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3,486,895

PROCESS FOR OBTAINING ARTISTIC EFFECTS IN PHOTOSOLUBLE DIRECT POSITIVE SILVER HALIDE EMULSIONS

Eugene Frederick Haugh, Old Bridge, N.J., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware
 No Drawing. Filed Apr. 29, 1966, Ser. No. 546,202
 Int. Cl. G03c 5/24, 7/00

U.S. Cl. 96-64

10 Claims

ABSTRACT OF THE DISCLOSURE

Process for forming images comprising (a) exposing a photosoluble silver halide emulsion layer imagewise so that the layer will have (i) areas of high exposure sufficient to form a photosoluble latent image, (ii) areas of intermediate exposure to form a developable latent image, and (iii) areas of no exposure insufficient to form a developable or photosoluble latent image, (b) treating the layer, prior to reducing the silver halide, with a silver halide solvent solution to effect solubilization of silver halide in areas (i) at a rate greater than in areas (ii) and (iii) until a positive image is formed, and (c) treating the layer with a developing solution to develop areas (ii) and not areas (iii). The process is useful in obtaining unusual and artistic effects, conversion of silhouette images to colored outlined images, and in two-color duplication of black and white originals.

This invention relates to a process for forming images from photosoluble silver halide emulsion layers.

The process of this invention comprises, in the order stated, the sequential steps of

(a) exposing a layer containing photosoluble silver halide crystals made relatively less soluble in a silver halide solvent by treatment with an organic compound capable of forming a silver salt of lower solubility in water than silver chloride, to an image producing pattern of actinic radiation so that the layer will have

(i) Areas of relatively high exposure, sufficient to form a photosoluble latent image,

(ii) Areas of intermediate exposure, sufficient to form a developable latent image, and

(iii) Areas of no exposure or relatively low exposure, insufficient to form a developable or photosoluble latent image,

(b) treating said layer prior to reducing the silver halide with an aqueous solution comprising a silver halide solvent, thereby effecting solubilization of the silver halide in image areas (i) at a rate substantially greater than in the less exposed image areas (ii) and (iii) until a positive image comprised of silver halide is formed; and

(c) treating said layer with a photographic silver halide developer solution to develop the latent image of intermediate exposure areas (ii) without developing the less exposed image areas (iii).

A "photosoluble latent image" results when a photosoluble layer is imagewise exposed to sufficient actinic radiation to render it soluble in an aqueous silver halide solvent at a rate substantially greater in exposed than in unexposed areas.

A "developable latent image" results when a photosoluble layer is imagewise exposed to sufficient actinic radiation to render it reducible to silver in a conventional aqueous photographic developer at a rate substantially greater in exposed than in unexposed areas.

Photosoluble silver halide emulsion layers useful in accordance with this invention are disclosed in Blake, U.S.P. 3,155,507. A very large number of organic compounds are disclosed as suitable for use in treating silver halide

emulsions to give them the desired properties. This Blake patent also describes qualitative testing procedures to determine whether or not a particular organic compound was satisfactory and quantitative tests useful in estimating the needed concentration of the organic compound.

Useful photosoluble silver halide layers are described in U.S. Patents of Blake, Nos. 3,155,514, 3,155,516, 3,155,517, 3,155,518 and 3,155,519, all patented Nov. 3, 1964; Celeste and Cohen, U.S. Patent No. 3,155,515 of Nov. 3, 1964; and assignee's copending application of Blake Ser. No. 444,022, filed Mar. 30, 1965, U.S.P. 3,377,169, Apr. 4, 1968; of Blake and Fan, Ser. No. 403,660 filed Oct. 13, 1964, U.S.P. 3,368,899, Feb. 13, 1968; and of Fan, Ser. No. 403,631 filed Oct. 13, 1964 U.S.P. 3,407,068 and Ser. No. 403,632 filed Oct. 13, 1964 U.S.P. 3,407,067, Oct. 22, 1968.

In carrying out a preferred embodiment of the invention, a photosoluble layer is prepared in a manner taught in U.S. 3,15,507. Typically, a gelatino-silver halide (especially silver chloride) emulsion is precipitated, ripened, and washed to remove soluble salts, all in a conventional manner. Then the emulsion is digested at a temperature of 150° F. to 200° F. in the presence of a selected organic compound, e.g., one of the aromatic mercaptans listed in said patent. Optionally, an optical sensitizing dye may also be present during this digestion as disclosed in the above Blake application, Ser. No. 390,460 U.S.P. 3,884,485, May 21, 1968. This photosoluble emulsion is then coated on a suitable support and dried. As disclosed in U.S. Patent 3,155,507, the organic compound (e.g., aromatic mercaptan) may be applied from solution as a treatment of the coated element rather than being added to the liquid emulsion prior to coating.

The photosoluble element thus prepared is exposed to at least three different levels of actinic radiation, one of which levels may include zero exposure. In the simplest embodiment of the invention, there is an area of relatively high exposure (i), an area of intermediate exposure (ii), and an area of relatively low or zero exposure (iii). The element is then treated with an aqueous solution of a silver halide solvent, e.g., a conventional photographic fixing solution containing Na₂S₂O₃. When the exposure levels are properly selected, the photosolubilized silver halide of area (i) will be removed by the silver halide solvent. Treatment with the solvent is stopped prior to the removal of any substantial quantity of silver halide in the less exposed areas (ii) and (iii).

An optional step of washing the element in water may follow treatment with the silver halide solvent. Next the element is treated with a conventional photographic developing solution of a concentration and for a period sufficient to develop the latent image in the remaining silver halide. Thus, the silver halide in the area of intermediate exposure, area (ii), will be reduced to a metallic silver image while the area of low or zero exposure, area (iii), will be essentially unaffected by the photographic developer solution. Optional washing and drying steps may follow the treatment with the developer solution. At this point the basic process of the invention has been completed and an element has been produced having three different, visually distinct areas: one area is transparent; in another area there is a black, metallic silver image; and in another area there is a silver halide image which, in the case of a silver chloride emulsion, is initially a white image. Such a simple embodiment of the invention is useful for such things as information analysis or masking and artistic effects.

In this process, the requirement of three different exposure levels is a minimum. There is no maximum limit of exposure levels since useful results may be obtained, for example, when the element is exposed through a continuous tone transparency. When there are more than

ditional processing steps which will be described in subsequent examples are capable of yielding many interesting results.

EXAMPLE II

Example I was repeated through the processing steps of treatment with silver halide solvent (fixing), washing, treatment with photographic developer, and washing, but omitting the final drying. At this point, the film was given a 15 second overall exposure using the same light as in the original, imaging exposure. The film was then treated for 2 minutes in the silver halide solvent solution used earlier but to which had been added 0.1 g. of KI per liter of solution. This was followed by a 3 minute water wash and drying in air.

The superimposed silver chloride positive image of Example I was thus removed by the extra fixing step and there remained only a black silver image. Highest optical densities of this silver image were found in areas of intermediate exposure while in the highest and lowest exposure areas there remained only clear gelatin.

EXAMPLE III

A sheet of the photosoluble film prepared in Example I was exposed as in that example except that the exposure time was increased to 10 seconds. The film was then processed at 70° F. starting with a one minute treatment in the silver halide solvent (fixing) solution of Example I and a 3 minute water wash. Then the film containing a positive silver halide image, was developed for one and a half minutes in a color developer solution having pH 11 at 80° F., and of the following formulation:

Water	-----ml---	800
Benzyl alcohol	-----ml---	6
Sodium hexametaphosphate	-----g---	1
Na ₂ SO ₃ (anhyd.)	-----g---	5
NaBr	-----g---	0.5
p-Aminodiethylanilinehydrochloride	-----g---	5
NaOH	-----g---	1
Na ₂ CO ₃ · 1 H ₂ O	-----g---	10
KI, 0.1% by wt. aqueous solution	-----ml---	10
Ethylenediamine	-----ml---	6
Water to make 1 liter.		

Per liter of the above color developer solution there had been added 2 g. of a cyan color coupler, N-(o-acetamidophenyl ethyl)-1-hydroxy-2-naphthamide. This treatment with color developer and cyan color coupler resulted in the formation of negative-positive³ images of both metallic silver and cyan dye in the areas of intermediate exposure (i.e., areas having a latent image).

After a 3-minute water wash, the film was given a 15-second flash exposure using the same light source as in the original, imaging exposure. With the remaining silver halide image thus fogged, the film was again developed for one and a half minute in the color developer solution described above to which, this time, there was added 2 g. per liter of a magenta color coupler, 2,4,6-trichlorophenyl-3-p-nitroanilino-2-pyrazoline - 5 - one. In this second color development step, the positive silver halide image was converted to both a black positive metallic silver image and a magenta positive dye image in the areas receiving the lowest image exposure.

After a 3-minute water wash, the black metallic silver images were removed and processing completed by treating for 3 minutes in a bleach solution, washing 2 minutes, fixing 3 minutes, washing 5 minutes and drying. The fixing solution was the same solution of silver halide solvent used in the first processing step following the imaging exposure except for the addition of 0.1 g. KI per liter of solution. The bleaching solution had the following formulation:

Water	-----ml---	800
Na ₂ SO ₄	-----g---	30
Na ₂ SO ₄	-----g---	45
K ₃ Fe(CN) ₆	-----g---	123
Water to make 1 liter.		
pH	-----	8.0-8.6

Upon completion of the above processing sequence, there resulted an artistically interesting color transparency comprising a positive magenta dye image and a superimposed negative-positive cyan dye image. Actually, the cyan image was a true negative image only at lower exposure levels and a positive image at higher exposure levels as discussed in the footnote in Example I.

EXAMPLE IV

Using another sheet of the photosoluble film of Example I, the processing sequence of Example III was varied by inserting an additional color development step with a yellow coupler. All other processing steps were identical to those described above but following the development with cyan coupler and the related washing step, the film was developed for one and a half minute in the above described color developer solution to which there was added 2 g. per liter of a yellow color coupler, 4 - (p-toluenesulfonyl-amino)-*o*-benzoylacetylacetonide. Apparently the latent image (in the areas of intermediate exposure) was not completely developed in the first development step when the cyan coupler was present; thus a positive yellow dye image was formed which blended with the cyan dye image to give a resultant positive dye image having a greenish color. The film was washed for 3 minutes in water and then processing was continued as described in Example III, i.e., flash exposed, developed with magenta coupler, bleached, fixed, etc. The resultant transparency, with its superimposed negative-positive⁴ and positive dye images, was similar to that described earlier but had a more pleasing overall appearance.

The processing sequence of this example was repeated except that the transparency through which the original exposure was made was a radiograph of a human head. The resultant copy of the radiograph exhibited potential utility for diagnostic purposes because the soft tissue area (corresponding to the high intensity region of the radiograph) was reproduced as magenta and bluish tones while bone areas gave green and clear areas. These color variations were much more apparent than the density variations in the original radiograph.

EXAMPLE V

Example II was repeated in all details except for the transparency through which the photosoluble film was given the original, imaging exposure. The transparency, in this case, was prepared from a lithographic negative and consisted of an image of large, block letters where there was no silver (transparent areas) against a background of black metallic silver of very high optical density. The exposure of the photosoluble film through this transparency resulted in highly exposed areas corresponding to the letters and areas of essentially zero exposure corresponding to the background of the transparency. Due to light scattering, there was a very thin line of intermediate exposure surrounding the highly exposed letter areas.

Treatment with the silver halide solvent caused removal of the silver halide in the highly exposed letter areas. If the film had been examined in white light one would have observed a positive copy of the original transparency except that the background areas would have been a white silver chloride image corresponding to the original black silver image. However, the film was kept in the dark while it was treated with the developer solution. The silver halide area contained a latent image (thin lines surrounding the transparent letter areas) where light scat-

³ See Footnote 1, Example I.

⁴ See Footnote 1, Example I.

tering effected an intermediate exposure and made the thin lines convertible by development from white silver halide to black metallic silver. Finally, the balance of the silver halide, in the areas of low exposure, was removed by the flashing (overall fogging) exposure followed by the second treatment with silver halide solvent.

The completely processed film, with silver halide having been removed from the areas of both high and low exposure, was left with only a thin line image of black metallic silver outlining the areas of each letter of the original image.

EXAMPLE VI

Example V was repeated through the steps of exposing, treating with a silver halide solvent to remove silver chloride in the heavily exposed areas, washing, treating with a silver halide reducing agent to develop the latent image (thin black line surrounding the transparent letter areas), and the washing step which followed.

At this point, the processing was altered. Instead of removing the remaining silver chloride, it was converted to silver iodide by soaking for two minutes in a 0.5% by weight aqueous solution of potassium iodide. After washing two minutes in water the film was soaked for ten minutes in a solution containing 0.5 g./liter of the dye Rhodamine B (CI Basic Violet 10). This magenta dye was thereby mordanted to the silver iodide image, representing the area of least exposure. The film was given a final two minute water washing and was dried in air. By such a method, an element could be toned to give practically any color desired.

The process of the present invention is applicable to any unfogged photosoluble element, e.g., as described in Blake, U.S. 3,155,507. Various types of silver halide crystals are disclosed in that patent as being suitable for use in preparing photosoluble elements, although silver chloride and silver chlorobromide are preferred.

The suitable photosoluble elements may be coated on any of the supports disclosed in U.S. 3,155,507, and may employ any of the binders, adjuvants, etc. as disclosed in that patent.

Many color couplers or color formers and toning solutions are known and described in prior patents and in the photographic literature. Suitable such compounds and compositions that are useful in accordance with this invention are described in "History of Color Photography" by J. S. Friedman, The American Photographic Publishing Co., Boston, Mass. (1947). Suitabue color coupling developing agents containing an unsubstituted amine group ($-NH_2$) are also described in the latter textbook.

The immediately apparent advantages of this invention are concerned with the multitude of unusual and artistic effects which can be obtained easily by modifying this simple basic process. Other practical applications, such as information analysis, two-color duplication of black and white originals to increase visual perception of low contrast detail, and conversion of a silhouette image to a colored outlined image useful in may making, are suggested. Working examples have been provided to illustrate the basic process itself with exposure, fixing and developing steps with numerous variations and additions. Many other variations will be apparent to those skilled in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process which comprises, in the order stated, the sequential steps of

(a) exposing a layer containing photosoluble silver halide crystals made relatively less soluble in a silver halide solvent by treatment with an organic compound capable of forming a silver salt of lower solubility in water than silver chloride, to an image producing pattern of actinic radiation so that the layer will have at least:

- (i) areas of relatively high exposure, sufficient to form a photosoluble latent image,
- (ii) areas of intermediate exposure, sufficient to form a developable latent image, and
- (iii) areas of no exposure or relatively low exposure insufficient to form a developable or photosoluble latent image;

(b) treating said layer prior to reducing the silver halide with an aqueous solution comprising a silver halide in image areas (i) at a rate substantially greater than in the less exposed image areas (ii) and (iii) until a positive image comprised of silver halide is formed; and

(c) treating said layer with a photographic silver halide developer solution to develop the latent image of intermediate exposure areas (ii) without developing the less exposed image areas (iii).

2. A process according to claim 1 wherein said layer has a gelatin binding agent for the silver halide grains.

3. A process according to claim 1 wherein the silver halide is silver chloride.

4. A process according to claim 1 wherein said organic compound is a mercaptan.

5. A process according to claim 1 wherein said organic compound is 2-mercapto-4-phenylthiazole.

6. A process according to claim 1 wherein the developer solution contains a color coupling compound.

7. A process according to claim 1 wherein after step (c) is completed the remaining silver halide is toned with a solution containing a mordanting dye.

8. A process according to claim 1 wherein after step (c) the silver halide is fogged and then treated in a color coupling developer solution.

9. A process according to claim 1 wherein the film is exposed to a silhouette image and after step (c) is completed the remaining silver halide is toned with a solution containing a mordanting dye.

10. A process according to claim 1 wherein a two-color image is produced by having a color coupling compound that produces a dye of certain color in the developer solution, and the developed element is re-exposed to actinic radiation and developed in a solution containing a color coupling compound that produces a dye of a different color than that produced in the first development.

References Cited

UNITED STATES PATENTS

2,908,570	10/1959	Meeussen	96—22 X
3,155,516	11/1964	Blake	96—64

OTHER REFERENCES

Mees, The Theory of the Photographic Process, 3rd ed., p. 88, Macmillan Co., 1966.

NORMAN G. TORCHIN, Primary Examiner

RICHARD E. FICHTER, Assistant Examiner

U.S. Cl. X.R.

96—22, 55

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,486,895 Dated Dec. 30, 1969

Inventor(s) Eugene Frederick Haugh

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 7, line 48, "Suitabue" should be --Suitable--.

Co. 8, (claim 1), line 17, after "halide", the following words should appear: --solvent, thereby effecting solubilization of the silver halide--; claim 4, line 29, "organis" should be --organic--.

SIGNED AND
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Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents