May 11, 1971 E. W. MILLER ET AL 3,578,450

DIFFUSION TRANSFER PRODUCTION OF REFLECTION POSITIVE WITH ALUMINUM STEARATE IN RECEPTIVE STRATUM

Filed April 22, 1968

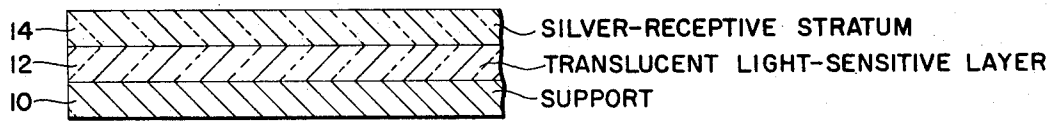


FIG. 1

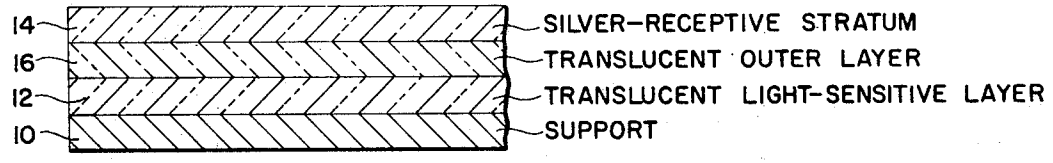


FIG. 2

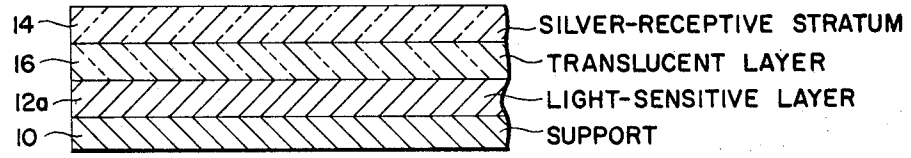


FIG. 3

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DIFFUSION TRANSFER PRODUCTION OF REFLECTION POSITIVE WITH ALUMINUM STEARATE IN RECEPTIVE STRATUM

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U.S. Cl. 96—29 12 Claims

ABSTRACT OF THE DISCLOSURE

Photographic products for forming a composite print viewable as a positive silver image, including a silver halide emulsion layer, an opacifying material in the emulsion layer and/or in an overlying layer, and an outer layer comprising a silver-receptive stratum, wherein the silver-receptive stratum includes a reagent comprising essentially aluminum stearate.

BACKGROUND OF THE INVENTION

The copending application of Edwin H. Land, Ser. No. 519,995 and the copending application of Edwin H. Land and Leonard C. Farney, Ser. No. 519,884, both filed Jan. 11, 1966, describe and claim photographic products and processes for forming a composite print comprising a negative image and a positive image, the print being viewable as a positive reflection print without separation of the respective images.

As is disclosed in these applications, a photographic film assembly including a layer containing a light opacity-providing material is exposed, e.g., to a light source on the same side of the support for the film assembly as the layer of opacity-providing material, and is then processed to form a negative image and a positive transfer image in a stratum situated above the layer of opacity-providing material. This material is present in an amount sufficient for masking effectively the negative image but not in an amount sufficient to preclude photoexposure of the light-sensitive material in the film assembly, so that there is formed a composite print which contains both a negative and a positive image but which is viewable by reflection as a positive reproduction of the original subject matter. The opacifying material further serves to provide the background for viewing the print by reflection.

In application Ser. No. 519,995, the layer of opacifying material is situated over a layer containing a light-sensitive silver halide emulsion; while in application Ser. No. 519,884, the opacifying material is situated in the same layer as the emulsion and may also be present in a second layer over the layer containing the silver halide emulsion. A silver-receptive stratum comprising a suitable matrix containing silver-precipitating nuclei may be provided over the opacifying material in the products contemplated by these copending applications.

In preparing the composite print, the outer surface of the silver-receptive stratum of the exposed element is contacted with an aqueous medium which may contain an alkaline material, a silver halide developing agent and a silver halide solvent, and this aqueous medium diffuses through to the silver halide emulsion layer to develop the negative image and in known manner to form an imagewise distribution of a soluble silver complex which is transferred, at least in part, by diffusion, to the silver-receptive stratum where it is reduced to provide a positive silver transfer image. The above-named ingredients may be contained initially in the aqueous medium, or in lieu thereof, any or all of them may be contained initially in one of the layers of the film unit, in

which event a solution of the same is obtained upon permeation of the aqueous medium. The aqueous medium may also include other reagents performing specific desired functions, e.g., preservatives, antifoggants, etc. and may also include a viscous film-forming reagent.

The aforementioned procedures are of particular use in the field of document duplication and they may be employed in conjunction with suitable apparatus for providing one or more copies of the original in a rapid and efficient manner.

The copending application of Leonard C. Farney and Richard Haberlin Ser. No. 723,002, filed concurrently, describes and claims certain improvements in the aforementioned film units wherein a macroscopic pigment is incorporated into the silver-receptive stratum. The inclusion of this pigment has been found to provide certain unexpected advantages, chief of which are: (1) altering the tone of the positive image; (2) faster absorption of processing liquid: (3) less staining of the highlights; and (4) more rapid development.

The present invention is somewhat related to the invention described and claimed in the last-named copending application in that it contemplates the addition to the silver-receptive stratum of a reagent which provides significant new advantages in addition to certain of those described above.

SUMMARY OF THE INVENTION

It has been found, quite surprisingly, that if aluminum stearate is included in the silver-receptive stratum of the above-mentioned film units, the resulting film unit exhibits markedly superior stability against heat and/or humidity, i.e., has a greater shelf life in a hot or humid environment than the film units not containing aluminum stearate, and that a composite print obtained from such a film unit has greater stability against degradative forces such as heat, humidity and the presence of sulfur. Moreover, the absorption rate of processing fluid is materially accelerated.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a partially schematic, partially enlarged fragmentary sectional view illustrating one film unit to which this invention is directed;

FIG. 2 is a similar view of another film unit; and

FIG. 3 is a similar view of still another film unit.

DESCRIPTION OF PREFERRED EMBODIMENT

In the preferred embodiment, the light-sensitive emulsion layer includes an opacifying material; the image-receiving layer comprises a gelatin matrix or a mixture of gelatin and colloidal silica, the receiving layer further including aluminum stearate and silver precipitating nuclei.

As was mentioned previously, this invention relates to novel products and processes for preparing a composite print viewable as a positive reflection print and, more particularly, to photographic products and processes such as are described and claimed in the aforementioned copending applications Ser. Nos. 519,995 and 519,884 wherein aluminum stearate is included in the silver-receptive stratum.

A primary object of this invention, therefore, is to provide novel products and processes of the foregoing description.

A further object is to provide novel products including a light-sensitive silver halide emulsion, an opacifying material in the same or an overlying layer, and an outer silver-receptive stratum including aluminum stearate.

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, and the product possessing the features, properties and the 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.

The invention will be more readily understood by reference to the accompanying drawing.

The photographic products to which this invention is directed include a light-sensitive silver halide emulsion layer, a layer of opacity-providing material which may be in the same layer as the emulsion, in an overlying layer, or both, and an outer silver-receptive stratum including silver precipitating nuclei providing a vigorous silver precipitating environment for reduction of a soluble silver complex transferred thereto to image silver.

In the embodiment shown in FIG. 1, the film unit comprises a support **10**, preferably opaque, having thereon a layer **12** including a light-sensitive silver halide emulsion and an opacifying material, and a silver-receptive stratum **14**.

In the embodiment shown in FIG. 2, an additional layer **16** of opacifying material is provided between layer **12** and stratum **14**.

The products shown in FIGS. 1 and 2 are described and claimed in the aforementioned copending application Ser. No. 519,884.

In the embodiment shown in FIG. 3, the support **10** contains a light-sensitive silver halide emulsion layer **12***a*, and the opacyifying material is contained in a layer **16** situated between layer **12***a* and silver-receptive stratum **14**. This last-named embodiment is described and claimed in the aforementioned copending application Ser. No. 519,995.

In all of these embodiments, the film unit is selectively exposed, e.g., through the outer stratum **14**, to provide a developable or latent image in the photosensitive layer. At some time thereafter, the element is developed by contacting the surface of stratum **14** with an aqueous medium which either contains the necessary ingredients for development or forms a solution of these ingredients after contact. In other words, the aqueous medium may comprise an aqueous processing composition including an alkaline material, a silver halide developing agent and a silver halide solvent or, in lieu thereof, any or all of these ingredients may be contained initially in one or more layers of the film unit. In either event, the aqueous medium permeates through stratum **14** (and any additional intermediate layers) to the photosensitive layer (**12** or **12***a*) to initiate development. In known manner, exposed and developable silver halide is reduced to form a negative image while an imagewise distribution of a soluble silver complex is formed in terms of unexposed or undeveloped areas of the emulsion. This imagewise distribution is transferred, at least in part, to stratum **14** where it is reduced to image silver to impart thereto a positive silver transfer image. The resulting composite print comprising the developed negative image and the overlying positive silver transfer image is viewable without separation as a positive silver reflection print, owing to the ability of the opacifying material to mask effectively the negative image.

Support **10** may be made of any of the materials heretofore used for such purposes, e.g., paper, a cellulose ester, etc. and is preferably opaque.

Layer **12** includes a light-sensitive silver halide emulsion, preferably a gelatino silver halide emulsion which upon development will form a negative silver image of relatively low density or covering power. It may, for example, be a mixed halide emulsion, e.g., a silver

iodobromide or chloroiodobromide emulsion, which possesses a relatively high speed as compared, for example, with the speed of silver chloride emulsions.

The opacifying material, which is preferably colorless or white, is at least permeable to, but substantially insoluble in the aqueous processing medium. As examples of useful opacifying materials, mention may be made of finely divided titanium dioxide, calcium carbonate, magnesium oxide, barium sulfate, etc. or mixtures of such materials.

Layer **16** of the embodiments shown in FIGS. 2 and 3 may comprise one or more of the aforementioned pigments dispersed in a suitable matrix such as gelatin.

The silver-receptive stratum provides a vigorous silver-precipitating environment and comprises, in addition to the aluminum stearate of this invention, at least one of the known silver-precipitating agents dispersed in a continuous vehicle or matrix. This vehicle or matrix may comprise a colloidal material such as gelatin, sodium carboxymethylcellulose, a siliceous material, e.g., one containing, in colloidal condition, oxides of silicon, particularly those in the form of silica acids, such as "Syton" (trademark of Monsanto Chemical Co. for a milky-white, stable 15% colloidal dispersion of silica in water); "Santocel" (trademark of Monsanto Chemical Co. for a light-weight porous silica aerogel from which the water has been removed by a process that does not destroy the original gel structure); or "Ludox" (trademark of E. I. du Pont de Nemours & Co. for an aqueous colloidal sol containing approximately 30% SiO_2 with less than 0.5% Na_2O as stabilizer), etc., or a mixture of such materials. One particularly useful carrier or matrix comprises a mixture of a colloidal silica such as those named above and gelatin, the ratio of gel to silica being on the order of from about 1:1 to about 1:10, a preferred range being on the order of from about 1:1 to about 1:5.

As examples of silver-precipitating nuclei, mention may be made of those heretofore known in the art, e.g., heavy metal sulfide and/or selenides, the colloidal noble metals, organic thio compounds, etc.

The layers or strata described above and shown in the illustrative drawing may also contain additional ingredients performing specific desired functions, as will be appreciated. For example, any or all of the ingredients essential to development may be contained in one or more of these layers, as heretofore noted.

The aluminum stearate included in the silver-receptive stratum need not be pure and most commercially available products in fact contain a certain percentage of stearic acid, e.g., from 2–14% acid. One such stearate is Aluminum Stearate No. 16, commercially available from Witco Chemical Co., understood to contain about 10–14% stearic acid, particle size about 96% through 200 mesh screen.

The amount of aluminum stearate employed may vary over a wide range and the invention accordingly contemplates use of an effective amount of stearate. As used herein and in the appended claims, the term "effective amount" denotes an amount sufficient to achieve beneficial results.

In a typical silver-receptive stratum, the aluminum stearate (or stearate-acid mixture) is present at a coverage on the order of from about 5–175 mgm. per square foot of surface area, from 10–100 mgm. per square foot being a preferred range. Such a stratum may contain from about 50–250 mgm. per square foot of other solids comprising the stratum, e.g., matrix, silver-precipitating nuclei, etc. In addition, it may contain a macroscopic pigment, as is described and claimed in the aforementioned copending application Ser. No. 723,002.

The following examples show by way of illustration and not by way of limitation the practice of the invention.

EXAMPLE 1

A film unit as shown in FIG. 1 was prepared in the manner disclosed in the aforementioned application Ser. No.

519,884. Layer **12** included a gelatino silver chloroiodobromide emulsion and titanium dioxide. Silver-receptive stratum **14** comprised of a silver-precipitating environment containing colloidal gold dispersed in a matrix of gelatin and colloidal silica, the ratio of gelatin to colloidal silica being about 1:3. Silver-receptive stratum **14** was applied over the translucent emulsion layer to provide a calculated coverage of 30 mgm. of gelatin and 90 mgm. of silica per square foot of surface area. This film unit was exposed and developed in the described manner to provide a composite print viewable as a positive silver reflection print, the tone of the positive image being characterized visually as black.

EXAMPLE 2

Example 1 was repeated, including in the silver-receptive stratum "Aluminum Stearate No. 16" at a calcuated coverage of about 77 mgm. per square foot of surface area.

EXAMPLE 3

The shelf (storage) life of film units prepared in the manner described in Examples 1 and 2 were compared by first storing the two for five days in an oven at 120° F. The units were then removed and employed to make positive images in the described manner, care being taken to maintain all exposing and processing conditions the same for control purposes. The resulting positive images were compared with those prepared in Examples 1 and 2. Comparing the prints obtained before and after stroage of the units it was readily observable that there was a significant loss of density, contrast and increase in D_{min} when the film unit of Example 1 is stored at these elevated temperatures; whereas little or no difference was observed with the unit containing the aluminum stearate. In one typical illustration comparing the quality of a print obtained from a film unit subjected to the above oven storage to one obtained from a like film unit which had not, with the film unit of Example 1 (no aluminum stearate) a loss of D_{max} from .84 to .74 was noted (approximately 12%) whereas with the aluminum stearate-containing film unit of Example 2, the loss was from .88 to .85, relatively insignificant. In addition, the toe region of the H and D curve of the first-named print became less sharp, losing contrast, the print exhibiting higher D_{mins}, whereas with the film unit containing aluminum stearate, no appreciable change was noted.

The foreging example demonstrates the significant improvement in stability of the film unit to elevated temperatures such as might occur in a truck, freight car, storage room, etc., when aluminum stearate is included in the silver-receptive stratum.

The following three examples together demonstrate the improvement in stability of a print obtained from a film unit of this invention.

EXAMPLE 4

Composite prints prepared in the manner described in Examples 1 and 2 were subjected to heat and humidity stability tests by storing them at 100° F. in an atmosphere of 80% relative humidity for 40 hours. The print obtained by the procedure of Example 1 (no stearate) showed noticeable yellowing, particularly in the highlight areas; whereas the print of Example 2 showed excellent stability. The difference was most noticeable to the eye.

EXAMPLE 5

The stability to sulfur was determined by suspending the respective prints prepared as in Examples 1 and 2 over an evaporating dish containing elemental sulfur in water for 16 hours at 140° F. thereby exposing them to sulfur vapor. Again, yellowing, particularly in the highlights, was readily observable in the print of Example 1; while no significant yellowing was noticeable with the print obtained from the film unit of this invention.

EXAMPLE 6

The tests of Examples 4 and 5 were combined by suspending the prints over the elemental sulfur at 140° F. in an atmosphere of 80% relative humidity for 16 hours, a severe stability test. The print of Example 1 yellowed most noticeably whereas the print of Example 2 exhibited a most pronounced increase in stability, yellowing only to a very slight extent.

According to the invention described and claimed in the aforementioned copending application Ser. No. 723,002, it was found that the absorption rate was materially increased by the addition to the silver-receptive stratum of a macroscopic pigment, e.g., titanium dioxide, calcium carbonate, etc. In other words, the addition of macroscopic pigment decreases the time required for a given amount of processing fluid to permeate through the surface of the silver-receptive stratum and, conversely, the amount absorbed in a given period of time is also increased.

A film unit containing aluminum stearate, namely a film unit as prepared in Example 2, was compared with film units in which the silver-receptive stratum contained calcium carbonate or titanium dioxide to determine whether the one containing stearate increased absorption at all and, if so, if it compared favorably with the pigment-containing film units which, as was shown in the aforementioned copending application, were superior in this respect to those which do not, e.g., a film unit as prepared in Example 1.

Quite surprisingly, the stearate-containing film unit was markedly superior to the above-noted pigmented film units.

The tests were conducted by determining the time required for a given weight of aqueous alkaline fluid to permeate an 8.5 x 11 inch film unit, the absorption time being determined by observation as the time required for the disappearance of surface gloss caused by application of the fluid to the surface of the silver-receptive stratum.

The amount of additive (pigment or stearate) per square foot of surface area and the results of these tests are as follows:

Additive to silver-receptive stratum	Amount (mgm./ft.²)	Absorption time	
		0.7 g.	0.6 g.
Aluminum stearate	77	5	3
Caldium carbonate	270	7	5
Titanium dioxide	77	10	7

Thus, for the amounts of aqueous alkaline liquid applied (0.7 g. and 0.6 g.), it was determined that the aluminum stearate increased absorption time faster than did calcium carbonate or titanium dioxide; whereas both of the latter pigments had previously been determined to increase absorption time over a film unit containing no pigment.

The increased absorption rate or, stated another way, the reduction in time required for the processing fluid to permeate through the silver-receptive stratum, provides certain significant advantages. The longer the liquid is on the surface of the unit during processing, the more tendency there is for staining of the highlight areas caused by aerial oxidation, particularly in the presence of elevated temperatures, e.g., the heating means for drying the print included in the exposing and developing apparatus disclosed in U.S. Pats. Nos. 3,282,153; 3,282,184; and 3,282,192. Hence the more rapid absorption rate eliminates or minimizes the tendency for stain.

Secondly, the more rapid absorption may materially increase the speed of positive image formation, thereby providing a positive silver image of a given desired density much more rapidly. Infrared silver development rate studies indicate that the presence of aluminum stearate does in fact speed up the initiation and rate of positive silver development.

Since certain changes may be made in the above product and process without departing from the scope of the in-

vention 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. In a photographic product for preparing a composite print viewable as a positive reflection print, said product comprising a layer containing a light-sensitive silver halide emulsion, a light opacity-providing material in said layer or in an overlying layer and a silver-receptive stratum including silver-precipitating nuclei dispersed in a continuous matrix, said light opacity-providing material being present in an amount sufficient for masking effectively a negative image formed in said emulsion layer by exposing said photographic product and developing said exposed product to form said negative image and a positive image in said silver-receptive stratum, whereby said composite print is viewable without separation as a positive silver reflection print; the improvement which comprises including in said silver-receptive stratum an effective amount of an additive consisting essentially aluminum stearate.

2. A product as defined in claim 1 wherein said additive comprises a major proportion of aluminum stearate and a minor amount of stearic acid.

3. A product as defined in claim 1 wherein said silver-receptive stratum contains from about 55 to about 425 mgm. of total solids per square foot of surface area and said additive is present in an amonut from about 5 to 175 mgm. per square foot of surface area.

4. In a photographic product for forming a composite print in which a positive image is formed in a stratum over a negative image, said composite print being viewable as a positive reflection print without separation of said two images, said product comprising a light-sensitive silver halide emulsion, said layer further including a light opacity-providing material, and a silver-receptive stratum above said emulsion layer, said opacity-providing material being present in an amount sufficient for masking effectively a silver image formed in said layer by exposing said photographic product and developing said exposed product to form said negative image in said layer and a positive transfer image in said silver-receptive stratum, the amount of said material being insufficient to preclude photoexposure of said silver halide, said material further being capable of providing a background for viewing said composite print by reflected light as a positive image; the improvement which comprises including in said silver-receptive stratum an effective amount of an additive consisting essentially aluminum stearate.

5. A product as defined in claim 4 wherein said additive comprises a major proportion of aluminum stearate and a minor amount of stearic acid.

6. A product as defined in claim 4 wherein said silver-receptive stratum comprises silver-precipitating nuclei dispersed in a continuous matrix comprising gelatin.

7. A product as defined in claim 4 wherein said silver-receptive stratum contains from about 55 to about 425 mgm. of total solids per square foot of surface area and said additive is present in an amount from about 5 to 175 mgm. per square foot of surface area.

8. In a photographic product for forming a composite print in which a positive image is formed in a stratum over a negative image, said composite print being viewable as a positive reflection print without separation of said two images, said product comprising a support having thereon a layer containing a light-sensitive silver halide

emulsion, said layer further including a light opacity-providing material, and a silver-receptive stratum above said emulsion layer, said silver-receptive stratum comprising silver-precipitating nuclei dispersed in a matrix of gelatin and colloidal silica, the ratio of gelatin to colloidal silica being from about 1:1 to 1:10, said opacity-providing material being present in an amount sufficient for masking effectively a silver image formed in said layer by exposing said photographic product and developing said exposed product to form said negative image in said layer and a positive transfer image in said silver-receptive stratum, the amount of said material being insufficient to preclude photoexposure of said silver halide, said material further being capable of providing a background for viewing said composite print by reflected light as a positive image; the improvement which comprises including in said silver-receptive stratum an effective amount of an additive consisting essentially of aluminum stearate.

9. A product as defined in claim 8 wherein said stratum contains from about 5 to about 175 mgm. of additive per square foot of surface area.

10. A product as defined in claim 9 wherein said additive is present in an amount sufficient to increase the shelf life of said product to a heated atmosphere and the stability of a positive print obtained therefrom to heat, humidity and the presence of sulfur.

11. A process for preparing a positive silver transfer image comprising exposing a product as defined in claim 1 to provide a developable image; applying an aqueous processing fluid to the surface of said exposed product; permeating said fluid through said silver-receptive stratum to said emulsion layer to develop said exposed emulsion and to form an imagewise distribution of a soluble silver complex in terms of unexposed areas of said emulsion; and transferring said imagewise distribution, at least in part, by diffusion, to said silver-receptive stratum where it is reduced to impart thereto a positive silver transfer image.

12. In a process wherein a photographic product including a layer containing a light-sensitive silver halide emulsion and a light opacity-providing material and an overlying silver-receptive stratum is exposed to form a developable image and said exposed product is developed by contacting the surface of said silver-receptive stratum with an aqueous fluid, said fluid permeating through said stratum to develop said image and to impart to said silver-receptive stratum a positive silver transfer image, said transfer image being viewable by reflected light, the improvement which comprises incorporating in said silver-receptive stratum before exposure of said product an additive consisting essentially of aluminum stearate in an amount sufficient to increase the stability of said image to heat, humidity and the presence of sulfur and to increase the absorption rate of said processing fluid through the surface of said stratum.

References Cited

UNITED STATES PATENTS

3,265,505 8/1966 Yudelson ---------- 96—29X

NORMAN G. TORCHIN, Primary Examiner

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U.S. Cl. X.R.

96—76