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Marchant et al.

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[54] **LASER STABILIZATION AND/OR PHOTODEVELOPMENT OF SILVER HALIDE MATERIALS**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 6,955, Jan. 29, 1970, now Defensive Publication No. T877,006

[52] **U.S. Cl.** ..... **96/27 R,** 96/27 E, 96/45.2, 96/50 R, 96/114.1

[51] **Int. Cl.** **G02c 5/04,** G03c 5/32, G03c 1/02

[58] **Field of Search** ..... 96/27 H, 61, 50, 45.2, 96/114.1, 27 E, 27 R

[56] **References Cited**

UNITED STATES PATENTS

3,144,332	8/1964	Brown et al.	96/27
3,224,877	12/1965	Jacobs	96/27
3,241,971	3/1966	Kitze	96/107
3,314,073	4/1967	Becker	96/27 H
3,392,020	7/1968	Yutzy et al.	96/114.1
3,418,122	12/1968	Cult	96/63
3,447,927	6/1969	Bacon	96/63
3,457,075	7/1969	Morgan	96/114.1
3,723,121	3/1973	Hauser	96/27 H

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Assistant Examiner—M. F. Kelley
Attorney, Agent, or Firm—Robert E. Knapp

[57] **ABSTRACT**

This disclosure relates to radiation-sensitive systems such as a silver halide radiation-sensitive system wherein a spot laser beam is used to stabilize an area of a silver halide radiation-sensitive element. In one aspect, the silver halide system preferably stabilized and/or photodeveloped by this technique contains silver halide grains having polyvalent metal ions occluded therein, preferably trivalent metal ions such as bismuth, iridium and the like, said system further comprising a halogen acceptor, such as a direct-print halogen acceptor, contiguous to the grains. In one preferred embodiment, a high-intensity, imagewise, light exposure which can be a laser light exposure is used to record an image on the silver halide layer when the emulsion is appropriately sensitized. A defocused laser is then used to heat-stabilize the silver halide in the image exposure areas; a laser of a second wavelength is used if the emulsion is laser-sensitized for the first exposure. Subsequent image exposures can then be made on the same photographic element followed by localized image stabilization. In certain instances, low-intensity laser beams or other localized light sources can be used to develop the image in localized areas after stabilization.

8 Claims, No Drawings

LASER STABILIZATION AND/OR PHOTODEVELOPMENT OF SILVER HALIDE MATERIALS

This is a continuation-in-part of U.S. application Ser. No. 6,955 of John C. Marchant and John R. Tinney, filed Jan. 29, 1970, now Defensive Publication No. T877,006.

This invention relates to methods of exposing, stabilizing and/or photodeveloping silver halide systems. In one aspect, this invention relates to a method of heat-stabilizing a print-out image record by using a laser beam as a heat source. In another aspect, a print-out system can be imagewise exposed by a high-intensity light or a laser beam, stabilized by a laser beam which is designed to provide heat in the element, preferably in the localized image-recording area, and then sequentially exposed and stabilized in additional regions of the element and/or photodeveloped to produce a visible image record. Another aspect relates to a process of imagewise exposing a silver halide radiation-sensitive material which is a photothermographic material and then exposing the imagewise exposed areas with a laser beam.

It is known in the art to make photographic systems which can be heat-stabilized. Such systems are disclosed in Bacon et al, U.S. Pat. No. 3,447,927 issued June 3, 1969; Stewart et al, U.S. Pat. No. 3,312,550 issued Apr. 4, 1967; Morgan et al, U.S. Pat. No. 3,457,075 issued July 22, 1969; McBride, U.S. Pat. No. 3,287,137 issued Nov. 22, 1966 and Yutzy et al, U.S. Pat. No. 3,392,020. The heat stabilization of systems of this type is generally carried out via hot platen systems such as disclosed in Colt, U.S. Pat. No. 3,418,122 issued Dec. 24, 1968 and Brown, U.S. Pat. No. 3,144,332 issued Aug. 11, 1964. Generally, the prior-art systems heat-stabilized the entire photographic element while stabilizing the imagewise-exposed area. It is desirable to provide a system which will allow for sequential imagewise exposures and stabilization of the localized imagewise exposure without affecting the non-exposed areas. A system of this type would allow for many data tracks to be superimposed or recorded on the same film strip, such as at intervals of time when comparison data tracks are recorded.

We have now discovered an improved process for exposing and stabilizing photographic heat-processable elements. Generally, the process relates to the use of a laser beam as a heat source for stabilizing selective areas of a radiation-sensitive element, such as a photographic element. A confined beam of a laser exposure can be directed over the same regions of the photographic element as the imagewise exposure such as, for example, in recording oscillograph traces.

One embodiment of the invention comprises a process comprising (1) imagewise exposing a silver halide radiation-sensitive material and (2) exposing the imagewise-exposed areas with a laser beam to heat the silver halide radiation-sensitive material.

In one preferred embodiment of this invention, the imagewise exposure is also carried out by a laser beam and the photographic system is spectrally sensitized to the wavelength of said laser beam. The laser beam used for the stabilization process is either a defocused beam of low intensity or of a wavelength to which the photographic recording system is not photographically sensitive.

In another highly preferred embodiment, the process of this invention is used to expose and stabilize a print-out silver halide emulsion containing silver halide grains having polyvalent metal ions and preferably trivalent metal ions occluded therein. A direct-print-type halogen acceptor is located contiguous to said grains.

The process of this invention is generally applicable to any photographic system which is heat-processable. Typical photographic heat-processable elements, i.e., those which do not require application of external liquid developing agents, are print-out elements as disclosed in Bacon et al, U.S. Pat. No. 3,447,927 issued June 3, 1969, elements such as disclosed in U.S. Pat. No. 3,392,020 issued July 9, 1968, direct-print elements as disclosed in McBride, U.S. Pat. No. 3,287,137 issued Nov. 22, 1966, and incorporated developer elements as disclosed in Stewart et al, U.S. Pat. No. 3,312,550 issued Apr. 4, 1967.

Preferred silver halide recording layers which are useful in elements processed in accordance with this invention comprise silver halide grains having polyvalent metal ions or atoms occluded therein. The silver halide grains having occluded polyvalent metal ions therein are generally obtained by precipitating in the presence of the polyvalent metal ions and preferably in an acid medium. Typical emulsions of this type are disclosed in Bacon et al, U.S. Pat. No. 3,447,927 issued June 3, 1969, and in Bacon, U.S. Pat. No. 3,531,291 issued Sept. 29, 1970. These emulsions are useful in recording electromagnetic radiation such as electrons, light, X-rays, etc. In certain preferred embodiments of this invention, the emulsion contains silver halide grains with trivalent metal ions occluded therein.

Typical silver halide compositions mentioned above contain a halogen acceptor which is generally contiguous with the silver halide grains in the system. Generally, suitable halogen acceptors are compounds which enhance the photolytic yield (as determined by radiographic analysis, for example) and/or the photolytic density of a print-out emulsion.

Another preferred photosensitive material which can be processed in accordance with this invention comprises an oxidation-reduction image forming combination comprising (i) an oxidizing agent, such as a heavy metal salt oxidizing agent, with (ii) a reducing agent and a photosensitive component, such as photosensitive silver halide which is believed to be a catalyst for the oxidation-reduction image forming combination. Photosensitive materials which can be processed in accordance with the invention include those described, for instance, in U.S. Pat. No. 3,672,904 issued June 27, 1972; Belgian U.S. Pat. No. 765,452, issued May 28, 1971; Belgian U.S. Pat. No. 765,451, issued May 28, 1971; Belgian U.S. Pat. No. 766,658, issued June 30, 1971; Belgian U.S. Pat. No. 766,590; Belgian U.S. Pat. No. 774,436, issued Nov. 12, 1971; Belgian U.S. Pat. No. 768,071, issued July 30, 1971; U.S. Pat. No. 3,666,477, issued May 30, 1972; Belgian U.S. Pat. No. 768,228, issued July 30, 1971; Belgian U.S. Pat. No. 772,371, issued Oct. 15, 1971 and the Product Licensing Index, Vol. 92, Dec. 1971, Item 9246. A useful photosensitive material comprises, for example, an oxidation-reduction image forming combination comprising (i) silver behenate and/or silver stearate with (ii) a reducing agent, such as a bis-beta-naphthol and photosensitive silver halide. An image in the photosen-

sitive material can be developed after imagewise exposure to light merely by heating the element to moderately elevated temperatures, such as from about 90°C. to about 250°C. for sufficient time to provide a desired image, e.g., from about 0.5 to about 90 seconds. This can be done by (1) imagewise exposing the described photosensitive material and (2) exposing the imagewise-exposed areas with a laser beam to heat the photosensitive material. The imagewise exposure of the described photosensitive material can be made with a laser beam and the subsequent exposure can be made with a defocused laser beam in only the areas of imagewise exposure with sufficient intensity to provide heating of those areas of the photosensitive material to a desired temperature, such as from about 90°C. to about 250°C.

The above-described emulsions can be coated on a wide variety of supports in accordance with usual practice. Typical supports for photographic elements of the invention include glass, metals, paper, polyethylene-coated paper, polypropylene-coated paper, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethyleneterephthalate film and related films of resinous materials and others. In one preferred embodiment wherein high temperatures can be used to process the elements of this invention, film supports are utilized which have a heat distortion temperature of at least 160°C. and more preferably of at least 180°C. in both the length and width directions of the support; heat-distortion temperature can be calculated according to ASTM-D–1637-61. Typical preferred supports of this embodiment are heat-set polyesters, for example, polyethylene terephthalates, cyclohexylenedimethylene terephthalates, etc.; high-temperature polyimides, heat-resistant polycarbonates and related film supports having high heat-distortion temperatures.

The laser sources useful in this invention include those generally known in the art. Typical useful lasers are described in "The Laser," Smith and Sorokin, McGraw-Hill, Physical and Quantum Electronics Series; and Roy A. Paananen, "Progress in Ionized-Argon Lasers," IEEE Spectrum, Vol. 3, page 88, June, 1966, which describes various types of lasers including the specific CO_2 continuous-wave laser used for the examples herein.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A radiation-sensitive gelatino silver chlorobromide photographic emulsion is prepared as described in Example 18 of U.S. Pat. No. 3,447,927 and coated on a heat-set polyester support at about 300 mg. Ag/ft^2.

Samples of this coating are then exposed imagewise 300 microseconds with a xenon flash unit, stabilized with a CO_2 continuous-wave laser having a beam power of 20 to 30 watts for 10 seconds with the total beam diffused optically to cover approximately 2 cm^2 of film. The sample is then photodeveloped 5 minutes at 6 inches from two 8-watt fluorescent lamps in a white reflector. Very good image discrimination is seen. The image has a Dmax of 1.80 and a Dmin of 0.29.

Similar results are obtained when the imagewise exposure is carried out with a laser source and the emulsion containing a sensitizing dye responsive to the wavelength of the laser radiation. The second laser beam is then of a different wavelength to avoid exposure of the silver halide emulsion.

EXAMPLE 2

Samples of the photographic emulsion prepared as described in Example 18 of U.S. Pat. No. 3,447,927 are coated on glass plates. Separate samples are then imagewise exposed with a laser beam or a xenon flash unit. A CO_2 continuous laser emitting at 10.6 microns with a 7- to 8-watt intensity to a spot size of 0.8 mm. is used to heat-stabilize the recorded image. A translation table moves the glass plate past the laser spot at a rate of 10 mm. per second. The sample is then photodeveloped 5 minutes at 6 inches from two 8-watt fluorescent lamps in a white reflector. Very good image discrimination is obtained.

EXAMPLE 3

A photothermographic element is prepared as follows:

A coating composition is prepared by mixing the following components:

Silver behenate (about 60–70% pure, impurities present are lower molecular weight fatty acids)	42.0 g
Behenic acid	32.0 g
Polyvinyl butyral	15.0 g
Acetone	250.0 ml
Toluene	250.0 ml
Phthalimide	8.5 g
NaBr (reacts with silver behenate to form silver bromide in situ)	2.4 g

After ball-mixing for 18 hours, 141 milliliters of the resulting dispersion is combined with the following solutions:

Acetone containing 0.08% by weight 3-ethyl-5-[(3-ethyl-2(3H)-benzothiazolyl-idene)isopropylidene]-2-thio-2,4-oxazolidinedione	4.4 ml
Acetone containing 6.25% by weight 2,2'-dihydroxy-1,1'-binaphthyl	52.5 ml

The composition is mixed and then coated on a water-resistant paper support and dried providing a photosensitive and thermosensitive element containing 60 milligrams of silver per square foot of support. The photosensitive element is exposed sensitometrically with tungsten light for 0.5 second. The resulting element is then heat stabilized employing a CO_2 continuous-wave laser with a beam power of 50 watts and a spot size of 1 mm. with a 200 microsecond exposure. Good image discrimination is obtained.

EXAMPLE 4

Similar results are obtained when the photothermographic element of Example 3 is exposed imagewise with a laser beam to which the photothermographic material is sensitive, rather than tungsten light, and then the photothermographic element is heated imagewise employing a laser beam to which the photothermographic material is not sensitive.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

1. A process comprising (1) imagewise exposing a silver halide radiation-sensitive material and (2) exposing the imagewise-exposed areas with a defocused laser beam to heat the silver halide radiation-sensitive material effectively.

2. A process according to claim 1 wherein the silver halide material is additionally photodeveloped to provide a visible image therein.

3. A process according to claim 1 wherein said silver halide material comprises silver halide grains having polyvalent metal ions occluded therein.

4. A process according to claim 1 wherein said silver halide material comprises silver halide grains having trivalent metal ions occluded therein and a direct-print halogen acceptor contiguous to said grains.

5. A process according to claim 1 wherein the imagewise exposure is made with a laser beam and said subsequent exposure is made with a defocused laser beam in only the areas of imagewise exposure with sufficient intensity to heat the emulsion effectively.

6. A process comprising (1) imagewise exposing with a laser beam a photothermographic element comprising a support having thereon an oxidation-reduction image forming combination comprising (i) silver stearate or silver behenate as an oxidizing agent with (ii) an organic reducing agent and photosensitive silver halide and (2) exposing the imagewise exposed areas with a defocused laser beam to heat the imagewise exposed areas of the photothermographic element to a temperature from about 80°C. to about 250°C. to provide a developed image.

7. A process comprising (1) imagewise exposing with a laser beam a photothermographic element comprising a support having thereon a layer comprising an oxidation-reduction image forming combination comprising (i) silver stearate or silver behenate with (ii) an organic reducing agent, and photosensitive silver halide, in a polymeric binder, and (2) exposing the imagewise exposed areas with a defocused laser beam to heat the imagewise exposed areas of photothermographic element to a temperature of at least 80°C. to provide a developed image.

8. A process as in claim 7 comprising (1) imagewise exposing with a laser beam a photothermographic element comprising a support having thereon a layer comprising an oxidation-reduction image forming combination comprising (i) silver behenate with (ii) a phenolic reducing agent, and photosensitive silver halide with a toner, a spectral sensitizing dye and a poly(vinyl butyral) binder for said layer, and (2) exposing the imagewise exposed areas with a defocused laser beam to heat the imagewise exposed areas of the photothermographic element to a temperature from about 80°C. to about 250°C. to provide a developed image.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,811,885 Dated May 21, 1974

Inventor(s) John C. Marchant and John R. Tinney

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

Cover page, column 2, line 3, "Robert E. Knapp" should read ---Richard E. Knapp---.

Column 2, lines 53-57, after "Belgian" delete "U.S.". Lines 59-60, after "Belgian" delete "U.S.".

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents