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PHOTOGRAPHIC PRODUCTS AND PROCESSES

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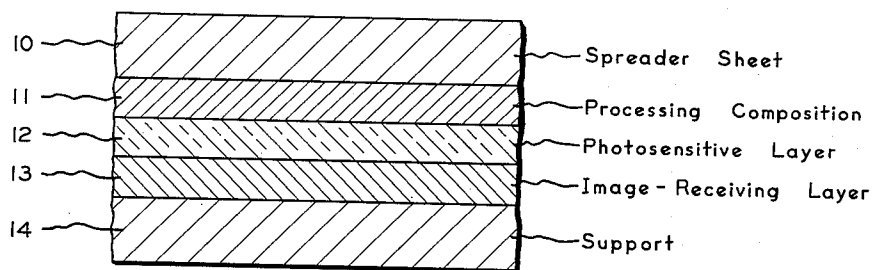


FIG. 1

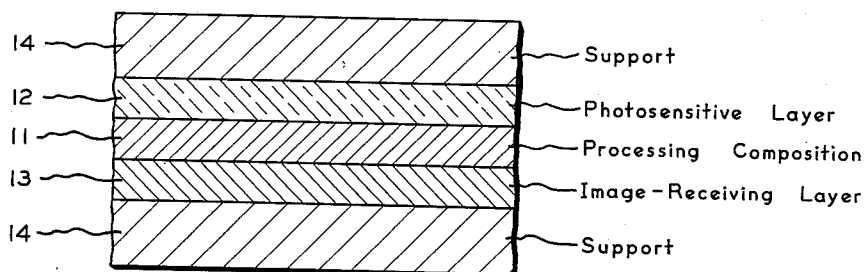


FIG. 2

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1

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PHOTOGRAPHIC PRODUCTS AND PROCESSES
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2 Claims. (Cl. 96-63)

This invention relates to photography and, more particularly, to novel photographic diffusion-transfer reversal processes and products for utilization therein.

In photographic diffusion-transfer reversal processes a latent image in a silver halide emulsion is developed and almost concurrently with such development a soluble silver complex is obtained by reaction of a silver halide solvent with the undeveloped silver halide of said emulsion. This complex is transferred in solution from the emulsion to a suitable print-receiving layer and the silver thereof is there precipitated to form the desired positive print in silver.

It is a primary object of the present invention to provide novel photographic products and processes whereby improved control of the transfer of image-forming components to a superposed image-receiving layer may be obtained.

A further object of the present invention is to provide photosensitive silver halide emulsions having incorporated therein integral matrices which provide structural stability sufficient to maintain said emulsions' physical integrity intact during processing.

A still further object of the present invention is to provide self-sustaining photosensitive silver halide gelatin emulsions.

Other objects of the present 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, and the product possessing the features, properties and relation of elements 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 a diagrammatic enlarged cross-sectional view illustrating the association of elements during one stage of the performance of a transfer process and showing, as one of the elements, an embodiment of the novel photosensitive elements of the present invention, the thickness of the various strata being exaggerated; and

FIG. 2 is a view similar to that of FIGURE 1 illustrating the association of elements during one stage of the performance of another transfer process and showing, as one of the elements, an embodiment of the novel photosensitive elements of the present invention.

The present invention comprehends improved processes and products of the type whereby a positive print is obtained in a single step by suitably treating an exposed silver halide emulsion containing a latent image with a processing composition. In one embodiment, the processing liquid is in a viscous condition and is spread in a liquid film between the photosensitive element comprising the silver halide emulsion and the print-receiving element comprising, preferably, a suitable silver precipitating layer. The processing composition effects development of the latent image in the emulsion and substantially contemporaneously therewith forms a soluble silver complex, for example, a thiosulfate or thiocyanate, with undeveloped silver halide. This soluble silver complex is, at least in part, transported in the direction of the print-

2

receiving element and the silver thereof is largely precipitated in the silver precipitating layer of said element to form therein a positive image in silver.

It has now been discovered that the aforementioned diffusion-transfer reversal processes may be substantially improved by the addition of deacetylated chitin to the photosensitive silver halide emulsion.

The term "deacetylated chitin" as utilized herein is intended to signify the product prepared by removing in whole or in part the acetyl groups from the polymeric acetamido derivative of a carbohydrate technically designated as chitin. It is also intended to include any other product substantially identical therewith, as for example, where such product is produced synthetically. The preparation of deacetylated chitin is well known in the art; see, for example, U.S. Patent No. 2,040,879, issued to G. W. Rigby on May 19, 1936.

The addition of deacetylated chitin to a photosensitive emulsion, preferably to a photosensitive silver halide gelatin emulsion, provides, when said emulsion is contacted with alkali, as for example, an alkaline photographic processing composition, a water-insoluble, substantially self-sustaining matrix. The deacetylated chitin matrix serves to maintain the wet photosensitive gelatin emulsion firm and undisturbed throughout processing operations, especially, when said processing operations take place at temperatures higher than normal. Where desirable, the concentration of deacetylated chitin disposed in the photosensitive silver halide gelatin emulsion may be of sufficient magnitude as to provide an integral single-layer element exhibiting sufficient internal support, subsequent to alkali contact, to be self-supporting, without requiring one or more separate supporting layers subsequent to said alkali contact. For example, according to the procedure subsequently described in regard to FIG. 1, the photosensitive emulsion may be temporarily affixed to a suitable image-receiving layer such that, subsequent to processing, the emulsion may be dissociated from the image-receiving layer to provide a single-stratum negative element exhibiting inherent structural stability. The separated emulsion layer may be mounted on another support, if desired. It must be noted that photosensitive elements of the present invention exhibit such substantial structural integrity during and subsequent to diffusion-transfer reversal processing in contradistinction to the previously known photosensitive emulsions. Addition of a sufficient amount of deacetylated chitin facilitates the utilization of a photosensitive silver halide gelatin emulsion, of a diffusion-transfer reversal process, subsequent to substantial exhaustive removal of unexposed silver halide, as a suitable negative for the production of prints by conventional photographic procedures.

The concentration of deacetylated chitin admixed with the photosensitive silver halide emulsion may be varied over a wide range according to the degree of rigidity desired, during and subsequent to processing, and the thickness and character of the photosensitive emulsion employed. It has been found that good results may be obtained by the use of about 10 to 35 cc. of a 5% solution of deacetylated chitin in 3% acetic acid per 50 cc. of a silver halide emulsion containing approximately 6% gelatin and 5% silver halide, that is, in the ratio, by weight, of about 1:1.7 to 1:6, inclusive, of deacetylated chitin to gelatin.

Although the following description is stated in terms of the preferred emulsion colloid binder, that is gelatin, it must be noted that the disclosure contained herein is also applicable to synthetic photosensitive silver halide binders, as for example, polyvinyl alcohol.

As illustrated in FIG. 1, one embodiment of the novel products of the present invention in the performance of

a transfer process comprises a spreader sheet 10, a layer 11 of relatively viscous processing agent, a photosensitive silver halide gelatin emulsion layer 12 containing deacetylated chitin, an image-receiving layer 13, preferably containing silver precipitating nuclei, such as the silver precipitating nuclei disclosed in U.S. Patent No. 2,698,237, issued December 28, 1954, to Edwin H. Land, and a suitable support layer 14. Support layer 14 may comprise an opaque material when a reflection print is desired or a transparent material when a transparency is desired.

Liquid layer 11 may be obtained by spreading a photographic processing composition, for example, in a manner disclosed in U.S. Patent No. 2,698,244, issued December 28, 1954, to Edwin H. Land. As disclosed in the last-mentioned U.S. patent, the liquid processing composition may be disposed in a rupturable container so positioned in regard to the appropriate surface, of the photosensitive silver halide emulsion, that upon compression by a spreader sheet 10, a substantially uniform layer 11 of processing composition is distributed over the surface, of said photosensitive emulsion 12, positioned distally in regard to image-receiving layer 13. The processing composition may be one of the film-forming processing compositions disclosed in U.S. Patent No. 2,543,181, issued February 27, 1951, to Edwin H. Land. It may comprise, for example, a developing agent such as hydroquinone, an alkali such as sodium hydroxide, a silver halide complexing agent such as sodium thiosulfate, and a high molecular weight film-forming thickening agent such as sodium carboxymethyl cellulose. All these materials are preferably in aqueous solution. These photographic agents are preferably contained in solution in the processing liquid prior to the spreading thereof as layer 11, but they may be in part or wholly added to the processing composition as it is spread between spreader sheet 10 and photosensitive silver halide emulsion 12, said agents being so located on or adjacent to the surface of said emulsion or spreader sheet as to be dissolved by or otherwise interacted with the liquid agent when the latter wets said surface.

In carrying out the aforementioned transfer process, the photosensitive silver halide emulsion 12 is exposed to a predetermined subject matter to form therein a latent image of said subject matter. A substantially uniform distribution of processing composition is distributed on the external surface of said emulsion, as for example, according to the previously described procedure. Processing composition reagents permeate into the photosensitive emulsion, contacting the deacetylated chitin disposed therein and substantially simultaneously therewith developing a latent image contained therein according to the point-to-point degree of exposure of said emulsion. Substantially contemporaneously with the development of the latent image, an imagewise distribution of soluble silver complex is formed from the unexposed silver halide within said emulsion. At least part of said silver complex, solubilized, is transferred, by imbibition, toward the print-receiving stratum 13 wherein said complex is reduced to elemental silver to provide a positive, reversed silver image of the latent image. Subsequent to substantial precipitative deposition of the positive silver image in image-receiving layer 13, dissociation of said layer 13 from the emulsion layer 12 may be effected.

The use of deacetylated chitin in a silver halide emulsion layer in a photographic embodiment similar to that shown in FIG. 1, whereby stripping of the silver halide emulsion layer from the image-receiving layer is facilitated, is illustrated in the following example.

Example 1

An image-receiving element of the type commercially available in Polaroid Land Picture Roll, type 42, com-

prising a support 14 and an image-receiving layer 13 containing silver precipitating nuclei, is coated with a photosensitive composition comprising:

	Cc.
5 Panchromatic-sensitized silver halide emulsion containing approximately 5% silver halide and 6% gelatin, by weight-----	50.0
Water -----	25.0
10 A solution of 5% high viscosity deacetylated chitin in 3% acetic acid-----	20.0
Pluronic L-44 (trade name of Wyandotte Chemicals Corp., Wyandotte, Michigan, for a nonionic polyoxypropylene polyoxyethylene condensate)-----	1.5

15 After drying, the photosensitive element is exposed and a processing composition of the type used in Polaroid Land Picture Roll, type 42, is spread between the photosensitive element and a superposed spreading sheet. After an imbibition period of approximately one minute, the spreading sheet is separated from the photosensitive element. In contradistinction to the heretofore known procedures, the emulsion layer is found to be sufficiently self-supporting to be simply pulled off without washing or using a stripping layer between the emulsion layer and the image-receiving layer. This increase in rigidity is a result of the inclusion of the deacetylated chitin.

If desired, the photosensitive silver halide gelatin emulsion layer 12 may be subjected to cleansing subsequent to dissociation, as for example, by washing with water. In addition, the inclusion of deacetylated chitin as a constituent component of photosensitive silver halide gelatin emulsion layer 12 provides substantial abrasion-resistant properties to said photosensitive emulsion layer 12 sufficient to substantially protect layer 12 from subsequent laceration and resultant degradation of the negative image.

FIG. 2 illustrates one embodiment of the novel photosensitive silver halide emulsions of the present invention in the performance of another transfer process, which comprises a support layer 14, a photosensitive silver halide gelatin emulsion layer 12 containing deacetylated chitin, a layer 11 of the previously noted viscous film-forming processing composition and an image-receiving layer 13, preferably containing silver precipitating nuclei.

As previously stated, layer 11 of processing composition may be distributed in a substantially uniform manner between photosensitive emulsion layer 12 and image-receiving layer 13, which may be accomplished in accordance with the procedures disclosed in the aforementioned U.S. Patent No. 2,543,181. For example, one or more rupturable containers may be attached to either photosensitive emulsion layer 12 and/or image-receiving layer 13 such that upon superposition of the respective layers 12 and 13 said container or containers are so positioned as to be capable, upon rupture, of releasing their contents in a substantially uniform layer between and in contact with an opposed surface of each of said layers. Rupture of the container or containers and spreading the contents thereof may be accomplished, for example, by compression between a pair of opposed, suitably gapped rollers.

In carrying out the aforementioned transfer process, the photosensitive silver halide emulsion 12 is exposed to a predetermined subject matter to form therein a latent image of said subject matter. The exposed emulsion is superposed on the image-receiving element 13 and the photographic processing composition 11 is spread between the opposed surfaces of said photosensitive emulsion 12 and said image-receiving element 13. Reagents permeate into the photosensitive emulsion 12, developing the latent image contained therein and forming a soluble silver complex from the unexposed silver halide. Soluble silver complex in solution in the reagent is transported from photosensitive emulsion layer 12, at least in part, by imbibition, toward print-receiving stratum 13 wherein the

complex is reduced to silver to provide the desired reversed, positive image. The lamination formed by the spreading of processing composition layer 11 between photosensitive emulsion 12 and print-receiving element 13 is kept intact for approximately 1/2 to 1 1/2 minutes, preferably 1 minute, and at the termination of this time interval print-receiving layer 13 is dissociated from emulsion 12, as for example, by stripping.

The utilization of a photosensitive silver halide gelatin emulsion containing deacetylated chitin provides an emulsion exhibiting substantially more adhesive bonding capacity between the surface of said emulsion and a film-forming processing composition containing an acidic film-forming agent, as for example, sodium carboxymethyl cellulose, than the adhesive bonding capacity exhibited between the image-receiving element and said processing composition. Thus, when print-receiving layer 13 is stripped from photosensitive emulsion 12 at the completion of processing, the film-forming processing composition remains substantially bonded to the photosensitive emulsion layer 12, thereby preventing the adherence of residual processing composition to print-receiving layer 13, which might result in possible stain formation and/or image degradation due in part to the constituent components thereof.

Where desired, removal of an acidic film-former containing processing composition adhering to the photosensitive element may be effected, as for example, by providing a suitable stripping layer, for example a suitable polymeric stratum, positioned between said element and said processing composition in accordance with known procedures, such that adhesive contact between the acidic film-former and the deacetylated chitin contained in the emulsion is avoided.

As an additional illustrative example of a photosensitive silver halide gelatin emulsion containing deacetylated chitin, mention may be made of the following:

Example 2

Dehydrated emulsion (Du Pont DH)-----grams--	50
Water -----cc--	50
5% deacetylated chitin (high viscosity) in 3% acetic acid solution -----cc--	15

Since certain changes in carrying out the above processes, and certain modifications in the products which embody the invention, may be made without departing from its scope, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative only and not in a limiting sense.

What is claimed is:

1. As a product, a photosensitive silver halide gelatin emulsion containing deacetylated chitin wherein the ratio, by weight, of deacetylated chitin to gelatin is from 1:1.7 to 1:6, inclusive.

2. In a photographic process, the step which comprises developing a latent image contained in an exposed photosensitive element, said element comprising a silver halide gelatin emulsion containing deacetylated chitin wherein the ratio, by weight, of deacetylated chitin to gelatin is from 1:1.7 to 1:6, inclusive, with an alkaline processing composition, for a time sufficient to develop said latent image to a silver image.

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