July 15, 1958 H. C. YUTZY ET AL 2,843,485

TRANSFER PROCESS OF PHOTOGRAPHIC PRINTING

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Fig. 1

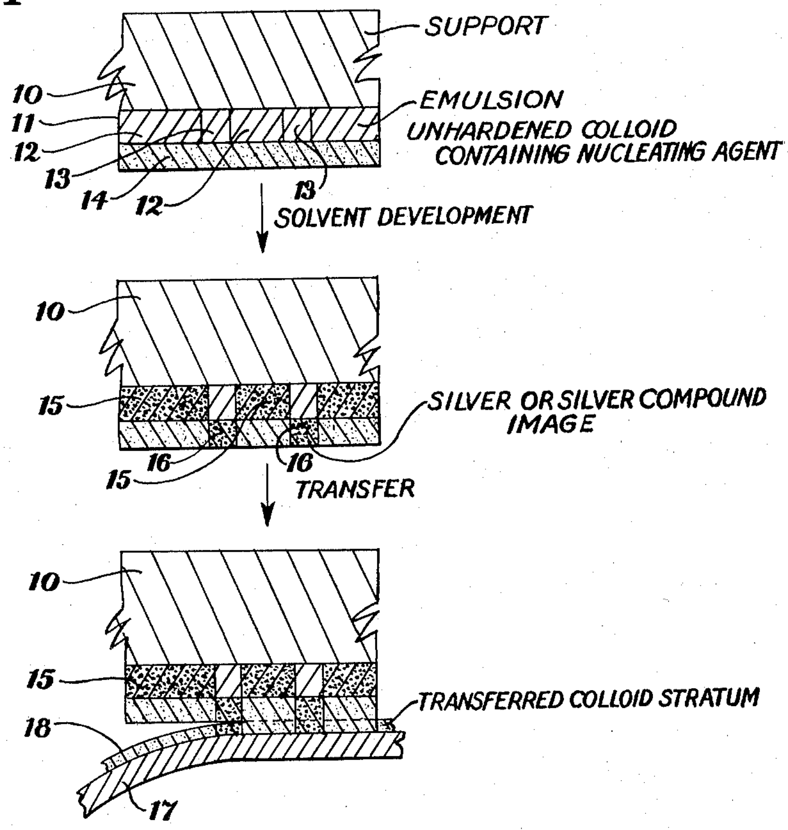
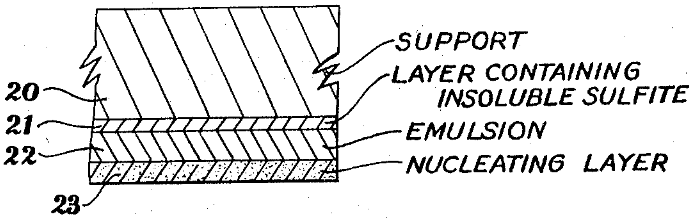


Fig. 2



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TRANSFER PROCESS OF PHOTOGRAPHIC PRINTING

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Original application May 3, 1952, Serial No. 285,855, now Patent No. 2,725,298, dated November 29, 1955. Divided and this application May 17, 1954, Serial No. 430,074

4 Claims. (Cl. 96—76)

This invention relates to photography and particularly to a transfer process of printing a photographic image.

This application is a division of U. S. application Serial No. 285,855, filed May 3, 1952, now U. S. Patent 2,725,298.

Various methods of forming an image in an unsensitized sheet by transfer from an originally sensitive layer have been described in the literature. In U. S. Patent 2,596,754, E. C. Yackel has described a procedure according to which a photographic image formed in an unhardened gelatin layer by conventional processing is transferred to a dry absorbent receiving sheet by squeegeeing the print, after processing, into contact with the dry absorbent surface, then stripping the two apart after a short interval of contact. In this process a stratum of the gelatin layer is adhered to the receiving surface and transferred leaving behind the remainder of the gelatin layer containing part of the image. Upon rewetting the gelatin layer successive transfers can be made. This method produces a negative transferred image if a positive is used to make the original exposure.

Processes involving solvent transfer methods have also been described in the literature, a review of these appearing in an article by Varden in the Photographic Society of America Journal, vol. 13, September 1947, page 551. These processes involve development of an exposed silver halide emulsion layer with a developing solution containing a solvent for silver halide. During or immediately following initial development the exposed emulsion layer is placed in contact with another layer, usually unsensitized, and the dissolved silver salts representing the positive image are then transported to the second layer and deposited as a positive image. This method gives a positive transferred image if a positive image is used for the original exposure.

We have now found that an image formed in the outer of two superposed strata by the solvent transfer method may be transferred to the receiving sheet by the method of U. S. Patent 2,596,754 and that several successive transfers may be made in this way to produce duplicate images. Our method involves in general the use as the sensitive material of a photographic element comprising a support having a silver halide emulsion layer thereon and an unhardened colloid layer overcoated on the emulsion layer so that the colloid layer is outermost. The colloid layer has dispersed therein an agent for promoting image formation, comprising physical development nuclei or a chemical precipitant for dissolved silver ions, so that the dissolved silver salts transported to the colloid layer from the silver halide emulsion layer during solvent development, are deposited and retained in a visible form in the colloid layer. The image thus obtained in the colloid layer may be transferred layerwise to an absorbent support and successive transfers of the colloid layer containing the image may be made on successive absorbent supports to produce duplicate images.

In the drawing,

Fig. 1 illustrates sectional views of the photographic elements at various stages in our preferred process, and

Fig. 2 is a sectional view of a modified form of the sensitive element used according to our invention.

The silver halide emulsion used in the sensitive element of our invention may be an ordinary unsensitized gelatino-silver halide emulsion, or an optically sensitized or chemically sensitized emulsion, in which the gelatin is substantially unhardened or hardened in such a way that it does not harden the colloid layer coated over it, as explained more fully hereinafter. The emulsion may contain a substantially non-diffusing developing agent of the tanning type as disclosed in Yackel U. S. Patent 2,592,368, or a non-tanning, substantially non-diffusing developing agent as described in U. S. Patent 2,716,059.

The colloid layer coated over the emulsion layer is a layer of water-susceptible or water-permeable colloid, such as gelatin or polyvinyl alcohol, containing an agent promoting image formation and capable of yielding with silver ion a dark-color silver substance, when the dissolved silver salts from the emulsion layer come in contact with it. This agent in the colloid layer may comprise either physical development nuclei or a chemical precipitant for dissolved silver ions, the following being suitable agents:

Colloidal silver
Colloidal sulphur
Stannous chloride
Sodium stannite
Sodium sulfide
Zinc sulfide
Cadmium sulfide
Arsenous oxide
Aminoguanidine sulfate
Aminoguanidine carbonate
Organic sulfiding agents, e. g.:
    Mercaptates
    Xanthates
    Thioacetates
    Thiourea or its derivatives
    Substituted hydrazines

The developing solution may be the usual and customary type of photographic developing solution containing hydroquinone, N-methyl-p-aminophenol sulfate, p-phenylene diamine, etc., or any mixture of these, as the developing agent and containing the usual ingredients such as alkali, potassium bromide and sodium sulfite. If the developing agent is incorporated in the emulsion layer the solution used to effect development may be a simple alkaline solution such as a sodium carbonate or sodium hydroxide solution. The developing solution must also contain a silver halide solvent such as sodium thiosulfate, sodium sulfite, ammonium hydroxide, ammonium sulfate, ammonium nitrate, ammonium chloride or a thiocyanate of an alkali metal. If the silver halide solvent is contained in the sensitive element as shown in Examples 3 and 4 hereinafter, the developing solution need not, of course, contain a silver halide solvent.

If a non-diffusing developing agent is to be used in the sensitive emulsion, any of the following compounds will serve for this purpose:

3,4-dihydroxy-diphenyl
2,5-dihydroxy-diphenyl
2,3-dihydroxy-diphenyl
5,6,7,8-tetrahydronaphthol hydroquinone
2-hydroxy-5-amino-diphenyl
3,4-diamino-diphenyl
Dodecyl catechol
Diamyl-hydroquinone
Lauryl hydroquinone

Our invention will be further illustrated by reference to the following specific examples.

Example 1

An ordinary photographic paper stock free from formaldehyde or other compound capable of hardening gelatin was coated with a high contrast contact speed gelatino-silver chloride emulsion substantially free of gelatin hardeners. On this photographic emulsion layer there was coated a layer of substantially unhardened gelatin containing colloidal zinc sulfide. This suspension was prepared as follows:

A. 157 cc. H_2O
23 cc. fused Na_2S—1 g. in 1000 cc. H_2O
B. 100 cc. $Zn(NO_3)_2 \cdot 6H_2O$—1 g. in 1000 cc. H_2O

B was poured into A at room temperature with rapid stirring. The mixture was quickly poured into 110 g. 20 percent gelatin (containing 10 cc. 7.5 percent aqueous saponin) at 40° C. The whole was held at 40° C. for coating.

This composite element was exposed to a positive original and the silver halide emulsion layer developed to a negative in a developing solution of the following composition:

	G.
N-methyl-p-aminophenol sulfate	10
Hydroquinone	10
Sodium sulfite, desiccated	50
Sodium metaborate	15
NaOH	15
KBr	0.5
$Na_2S_2O_35H_2O$	5
Urea	20
Chlorobenzotriazole	0.5
Water to 1 liter.	

After development for approximately one minute there was formed in the nucleating layer a positive image. The sheet was removed from the developer solution, squeegeed to remove excess developer and pressed into contact with a sheet of absorbent paper, for example, an ordinary bond typewriter paper. After a few seconds the photographic sheet was stripped from the receiving paper, which was found to carry a positive image representing a stratum of the total positive image formed in the overcoated nucleating layer.

The original photographic layer carrying the negative and the remainder of the nucleating layer with the positive image was rewet in the developer solution, squeegeed and rolled into contact with a second sheet of receiving paper, then stripped as before leaving another portion of the image on the second receiving sheet. This operation could be repeated several times.

The incorporation of from 1 to 20 percent of urea in the developing bath to increase the softness of the gelatin image was found to be advantageous.

Example 2

An ordinary photographic paper stock was coated with a high contrast contact speed gelatino-silver chloride emulsion hardened with 4.9 cc. of 20 percent formaldehyde solution per kilogram of emulsion. On this emulsion layer there was coated a layer of polyvinyl alcohol containing cadmium sulfide prepared as follows:

A. (46 g. 17% polyvinyl alcohol) melted at 80° C. (234 cc. H_2O) cooled to 40° C.
40° C. (14.4 cc. Na_2S solution (1.0 g. fused Na_2S per 100 cc. solution in H_2O)
B. 45.6 cc. $CdCl_2.2\frac{1}{2}H_2O$ solution (1.0 g./100 cc.), room temperature

B added to A with rapid stirring. Finally 10 cc. 7.5% aqueous saponin added. Dispersion held at 40° C. for coating.

This **composite** element after exposure to a positive

image and development in the developer of Example 1 was squeegeed to remove excess developer and rolled into contact with an absorbent receiving sheet. The positive image formed in the polyvinyl alcohol layer was transferred to the receiving support, yielding a direct positive image.

The advantage of this element is that conventional photographic emulsions with conventional hardening agents such as formaldehyde may be used. Such gelatin hardeners have little hardening action on polyvinyl alcohol so that the polyvinyl alcohol layer retains the proper physical characteristics for a transfer to the receiving sheet.

Example 3

A photographic paper support free from formaldehyde or other gelatin hardeners bearing instead of the usual baryta coat a similar layer made with barium sulfite instead of barium sulfate was coated with the emulsion layer of Example 1 containing 12 g. of 3,4-dihydroxy diphenyl per kilogram of emulsion and also the nucleating layer of Example 1. The nucleating layer could also be coated on a separate sheet and squeegeed into contact with the emulsion layer just prior to the development process. The barium sulfite layer was made as follows:

A.	H_2O (65° C.)	750 cc.
	$BaCl_2.H_2O$	213 g.
B.	H_2O (boiling)	1500 cc.
	Na_2SO_3	120 g. (10% excess)

"A" was run into the boiling solution "B" over a 20-minute period. The mixture was boiled 30 minutes longer, then allowed to settle 3 hours. The mixture was filtered by suction (required 2½ hours).

The wet $BaSO_3$ from above (310 g.) was dispersed in 264 cc. of water containing 45 cc. of 7.5% aqueous saponin. The mixture was heated to 40° C. and 206 g. 10% gelatin was added. This was held at 40° C. for coating.

This element was exposed to a positive layer image and developed for about one minute in the following solution:

	G.
$Na_2CO_3.H_2O$	50
NaOH	15
Urea	100
Water to 1 liter.	

The theory of development of this element is as follows: When the exposed silver halide layer is brought into contact with the developing solution, development is initiated and carried well toward completion as the developing solution penetrates the colloid layer, the concentrations of silver halide solvent no higher than those used in conventional development. This allows development to a negative image before appreciable solution and subsequent transfer of silver halide to the nucleating layer via silver halide solvent occurs. As the developing solution penetrates through the emulsion to the under-coated barium sulfite layer the carbonate and hydroxyl ions in the developing solution react with the barium sulfite to produce barium carbonate and barium hydroxide, thus liberating the sulfite ion as the alkali salts and these diffuse back through the emulsion layer to the nucleating layer to effect the usual silver halide transfer.

It is also desirable in this case to add some neutral sulfate such as sodium sulfate to the developer since barium sulfate is considerably less soluble than the carbonate, hydroxide or sulfite and will effect a more nearly complete conversion of the barium sulfite to sulfate, thus liberating the soluble sulfite more efficiently.

Other solvent systems may be substituted for the barium sulfite such as calcium or strontium sulfite. Other examples of solvents are slightly soluble or non-wandering ammonium salts or amines. Long-chain amines may be included in the undercoat by coating high molecular resins in the layer as complexes with the amines, the complexes being broken up by the action of the alkali in the developer.

A separate receiving sheet bearing the nucleating layer may be used in conjunction with a conventional silver halide paper, by incorporating the insoluble or nonwandering solvent in the nucleating layer or under the nucleating layer on the receiving sheet. It will be apparent also that the silver halide emulsion may contain a substantially non-diffusing developing agent as described in Example 3, the chemical energy required for formation of the positive image being obtained from suitable reagents in a second layer either overcoated on the emulsion layer or coated on a second transfer sheet.

In the process of Example 1 in which both emulsion and nucleating layer were unhardened it has been found that there is some tendency for the fracture to occur at the paper base during transfer to the receiving sheet, resulting in unwanted transfer of all of the layers. This can be prevented by incorporating in the baryta layer or in a layer beneath the sensitive emulsion layer a completely exposed silver halide emulsion having therein an issoluble tanning developing agent. During development the completely exposed or fogged bottom layer is rapidly developed and tanned at the same time thus hardening the bottom layer and causing it to adhere more strongly to the paper support. This layer may contaian the usual baryta or it may contain barium sulfite as described in Example 3. The black density developed in the barium sulfite layer does not affect the transfer results. The following example illustrates a coating made in this way.

Example 4

A paper support was coated with a suspension of barium sulfite, silver chloride emulsion, and 4-phenyl catechol as a tanning developing agent. This layer was thoroughly flashed to white light before subsequent coating. Over this layer there was coated a gelatino-silver chloride emulsion also containing 4-phenyl catechol. Over the emulsion there was coated a gelatin layer containing zinc sulfide.

After exposure to an image this material was developed for two to three minutes in an alkaline solution. This caused (1) complete development of the silver in the bottom layer accompanied by tanning of the gelatin in the layer, (2) development of the negative image in the photosensitive layer and solution of the undeveloped silver halide in this layer by the sulfite ion from the bottom layer and (3) diffusion of the silver sulfite complex to the top layer where the silver was deposited as silver sulfide in the form of a positive image. When successive fractions of the top layer were transferred to a receiving support there was little if any tendency for all of the layers to transfer at once.

Our invention will now be described by reference to the accompanying drawing. As shown in Fig. 1 a support **10** has coated thereon a silver halide emulsion layer **11** having exposed portions **12** and unexposed portions **13**, an unhardened colloid layer **14** containing a nucleating agent which is coated over the emulsion layer **11**. Upon solvent development of this material a silver image **15** is formed in layer **11** and a silver or silver compound image **16** is formed in the nucleating layer by solvent transfer. When this element is rolled into contact with a receiving sheet **17** a portion **18** of the nucleating layer carrying the image is transferred to the sheet **17** as shown in the final stage of Fig. 1.

Fig. 2 illustrates the modification of our material in which a support **20** is coated with a layer **21** containing an insoluble sulfite, an emulsion layer **22** and a nucleating layer **23**.

Where we refer to a "substantially unhardened" gelatin emulsion layer we mean a layer that is not harder than would be the case with gelatin contining 0.25 ounce of formaldehyde (40 percent, diluted 1 to 3 with water) per pound of gelatin when freshly coated, or 0.1 ounce of the formaldehyde solution per pound of gelatin for a sample aged 3 to 6 months.

Where we refer to "transferring a continuous stratum of the emulsion layer" we mean that a thin layer of the total surface area of the photographic element is carried off onto the receiving support.

It will be understood that the modifications and equivalents included herein are by way of example only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. A light-sensitive photographic element comprising a support having thereon at least two layers including a substantially unhardened gelatino-silver halide emulsion layer having a dihydroxy diphenyl developing agent incorporated therein, and a layer of unsensitized, substantially unhardened gelatin containing a chemical precipitant for dissolved silver ions coated directly on said emulsion layer and attached to said emulsion layer to permit transfer of dissolved, undeveloped silver ions from said emulsion layer to said gelatin layer containing said chemical precipitant for dissolved silver ions, upon exposure and development of said emulsion layer in a solvent developer, and to form a reversed photographic image in said stratum containing said chemical precipitant for dissolved silver ions, and to permit transfer of a stratum of said gelatin layer containing said reversed photographic image to a dry, absorbent surface, said gelatin layers being not harder than a gelatin layer containing ¼ ounce of formaldehyde per pound of gelatin.

2. The element of claim 1, in which the chemical precipitant is cadmium sulfide.

3. The element of claim 1, in which the chemical precipitant is zinc sulfide.

4. The element of claim 1, in which the support is a paper support, and a layer of gelatin containing an alkaline earth metal sulfite is located between said support and said emulsion.

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