned images, thereafter removing said tanned negative image and soluble emulsion by treatment with hot water leaving a positive relief image on said support.

3. The method of making a direct-positive photographic relief image which comprises uniformly exposing to light from the support side a stratum of a single substantially unhardened gelatino-silver halide emulsion layer containing a light-absorber coated on a transparent support substantially impermeable to photographic developing solution, then image-wise exposing another stratum of the emulsion layer from the side opposite the support leaving an unexposed stratum of soluble emulsion separating said exposed regions, developing the exposed element in a tanning developer composition to simultaneously form a positive silver and tanned gelatin image adjacent the support, a negative silver and tanned gelatin image in the region of the image exposure, and a stratum of soluble emulsion separating said tanned images, thereafter, removing said tanned negative image and soluble emulsion by treatment with hot water leaving a positive relief image on said support.

4. The method of making a direct-positive photographic relief image in a film having two substantially unhardened gelatin-silver halide emulsion layers superposed on a transparent support substantially impermeable to photographic developing solution, which comprises uniformly exposing to light an emulsion stratum adjacent the support without exposure of said outer emulsion layer, image-wise exposing an outer stratum of said outer emulsion layer leaving unexposed soluble emulsion separating the exposed strata, developing the exposed element in a tanning developer composition to simultaneously form a positive silver and tanned gelatin image adjacent the support, a negative silver and tanned gelatin image in the region of the image exposure, and a stratum of soluble emulsion separating said tanned images, thereafter, removing said tanned negative image and soluble emulsion by treatment with hot water leaving a positive relief image on said support.

5. The method of making a direct-positive photographic relief image in a film having two substantially unhardened gelatino-silver halide emulsion layers on a transparent support substantially impermeable to photographic developing solution, the outermost emulsion layer having appreciably greater sensitivity, which comprises uniformly exposing to light an emulsion stratum adjacent the support without exposure of the outermost emulsion layer, imagewise exposing an outer stratum of said outermost emulsion layer leaving a stratum of unexposed soluble emulsion separating the exposed regions, developing the exposed element in a tanning developer composition to simultaneously form a positive silver and tanned gelatin image adjacent the support, a negative silver and tanned gelatin image in the region of the image exposure, and a stratum of soluble emulsion separating said tanned images, thereafter, removing said tanned negative image and soluble emulsion by treatment with hot water leaving a positive relief image on said support.

6. The method of making a direct-positive photographic relief image in a film having two substantially unhardened panchromatic gelatino-silver halide emulsion layers superposed on a transparent support substantially impermeable to photographic developing solution, the outermost emulsion layer having appreciably greater sensitivity than the other emulsion, said other emulsion containing a light absorber, which comprises uniformly exposing to light an emulsion adjacent the support without exposure of the outermost emulsion layer, imagewise exposing an outer stratum of said outermost emulsion layer leaving unexposed soluble emulsion separating the two exposed regions, developing the exposed element in a tanning developer composition to simultaneously form a positive silver and tanned gelatin image adjacent the support, a negative silver and tanned gelatin image in the region of the image exposure, and a stratum of soluble emulsion separating said tanned images, thereafter, removing said tanned negative image and soluble emulsion by treatment with hot water leaving a positive relief image on said support.

7. The method of making a direct-positive photographic relief image which comprises uniformly exposing to light a stratum of substantially unhardened gelatino-silver halide emulsion layer coated on a transparent support substantially impermeable to photographic developing solution from the support side, exposing another stratum of substantially unhardened gelatino-silver halide emulsion from the side opposite the support to a color-separation image of a color-transparency, in registry exposing said sensitive element from the support side through said transparency to a wavelength of light improperly absorbed by images of said color transparency leaving some unexposed soluble emulsion separating said color-separation image region from other exposed regions, developing the element in a tanning developer composition to simultaneously form a color-corrected positive silver and tanned gelatin image adjacent the support, a negative silver and tanned gelatin image outermost, and a stratum of soluble emulsion separating said tanned images, removing said tanned negative image and soluble emulsion by treatment with hot water leaving a color-corrected positive relief image on said support.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,993,576	Troland	Mar. 5, 1923
2,218,229	Carroll	Oct. 15, 1940

FOREIGN PATENTS

Number	Country	Date
716,428	France	Oct. 6, 1931

OTHER REFERENCES

Ricketts, British Journal of Photography, June 5, 1914, page 446.