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PHOTOGRAPHIC PROCESS FOR FORMING
A POSITIVE TRANSFER IMAGE
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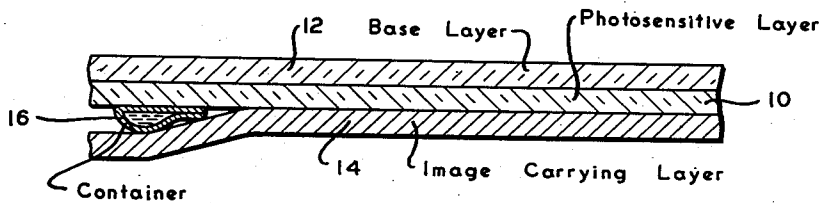


FIG. 1

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PHOTOGRAPHIC PROCESS FOR FORMING A POSITIVE TRANSFER IMAGE

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4 Claims. (Cl. 95—88)

1

This application relates to photography, and to novel photographic processes in general.

This invention relates more particularly to processes of the type where a positive image is formed from a latent negative image in a silver halide photosensitive layer by creating positive image-forming components under the selective control of the development of the latent image and by utilizing these image-forming components for creating the positive image. With such processes, staining of the highlights of the positive image is sometimes encountered due to the existence of unused developer in stain-forming condition in said highlights.

It is a principal object of the present invention to provide improved processes of the above type and improved products for use with such processes whereby staining of the highlights of the positive image is prevented.

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

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

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

Figure 1 is an exaggerated cross-sectional view of a preferred composite photographic film unit embodying the present invention.

In the photographic processes with which this invention is particularly involved, a sheet of photosensitive material, preferably a silver halide, is exposed to actinic light to create therein a latent negative image. This latent image is developed and a positive image thereof is formed on an image-carrying layer, preferably by creating between the two layers a uniform film of a viscous alkaline developer solution containing a substance capable of forming positive image-forming components. This latter substance, in a preferred form of the invention, comprises a silver halide solvent such as sodium thiosulfate. With such a film of liquid composition between the exposed

2

photosensitive layer and the image-carrying layer, the developer therein develops the exposed photosensitive material and the silver halide solvent forms soluble complex ions with the unexposed photosensitive material. These complex ions are dissolved and are transported to the surface of the image-carrying layer where they are converted, by the developer, to colloidal particles comprising silver, these particles constituting a positive image of the latent negative image.

The creation of this layer of liquid, including the developer, is a mechanical process and subject to considerable variation as the result of different conditions of temperature, etc., during the spreading of the liquid. Therefore, it is desirable, in most cases, to include in the layer of liquid composition more developer per unit area than would ordinarily be required to just develop the exposed photosensitive material so as to fully cover and develop the negative image. Much of the excess developer remains on the image-carrying layer containing the positive image.

The principal feature of the present invention is the prevention of any stain due to oxidation of any excess developer which may exist in the highlights of the positive image. This is accomplished in the preferred form of the invention, by providing a strong antioxidant in the liquid composition or on one of the layers in position to be dissolved by the liquid composition as it spreads between these layers. This antioxidant is preferably one whose oxidation product is white or colorless and also one which has at least the ability to reduce the silver complexes to silver and preferably has some ability for assisting in developing the latent negative image.

In a preferred form of the invention the antioxidant is included on the image-carrying layer and its effectiveness is increased by use in combination with a substance of acid reaction.

Referring now to Fig. 1 there is shown a preferred form of a film unit embodying the present invention. In Fig. 1 there is provided a photosensitive layer 10, preferably carried by a suitable base layer 12, and an image-carrying layer 14. Between these two layers there is preferably positioned the container 16 having therein a liquid composition.

In a preferred modification of the invention the photosensitive layer 10 comprises a silver halide

ide photosensitive material coated upon a suitable cellulosic film base 12. The image-carrying layer comprises, in a preferred form, a sheet of baryta paper which has been treated by coating thereon a thin layer of a material prepared as set forth in the following nonlimiting example:

Example 1

The following ingredients are placed in a mechanical mixer and preferably added in the order named, while being continuously mixed:

192 cc. of a 40% water solution of neutral lead acetate
30 gm. of silica aerogel ("Santocel C" Monsanto)
50 cc. of a 1/5% water solution of sodium sulfide
25 cc. of a 2% water solution of sodium sulfide
66 cc. of a 1% water solution cupric acetate
36 cc. of a 15% water solution of ascorbic acid.

When an extremely stable picture is desired, it is preferred, in some cases, to place the coating of Example 1 on a sheet of baryta paper which has been previously dipped as set forth in the following nonlimiting example:

Example 2

A sheet of baryta paper is run through a 1/4% neutral lead acetate bath for 1 minute, dried, run through a 1/40% sodium sulfide bath for 2 seconds, dried, and then run through a bath containing 1% neutral lead acetate, 10% cadmium acetate and 30% zinc nitrate for 1 minute.

It is also possible to use, in place of the baths of Example 2, a single bath containing cadmium acetate, neutral lead acetate, and zinc nitrate.

A liquid composition in the container 16 preferably comprises a developer such as hydroquinone, an alkali such as sodium hydroxide, a silver halide solvent such as sodium thiosulfate, a preservative such as sodium sulfite, and a film-forming material, which in a preferred form is sodium carboxymethyl cellulose. There is also included a sufficient amount of water to carry the above-mentioned elements in solution. A suitable liquid composition may comprise:

Example 3

	Grams
Water	1860
Sodium carboxymethyl cellulose	93
Sodium sulfite	78
Sodium hydroxide	74.6
Sodium thiosulfate	14.5
Citric acid	38.5
Hydroquinone	52

Various equivalents may be used in the above-mentioned liquid composition and it is equally possible to substitute, for the film-forming sodium carboxymethyl cellulose, other film-forming materials such as other alkali-inert, water-soluble polymers, for example hydroxyethyl cellulose, polymethacrylic acid, and aluminum carboxymethyl cellulose. Equally, other developers, preservatives, alkalies, and silver halide solvents may be used, and other substances such as restrainers may be added where desired.

In the use of the embodiment of the invention shown in Fig. 1, the photosensitive layer 10 is exposed to actinic light, either through the base layer 12, or by separating the photosensitive layer 10 and the base layer 12 from the remainder of the film unit to allow direct exposure of the photosensitive layer 10 by light which does not pass through any of the other

layers of the film. The film unit is then processed by applying a mechanical stress thereto for the purpose of releasing the liquid composition from the container 16 and spreading it in a uniform thin layer between the photosensitive layer 10 and the image-carrying layer 14 to form an image-receiving layer. This may be most readily accomplished by passing the film unit through a pair of pressure rollers, the container end going first. The action of the pressure rollers releases the liquid composition and spreads it in a uniform thin layer. The developer in the liquid composition develops the latent negative image in the photosensitive layer and the silver halide solvent forms with the unexposed portions of the photosensitive layer soluble silver complexes. The silver halide complexes migrate to the image-carrying layer where they are converted into insoluble particles comprising silver by the joint action of the developer, the ascorbic acid and the lead sulfide on the surface of the image-carrying layer.

The positive image on the image-carrying layer is next separated from the photosensitive layer and there is found to exist a stable positive image on the surface of the image-carrying layer. The stability of the positive image with respect to heat, moisture, and radiation is believed to be due, at least partially, to the antioxidant characteristics of the ascorbic acid which prevents oxidation of any excess developer in the highlights of the positive image. This effect, in some cases, is noticeably increased when the alkalinity of the positive image is lowered to a neutral or acid condition by the inclusion on the image-carrying layer of a substance of acid reaction such as the metal salts described in Example 2.

Other antioxidants may be used on the image-carrying layer in place of, or in addition to, the ascorbic acid in Example 1, as set forth in the following nonlimiting examples:

Example 4

The mixture of Example 1 is modified by replacing the ascorbic acid with 17 cc. of a 15% water solution of aminoguanidine.

Example 5

The mixture of Example 1 is modified by replacing the ascorbic acid with 12 cc. of a 15% water solution of aminourea.

Another example of the use of ascorbic acid is set forth below when the listed ingredients are mixed and applied as in Example 1.

Example 6

192 cc. of a 40% water solution of neutral lead acetate
30 g. of silica aerogel
60 cc. of a 1% water solution of sodium sulfide
36 cc. of a 15% water solution of ascorbic acid

A baryta image-carrying layer is prepared for receiving the above mix by dipping for about 30 seconds in a water solution containing by weight 10% cadmium acetate, 1% lead acetate and 30% zinc nitrate.

While it is preferred that the antioxidant be included on the image-carrying layer or be associated with the film unit or some other layer in position to be dissolved by the liquid composition, this is not essential, and satisfactory results have been achieved by including the antioxidant, such as ascorbic acid, in the liquid composition.

5

In general it is desirable to include the anti-oxidant on the image-carrying layer since, during the most critical portion of the development of the negative image, i. e., the initial development, the strongly alkaline solution of the developer is unaffected by the presence of the antioxidant which is being dissolved from the image-carrying layer; therefore its initial effect on the negative is not restrained by the antioxidant. This gives an undiminished capability for the developer in its initial stage of the process for the development of the negative image. As the development of the negative proceeds, the antioxidant is dissolved, thus somewhat restraining the capability of the developer. However, at this point the positive image is also forming which acts to localize the precipitation of silver from the silver complexes, thereby removing the necessity for extremely rapid and accurate development of the negative image. This antioxidant also assists in reducing the silver complexes to silver on the image-carrying layer; thus it acts as a developer for the positive image along with those portions of the developer which are unaffected by development of the negative image.

While a preferred form of the invention has been described, it should be pointed out that various modifications thereof are within the broad scope of the invention. For example, certain of the materials normally carried in the liquid composition may be included on the various layers of the film unit in position to be dissolved by the liquid as it is spread through the film unit. As an example of this, the sodium thiosulfate may be included on the image-carrying layer, and in some cases this modification of the invention is preferred.

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

What is claimed is:

1. A photographic process for forming, by transfer, a positive print of a latent image contained in the silver halide emulsion of a photosensitive element wherein a single application of liquid to said element is effective to give a finished print of improved stability, which process comprises the steps of bringing a relatively uniform layerwise distribution of a processing liquid into contact with the photosensitive element so as to permeate said emulsion with said liquid, said layerwise distribution of processing liquid providing the entire mass of liquid for performing said processing; causing said liquid to permeate said photosensitive element while a print-receiving element is superposed therewith and providing, as reagents in said processing liquid, a silver halide developer characterized by its propensity for oxidizing in an alkaline environment to form stains, a silver halide solvent capable of forming transferable soluble silver complexes with the unexposed silver halide of said emulsion, an alkali

6

and ascorbic acid, the oxidation characteristics of the latter being such that it serves as an anti-oxidant for said developer, said ascorbic acid being capable of cooperating with said developer in the reduction of the silver of soluble silver complexes; developing said emulsion layer with said processing liquid and transferring from said emulsion layer, by imbibition, at least part of said soluble silver complexes onto a print-receiving stratum supported by said print-receiving element; reducing by said processing liquid the silver ions of said soluble silver complexes to silver in said print-receiving stratum to form an image in silver which is a positive of the subject matter of the latent image developed in the silver halide emulsion; and separating said stratum with said print-receiving element from said photosensitive layer, a quantity of said ascorbic acid being permanently retained in said stratum and inhibiting such residual amounts of said silver halide developer as may be in said stratum from forming stains therein.

2. The process of claim 1 wherein the developer is hydroquinone.

3. The process of claim 1 wherein the layerwise distribution of processing liquid is obtained by spreading the mass of processing liquid between the photosensitive element and the print-receiving element and wherein said reagents are contained in the processing liquid prior to its spreading.

4. The process of claim 1 wherein the ascorbic acid is initially carried in solid form upon one of said elements and is dissolved in the processing element during the confinement of said liquid between the outer surfaces of said elements.

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