Fig. 1

Silver-receptive stratum
Translucent light-sensitive layer
Support

Fig. 2

Silver-receptive stratum
Translucent outer layer
Translucent light-sensitive layer
Support

Fig. 3

Silver-receptive stratum
Translucent layer
Light-sensitive layer
Support
DIFFUSION TRANSFER PRODUCTION OF REFLECTION POSITIVE WITH MACROSCOPIC PIGMENT IN RECEPTIVE STRATUM


Continuation of abandoned application Ser. No. 723,002, Apr. 22, 1968. This application Apr. 7, 1971, Ser. No. 132,081

Int. Cl. G03c 1/48, 5/54

U.S. Cl. 96—29 R

5 Claims

ABSTRACT OF THE DISCLOSURE

Photographic products for forming a composite print viewable as a positive silver image, including a silver halide material, 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 macroscopic pigment.

This application is a continuation of Ser. No. 723,002 filed Apr. 22, 1968, now abandoned.

BACKGROUND OF THE INVENTION

The copending application of Edwin H. Land, Ser. No. 519,995 was abandoned and the copending application of Edwin H. Land and Leonard C. Farney, Ser. No. 519,884, now abandoned, 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 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 as a reflection image 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 alkali halide, a silver halide developer 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.

In the practice of the invention it is, of course, most desirable that one obtain a composite print in which the positive image possesses the desired tone, clean highlight areas free of stain, and that the image be characterized as having good density and contrast. Image tone providing neutral, e.g., black or blue-black, is found by most to be preferable generally to brown or sepia images.

SUMMARY OF THE INVENTION

The present invention contemplates a novel silver-receptive stratum in the aforementioned products which includes silver precipitating nuclei contained in a suitable matrix and which further includes an effective amount of a macroscopic pigment. The macroscopic pigment tends to alter the tone of the transfer image, i.e., acts as a toning agent capable of providing a silver image of a more desirable tone, and provides further advantages including more rapid absorption of the processing fluid, less tendency for stain, less tendency for silver in the highlight areas, and more rapid development. The pigment so added may be inorganic or organic. Combinations of pigments are also contemplated. The pigment so added should be photographically innocuous, i.e., should not adversely affect the photographic system upon which image formation is predicated, nor should it affect adversely, at least to any appreciable extent, the shelf life of the film unit. Moreover, as will be apparent, it should be compatible with the contemplated color of background for viewing the print. In other words, where a white background is contemplated, the pigment should be substantially white.

BRIEF DESCRIPTION OF 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 a colloidal silica, the receiving layer further including silver precipitating nuclei and one or more macroscopic pigments. Other materials performing specific desired functions may also be included in this layer.

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 Serial Nos. 519,995 and 519,884 wherein a macroscopic pigment 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 ma...
3,705,804

**Material in the same or an overlying layer, and an outer silver-receptive stratum including a macroscopic pigment.**

Still another object is to provide novel products of this description wherein the silver receptive stratum includes a macroscopic pigment or mixture of pigments for altering the tone of the silver transfer image formed in or on this stratum to a more desired tone.

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 the macroscopic pigmented 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 to form a visible silver image.

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. 159,824.

In the embodiment shown in FIG. 3, the support 10 contains a light-sensitive silver halide emulsion layer 12a, and the opacifying material is contained in a layer 16 situated between layer 12a 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 support 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 alkali, 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 12a) 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 reflection 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 gelatin 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 vigorous silver-precipitating environment and comprises, in addition to the macroscopic pigment 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 carboxymethylcellosolve, a silicate 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 lightweight 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<sub>2</sub> with less than 0.5% Na<sub>2</sub>O 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.

As examples of silver-precipitating nuclei, mention may be made of those heretofore known in the art, e.g., heavy metal sulfides 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 macroscopic pigments contemplated by this invention may be selected from a wide list of known material, e.g., titanium dioxide, calcium carbonate, barium sulfate, Wollastonite (CaSiO<sub>3</sub>), talc [Mg₃Si₄O₁₅(OH)₄]Si<sub>2</sub> clays such as kaolinite (an aluminum silicate clay), and the like. Preferably are the white mineral pigments, e.g., the oxides, silicates, carbonates, etc. As used herein and in the appended claims, the term "macroscopic" is employed in its ordinary meaning to denote pigments having a particle size visible to the naked eye as distinguished from microscopic or colloidal substances, e.g., the colloidal silver halide of the herefore noted layer, the ratio of the matrix or vehicle, for the precipitating nuclei in this stratum. These macroscopic pigments preferably have a mean particle size from about 0.1μ to about 10μ.

As was mentioned previously, the matrix for silver-receptive stratum 14 preferably comprises gelatin or a mixture of gelatin and another substance, e.g., a siliceous material. In such a layer, the ratio of the macroscopic material to be on the order of from about 1:1 to 1:10, a preferred range being on the order of from about 1:1 to about 1:5. The amount of macroscopic pigment which
may be included in the practice of this invention should have a lower limit calculated to achieve the desired results, the upper limit being determined preferentially at just below the point at which staining or flakes of the layer is caused by having too much pigment. The ratio of pigment to gel in the preferential strata is from about 2:1 to about 12:1, particularly good results being observed with ratios of from about 2:1 to about 8:1.

In a typical product contemplated by this invention, stratum 14 may contain, for example, from about 90 to 850 mg. of total solids (dry weight) per square foot of surface area. The macromolecular pigments in the stratum may be of the order of from about 40 to about 600 mgm. per square foot. In addition, the silver-receptive stratum may contain effective amounts of an additive comprising essentially aluminum stearate, as is described and claimed in the copending application of Edgar W. Miller and Harry A. Smith, Ser. No. 723,003, filed concurrently, now Pat No. 3,578,450.

Prior to the present invention a skilled worker desiring to alter the tone of the silver transfer image would have contemplated selection of one of the known toning agents for this purpose. It has been found quite unexpectedly that the addition of the macroscopic pigment functions as a toning agent, thereby providing a novel means of altering the tone of the silver transfer image to a more desired tone. By way of example, calcium carbonate tends to make the image more brown; while titanium dioxide tends to make it more blue. Mixtures of the two give intermediate tones, depending, of course, upon the ratios employed.

In addition to functioning as a toning agent, the pigment materially increases the absorption rate at which the processing liquid permeates the surface of the film unit. This in turn 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 of the apparatus for exposing and developing the film units 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 rate has been shown by infrared silver development rate analyses to increase the rate of negative image formation which in turn minimizes the unwanted transfer of silver halide from exposed areas to increase the D_max and lower the D_A or contrast. In other words, in a silver diffusion transfer system, it is more desirable that exposed and developable silver halide be reduced before it can be dissolved by the solvent-completing agent to form a soluble silver complex which can transfer to the silver-receptive stratum to give unwanted image silver in the highlights.

Thirdly, these studies show that the more rapid absorption materially increases the speed of positive image formation, thereby providing a positive silver image of a given density much more rapidly. Apart from the broad general photographic applications of these units of this invention, if one contemplates documentary duplication apparatus by which one or more copies of successive documents are desired, the advantage of reducing the time required for the unit to be in the processing apparatus will be readily apparent.

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

Example 1

A film unit as shown in Fig. 1 was prepared in the manner disclosed in the aforementioned Ser. No. 5,384, Layer 12 included a gelatin no silver chloro-iodobromide emulsion and titanium dioxide. Silver-receptive stratum 14 comprised 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

The procedure of Example 1 was repeated several times, each time adding a given amount of calcium carbonate to the silver-receptive stratum coatings, the amounts of calcium carbonate added being such as to give the following calculated coverage per square foot of surface area: (1) 45 mgm.; (2) 77 mgm.; (3) 170 mgm.; and (4) 270 mgm. Exposure and development in the same manner as Example 1 provided composite prints of comparable quality. The tone of the positive image in each instance was altered from the black of Example 1 to a brownish black.

Example 3

Example 1 was repeated, adding titanium dioxide to the silver-receptive stratum at a calculated coverage of 77 mgm. per square foot. The positive image of the resulting composite print was a bluish-black in tone.

Example 4

Example 3 was repeated, changing the concentration of titanium dioxide to a calculated coverage of 225 mgm. per square foot. The resulting positive image was of bluish tone.

Example 5

Example 1 was repeated, adding to the silver-receptive stratum calcium carbonate at a calculated coverage of 127.5 mgm. per square foot and titanium dioxide at a calculated coverage of 42.5 mgm. per square foot. The resulting positive image was black in tone, being somewhat more neutral in tone than the image prepared in Example 1.

Example 6

Example 5 was repeated, varying the amounts to 97.5 mgm. per square foot of calcium carbonate and 77.5 mgm. per square foot of titanium dioxide. The positive image was again blue-black in tone.

Example 7

Example 1 was repeated, adding to the silver-receptive stratum kaolinite clay at a calculated coverage of 87.5 mgm. per square foot and 15.5 mgm. per square foot of titanium dioxide. The resulting positive image was brown in tone.

Example 8

Example 1 was repeated, adding to the silver-receptive stratum 77 mgm. per square foot of Wollastonite. The resulting positive image was brown-black.

Example 9

Example 1 was repeated, adding talc at a calculated coverage of 270 mgm. per square foot. The resulting positive image was brown-black.

As was mentioned previously, the presence of the pigment also materially reduces the absorption time, i.e., the time it takes for a given quantity of an aqueous alkaline medium applied thereover to impregnate or permeate through the outer surface of the film unit.

To illustrate this advantage of the present invention, the absorption time with film units with or without pigment in the silver-receptive stratum were measured, employing in each instance a given amount of alkaline medium, namely 0.8 g. of such a medium applied over the surface of an 8.5 x 11 inch film unit. The absorption time was measured as the time from application for the
disappearance of surface gloss on the film unit, as determined visually. With no added pigment, with a typical film unit of the type previously described and illustrated in FIG. 1, the absorption time was on the order of 14 seconds or more. By incorporating calcium carbonate in the silver-receptive stratum at a calculated coverage of 75 mgm. per square foot of surface area, the absorption time was cut to about 9 seconds. Greater amounts of pigments gave still greater reductions in absorption time. For example, the addition of 300 mgm. per square foot reduced the absorption time to 6–7 seconds; while 600 mgm. per square foot reduced it to about two seconds. Titanium dioxide was found not to reduce the absorption time quite as much as did calcium carbonate. Yet, incorporation of titanium dioxide at a calculated coverage of about 75 mgm. per square foot of surface area reduced the absorption time to about 11 seconds, whereas greater amounts again gave greater reductions, e.g., 300 mgm. per square foot reduced the absorption time to about 8 seconds. Conversely, as would be anticipated by the foregoing discussion and data, the amount of aqueous alkaline medium absorbed in a given period of time was also markedly increased.

Infrared silver development rate studies were also conducted to determine the amount of reduced silver in the positive and in the negative images at several time intervals during development. These studies gave dramatic evidence of the more rapid development obtained as a function of the addition of pigment. For example, in a typical film unit of FIG. 1 containing no added pigment, it took about six seconds before positive silver formation could be observed, about 50% of the maximum negative silver density being obtained in about 2.1 seconds. With the addition of calcium carbonate at a calculated coverage of about 270 mgm. per square foot, positive silver formation was noted in three seconds, 50% of the negative silver density being obtained in about 6/20 second. In the first film unit with no added pigment, positive silver build-up was still climbing toward the maximum density levels at 15 seconds, whereas with the second film unit containing the calcium carbonate, the positive silver build-up leveled off at less than 9 seconds.

These development rate studies would indicate to one skilled in the art that negative development and/or processing time for forming the composite print are materially reduced. Not only does this mean that positive reproductions can be achieved more rapidly; it also means that cleaner D met can be obtained.

From the foregoing description and illustrative examples, it will be apparent that the addition of an effective amount of a macroscopic pigment to the silver-receptive stratum of the aforementioned photographic products provides significant advantages.

As used herein and in the appended claims, the term “effective amount” denotes an amount sufficient to achieve beneficial results.

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 limiting sense.

What is claimed is:

1. 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-opacifying material, and a silver-receptive stratum above said emulsion layer, said silver-receptive stratum comprising silver-particle precipitating nuclei dispersed in a matrix of gelatin and colloidal silica, the ratio of gelatin to colloidal silica being from about 1.5:1 to 1:10, said opacifying 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 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 a macroscopic pigment having a mean particle size of from about 0.1a to about 10µ and wherein the ratio of macroscopic pigment to gelatin in said stratum is from about 2:1 to about 12:1.

2. A product as defined in claim 1 wherein said stratum contains from about 40 to about 600 mgm. of pigment per square foot of surface area.

3. A product as defined in claim 1 wherein said pigment is calcium carbonate, wollastonite, titanium dioxide, barium sulfate, calcium silicate, talc, silica, an aluminum silicate clay, or a mixture of said compounds.

4. A product as defined in claim 1 wherein said amount of macroscopic pigment present is sufficient to alter the tone of said positive image formed in said stratum and to increase the absorption rate of an aqueous liquid applied to the surface of said stratum.

5. A process for preparing a positive silver transfer image comprising exposing a product as defined in claim 1 to provide a developing image; applying an aqueous alkaline 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.

References Cited

FOREIGN PATENTS

545,678 3/1956 Belgium ...................... 96—29
893,652 4/1962 Great Britain .................. 96—29

NORMAN G. TORCHIN, Examiner

W. H. LOUIE, Jr., Assistant Examiner

U.S. Cl. X.R.

96—76 R