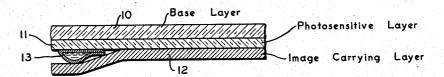
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SILVER HALIDE DEVELOPER CONTAINING A FILM-FORMNG PLASTIC AND A WATER INSOLUBLE FINELY COMMINUTED SOLID SUBSTANCE Filed Nov. 29, 1946



UNITED STATES PATENT **OFFICE**

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SILVER HALIDE DEVELOPER CONTAINING A FILM-FORMING PLASTIC AND A WATER INSOLUBLE FINELY COMMINUTED SOLID SUBSTANCE

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15 Claims. (Cl. 95-88)

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This invention relates to photography and more particularly to novel photographic film units and processes.

A principal object of the present invention is to provide a novel photographic process of the type wherein a viscous film-forming material is utilized in forming an image-receiving layer for the purpose of receiving a positive image of a subject image, and wherein said image-receiving layer has a greater resistance to cracking.

Another object of the present invention is to provide a process for forming an image-receiving layer of the above character having a matte surface, by the use of a finely comminuted substance.

Another object of the invention is to provide a 15 photographic material comprising a water solution of a developer, a film-forming material, and a water-insoluble substance capable of giving a matte surface to a film formed by the film-forming material.

Another object of the invention is to provide a composite photographic film unit comprising a photosensitive layer, a container having therein a liquid composition including a film-forming material, an image-carrying layer, and a substance capable of imparting a matte surface to a film formed by said film-forming material when said liquid is spread in contact with said imagecarrying layer.

These and other objects of the invention will in 30 part be obvious and will in part appear hereinafter.

The invention accordingly comprises the product possessing the features, properties and the relation of components and the process involving 35 the several steps and the relation and the 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 40 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.

This invention relates generally to novel photographic processes of the type wherein a photosensitive layer is subjected to a predetermined processing by having spread adjacent thereto and preferably in contact therewith a layer of a liquid 50 processing agent comprising as an ingredient thereof a film-forming material, the latter material being adapted to provide adjacent said photosensitive layer a dimensionally stable solid film. In its preferred form the processing carried 55 the formation of a stable film.

out by said composition is effective to develop a latent image in the photosensitive layer and to provide in said film, or in said film and a layer associated therewith, a visible positive image of the subject matter to which said photosensitive layer was subjected in the formation of the latent image.

In a preferred modification of the present invention, the process comprises creating within a film unit, containing said photosensitive layer, a layer of liquid composition including a solvent for a developer and a film-forming material, causing said film-forming material to create a solid, substantially dimensionally stable film having a matte surface, developing said latent image in said photosensitive material by means of said developer, creating positive image-forming components under the selective control of said development, transferring said positive imageforming components to said formed film and converting said components to a visible positive image at least partially in said formed film.

A preferred film unit for use with such a process comprises a layer of photosensitive material such as a noble metal halide, for example, a silver halide, another layer, and a container having therein a liquid composition and positioned for discharge of its liquid content between said layers. The liquid composition preferably comprises an alkaline aqueous solution of a developer such as hydroquinone, a silver halide solvent such as sodium thiosulfate, a preservative such as sodium sulfite, a film-forming material such as sodium carboxymethyl cellulose, and a relatively insoluble inert colloidal substance capable of imparting a matte surface to a film formed by means of the film-forming material. The other layer in the film unit preferably serves as a carrier for the final positive image and is hereinafter referred to as an image-carrying layer.

This preferred type of film unit is shown in the drawing wherein there is provided a base layer 16 adapted to carry on one surface thereof a photosensitive layer 11. There is also provided an image-carrying layer 12 which may be suitably joined to the base layer 10. Between the imagecarrying layer 12 and the photosensitive layer 11, there is positioned a container 13, adapted to have therein the liquid composition. This container can be attached to either the photosensitive layer 11 or the image-carrying layer 12. On the upper surface of the image-carrying layer 12, there is preferably incorporated a material such as lead acetate which aids, among other things,

The base layer 10 is preferably made of a suitable film base material such as a cellulosic ester, or mixed ester such as cellulose nitrate, cellulose acetate, cellulose acetate propionate, or other substances capable of supporting a photosensitive emulsion.

The image-carrying layer 12, in a preferred embodiment of the invention, is formed of a photographic material known in the art as baryta paper. This layer is preferably permeable to 10 the liquid composition and may also be manufactured from other substances such as gelatin or paper. It may also be made of regenerated cellulose, polyhydroxy alkanes such as polyvinyl alcohol, sodium alginate, certain of the cellulose 15 ethers such as methyl cellulose, and their derivatives such as sodium carboxymethyl cellulose or hydroxyethyl cellulose, carbohydrates such as gums or starch, and mixtures of these materials where the latter are compatible.

In a preferred embodiment of the invention, this film-forming material adheres strongly to the image-carrying layer and forms therewith an inseparable coating.

The film-forming material may comprise a 25 high molecular weight polymer preferably from the class consisting of the water-soluble, alkaliinert polymers such as hydroxyethyl cellulose. sodium carboxymethyl cellulose and polymethacrylic acid. Such other cellulosic ethers as 30aluminum carboxymethyl cellulose may also be satisfactorily used for this purpose. In accordance with the present invention there is included in the above-described liquid composition an inert substance, such as silica aerogel, fuller's 35 earth, diatomaceous earth, kieselguhr, and wood flour. In general, it may be stated that these inert substances should have the ability of forming a more or less discontinuous film. The property of these substances to make the film more 40 or less discontinuous also seems to aid in preventing the cracking of the film. This is particularly true when a thick film is created and a film-forming material is used of the type such as sodium carboxymethyl cellulose which crosslinks with metals, such as lead, to form a very brittle film.

In the use of inert substances of the above type which have high absorptive characteristics, it has been found that when they are added to the liquid composition they should be first treated so as to remove any absorbed air, since the oxygen in the air may have a deleterious effect upon the liquid composition. It has been found that some substances, such as Santocel, which is a silica aerogel, may cause considerable oxidation of the developer in the liquid composition even though the mixture is prepared under an inert atmosphere. This silica aerogel may be deoxygenated by repeatedly evacuating and then blowing in nitrogen. Other methods of removing absorbed oxygen are equally valuable.

Several nonlimiting examples of preferred liquid compositions for use in the present invention are as follows:

Example 1

Hydroquinone	_grams	13.5	
Sodium thiosulfate	do	3.75	
Sodium sulfite	do	13.5	
Sodium carboxymethyl cellulose _	do	25	
Sodium hydroxide	do	19.5	
Water	cc	495	
Wood flour	_grams	20	

Hydroquinonegrams_	27.2
Sodium thiosulfatedo	
Sodium sulfitedo	13.5
Sodium carboxymethyl cellulosedo	63.9
Sodium hydroxidedo	19.5
Watercc_	
Santocel micropulverizedgrams_	1.4

Other inert materials such as fuller's earth and kieselguhr may be incorporated in liquid compositions of the type described above and they are preferably added in the ratio of about 1 part, or less, of the added material to 25 parts of the liquid composition.

When the film unit of the type described in connection with the drawing is used, the photosensitive layer 11 is exposed to actinic light either through the transparent base layer 10 or, if the base layer be opaque, the photosensitive layer may be exposed by moving either the photosensitive layer 11 or the image-carrying layer 12 and exposing the photosensitive layer directly without any of the light passing through any of the layers of the film unit.

The composite film unit is then processed by the application of a mechanical stress to the film unit for the purpose of releasing the liquid composition from the container 13 and spreading this liquid composition in a uniform thin film between the photosensitive layer !! and the image-carrying layer 12. The developer in the liquid composition develops the exposed photosensitive material and the silver halide solvent forms soluble image-forming complexes with the unexposed and undeveloped photosensitive material. Meanwhile, the film-forming material is forming a dimensionally stable image-receiving layer which preferably adheres to the imagecarrying layer. The image-forming complexes are transferred to this image-receiving layer where they are developed to a positive image by unused developer in the liquid composition.

The added inert material makes the formed film more or less discontinuous and thereby imparts to the formed film a greater resistance to cracking. Since the inert substance, such as Santocel, has a low refractive index, and imparts to the formed film a more or less rough surface, this surface has an excellent matte finish.

While the preferred liquid composition described above includes all or most of the active materials for forming the positive image, this requirement is not essential and one or more of the materials in the liquid may be included in solid form in the film unit in position to be dissolved by the liquid as it is spread through the film unit.

Since certain changes may be made in the above product and 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 limited sense.

What is claimed is:

A photographic product for forming transfer prints comprising a rupturable container holding a liquid, and a sheet support on which said container is mounted, said sheet support providing a spreading surface having a liquid-receiving area adjacent said container onto which said liquid is spreadable directly from said container, the liquid in the container comprising a silver halide developer, a solvent including water

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for said developer, a water-soluble silver halide solvent, a water-soluble film-forming plastic in solution and a water-insoluble finely comminuted solid substance chemically inert to the contents of said liquid in suspension, said finely 5 comminuted substance having a low refractive index, the container contents, when spread on said liquid-receiving area, being sufficient in amount and capable of forming a transfer print of a latent image contained in an area of silver 10 halide emulsion equivalent to said liquid-receiving area, said finely comminuted substance imparting to the solid plastic film that is obtained upon the drying of the liquid a matte surface and a greater resistance to cracking.

2. The product of claim 1 wherein the finely comminuted substance is silica aerogel.

3. The product of claim 1 wherein the finely comminuted substance is diatomaceous earth.

4. The product of claim 1 wherein the finely 20 comminuted substance is wood flour.

5. A photographic processing composition for forming transfer prints of latent images contained in silver halide emulsions, which composition comprises a silver halide developer, a sol- 25 vent including water for said developer, an alkali, a water-soluble silver halide solvent, a watersoluble film-forming plastic, said plastic forming a solid film upon removal of the liquid content of said composition, and a water-insoluble finely 30 comminuted solid substance chemically inert to the developer, alkali, silver halide solvent and plastic, said composition, when spread in a thin layer between a photosensitive silver halide emulsion containing a latent image and a print- 35 receiving layer, being capable of forming a transfer print of said latent image and of forming a solid film of said plastic throughout the spread area when the liquid content of the composition has been absorbed and evaporated therefrom, said 40 finely comminuted substance imparting a matte surface to said film and increasing the resistance thereof to cracking.

6. The composition of claim 5 wherein the finely comminuted substance is silica aerogel.

7. The composition of claim 5 wherein the finely comminuted substance is diatomaceous earth.

8. The composition of claim 5 wherein the finely comminuted substance is wood flour.

9. In a method of forming transfer prints of a latent image contained in a predetermined area of a silver halide layer of a photosensitive sheet material wherein a viscous liquid processing agent, containing all of the liquid for effecting the formation of the transfer print and also containing a solid film-forming colloid, is spread in a layer between said photosensitive sheet material and another sheet material, the liquid from said processing agent being absorbed by said photosensitive sheet material and during absorption distributing to said photosensitive layer photo-

graphic material, including a silver halide developer, for forming a transfer print of said latent image and wherein the absorption of the liquid from the layer of processing agent increases the concentration of the solid film-forming colloid between said sheet materials and produces between said sheet materials a coating of said colloid for receiving part at least of said transfer print, said colloid normally solidifying to form a solid film having a glossy surface, the improvement in said method which comprises the step of dispersing in the liquid processing agent, prior to the solidification of its colloid, a finely comminuted solid substance relatively insoluble and inert in the processing agent and having a low refractive index, said substance imparting a matte surface to the solid film formed from the colloid and increasing the resistance of said film to cracking.

10. The method of claim 9 wherein the finely comminuted substance is dispersed in the processing agent prior to the spreading thereof.

11. The method of claim 10 wherein the photographic material for forming the transfer print includes a silver halide solvent as well as the silver halide developer.

12. The method of claim 11 wherein the silver halide developer and the silver halide solvent are contained in the liquid processing agent prior to the spreading thereof.

13. The method of claim 9 wherein the finely comminuted substance is silica aerogel.

14. The method of claim 9 wherein the finely comminuted substance is diatomaceous earth.

15. The method of claim 9 wherein the finely comminuted substance is wood flour.

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