

[54] **PROCESS FOR THE PRODUCTION OF
CONTOUR LINE IMAGES**

[75] Inventors: **Edwin Hendrik Hazenbosch,**
Mechelen; **Albert Lucine Poot,**
Kontich, both of Belgium

[73] Assignee: **Agfa-Gevaert, Mortsels, Belgium**

[22] Filed: **Sept. 9, 1974**

[21] Appl. No.: **504,260**

Related U.S. Application Data

[63] Continuation of Ser. No. 296,082, Oct. 10, 1972,
abandoned.

[30] **Foreign Application Priority Data**

Oct. 11, 1971 United Kingdom..... 47316/71

[52] **U.S. Cl.** **96/27 R; 96/27 E; 96/90 R;**
96/115 P

[51] **Int. Cl.²** **G03C 5/04; G03C 5/24**

[58] **Field of Search** **96/27 E, 27 R, 48 R, 90 R,**
96/115 P

[56]

References Cited

UNITED STATES PATENTS

3,476,562	11/1969	Yamada et al.....	96/90 R
3,503,745	3/1970	Yamada et al.....	96/90 R
3,607,266	9/1971	Yamada et al.....	96/48 R

Primary Examiner—Won H. Louie, Jr.

Attorney, Agent, or Firm—William J. Daniel

[57]

ABSTRACT

A photographic process for forming contour line images with a recording layer containing particles of intimately mixed N-vinyl carbazole and carbon tetrabromide that are in effective contact with a dye base and are dispersed in a hardenable hydrophilic colloid binder. The dye base is preferably a styryl dye base. The recording layer may contain colouring matter in the form of dyes or coloured pigments. Contour line images are produced that either are of low opacity on an optically dense recording layer image background or have a relatively high opacity as compared with the image recording layer background.

10 Claims, No Drawings

PROCESS FOR THE PRODUCTION OF CONTOUR LINE IMAGES

This is a continuation of Ser. No. 296,082, filed Oct. 10, 1972.

The present invention relates to the photographic production of contour line images.

The production of photographic images characterized by equidensity contour lines is known already e.g. from the United Kingdom Patent Specification 1,248,071.

According to the invention described in the above United Kingdom Patent Specification equidensity contour line images are produced in a wet development processing wherein an image-wise exposed photographic silver halide emulsion material is used containing a mixture of silver halide grains having a different photosensitivity, halide composition, and solubility.

The present invention provides a process for the production of photographic contour line images wherein silverless photographic materials are used that do not need a wet chemical development.

The recording material applied in the present invention comprises a hydrophilic colloid medium containing dispersed discrete particles of an intimate mixture of N-vinylcarbazole and carbon tetrabromide in effective contact with a proper amount of a hydrogen bromide acceptor e.g. a dyestuff salt precursor such as a dye base preferably a styryl dye base.

A photographic material comprising these ingredients has been described already in the United Kingdom Patent Specification 1,065,548.

It has now been found that the above described recording material is suited for the production of different types of contour line images.

According to a first mode of operation of the present invention a contour line image having relatively low opacity (optical density less than 0.25) coloured or practically white contour lines on an optically dense recording layer image background (optical density at least 0.5) is obtained.

For that purpose in a first step a recording layer containing a styryl dye base and particles of intimately mixed N-vinylcarbazole and carbon tetrabromide dispersed in a hardenable hydrophilic colloid binder, e.g. gelatin, is given an image-wise exposure to active electromagnetic radiation of an intensity sufficient to form a print-out image. At the edge of the print-out image area narrow contour lines having a color different from that of the more central parts of the print-out image area are formed.

It is assumed that the hydrogen bromide produced in the exposed parts laterally diffuses beyond the edges of the exposed parts and is captured by the styryl dye base forming a red styryl dye salt around said parts. In the exposed parts themselves the hydrogen bromide is probably consumed in a dye-forming reaction using up the N-vinylcarbazole contained in the dispersed carbon tetrabromide N-vinylcarbazole droplets.

In a second step the recording layer is overall exposed to active electromagnetic radiation e.g. white light emitted by incandescent bulbs and obtains a colouration in the initially non-exposed portions. The clearly visible red coloured contour line remain, in other words, are not affected by this exposure.

In a third step the recording material is overall heated, e.g. in the range of 100°–150°C, whereby the

areas corresponding with the red coloured contour lines are bleached substantially. As a result thereof a contour line image having white to pale yellow contour lines on a dark brown image background is obtained.

According to a second mode of operation a contour line image having coloured contour lines of relatively high opacity (optical density at least 0.5) as compared with the low opacity (optical density lower than 0.25) image recording layer background is formed by a procedure comprising all the steps described in the first mode of operation but followed by two subsequent additional steps viz. (1) the overall intensive exposure with ultra-violet radiation of the recording layer, whereby the pale yellow contour lines become darker and finally turn dark brown and (2) the wash-off treatment of the recording layer, whereby the layer portions that do not correspond with the contour lines are removed selectively leaving a contour line image having intensively coloured contour lines on a background having the colour of the support, to which the recording layer has been applied.

When the recording layer incorporates colouring matter, e.g. already applied in the coating stage in the form of dyes or coloured pigments, said exposure to intensive ultra-violet radiation is not necessary for obtaining a coloured contour line image in the subsequent wash-off step. The colour of the contour line is then the same as the colour of the applied pigment or dye.

The heating step, whereby the contour lines are bleached substantially according to the first mode of operation, may proceed with the common means suited for that purpose, e.g. heated rollers, hot glazing plate, hot air current and the like.

In the second mode of operation the wash-off treatment of the water-permeable colloid portions may proceed advantageously with running water (tap water at a temperature of 20°–60°C) whilst applying some mechanical friction.

The recording materials applied in the above two modes of operation preferably consist of a support onto which the hydrophilic colloid medium has been applied in the form of a layer.

The hydrophilic film-forming binder or binder mixture into which the combination of said aromatic N-vinyl compound and photosensitive organic polyhalogen compound is dispersed preferably consists of or mainly contains a water-soluble film-forming colloid containing active hydrogen atoms as are present, e.g., in hydroxyl groups and amino groups. Both qualitative characterization and quantitative determination of active hydrogen can be carried out by the procedure known as the Zerewitinoff active hydrogen determination. Hardenable hydrophilic colloids containing active hydrogen atoms are, e.g., polyvinyl alcohol, polyacrylamide or gelatin, and other film or stratum-forming protein type colloids.

In the present invention best results are obtained with aldehyde-hardenable hydrophilic water-soluble colloids that possess the property of sol-gel transformation such as gelatin.

In the two modes of operation the recording layer contains the N-vinylcarbazole and carbon tetrabromide in a preferred molar range of 40:60 to 75:25.

The hardenable hydrophilic colloid binder is present for preferably 60 parts by weight with respect to 100 parts by weight of the mixture of N-vinylcarbazole and carbon tetrabromide.

According to a preferred embodiment for preparing the recording material the carbon tetrabromide before its incorporation into the coating composition is first dissolved in a high-boiling organic liquid, e.g. ethylene glycol monomethyl ether, and in that state dispersed in the hydrophilic colloid medium in which it comes in intimate contact with the aromatic N-vinyl compound.

The hydrogen bromide acceptor, which is preferably a spectral sensitizing dye base such as a styryl dye base, is incorporated preferably into the recording layer composition in the form of a solution in a solvent that is miscible with water so that it becomes very homogeneously distributed throughout the hydrophilic colloid and can come in intimate contact with the complex formed by the carbon tetrabromide and N-vinylcarbazole compound.

The molar ratio of hydrogen bromide acceptor such as a styryl dye base to photosensitive carbon tetrabromide is preferably in the range of 0.0001 to 0.01.

In the absence of any spectral sensitizing agent the recording layer has an inherent sensitivity to ultra-violet radiation. The presence of a spectral sensitizing agent such as a styryl dye base extends that spectral sensitivity into the visible spectrum, so that it is not necessary to apply an ultra-violet radiation source in the initial image-wise exposure.

A survey of suitable sensitizing agents for the photosensitive compositions used according to the present invention is given in the French Patent Specification 1,574,740 and in the U.S. Pat. No. 3,503,745.

Preference is given to the use of so-called spectrally sensitizing dye bases, more particularly those of the styryl and azastyryl type, e.g. 4-(p-dimethylaminostyryl)-quinoline and 2-(p-dimethylaminostyryl)-quinoline.

These dye bases yield dye salts that are good red sensitizers for the photopolymerization of aromatic N-vinyl compounds (see Yamada et al.; Camera Speed Photopolymerization System - Part II, Dye-sensitization and Latensification in the Basic Photopolymerization Emulsion - Preprints SPSE Congress, Los Angeles, May 12-16 (1969)).

The photosensitive coating composition can be applied to any type of support known from the photographic art, e.g. a transparent resin support and a transparent or opaque paper support. Optionally the support is provided with a subbing layer known in the art for hydrophilic colloid layers such as gelatin colloid layers.

The present invention is further illustrated by the following examples.

The percentages and ratios are by weight unless otherwise indicated.

EXAMPLE 1

Preparation of the recording material

64 g of gelatin were dissolved at 50°C in 240 ml of water and to this solution 2 ml of a 5% aqueous solution of the wetting agent TERGITOL 4 (7-ethyl-2-methyl-4-undecanol ester of sodium hydrogen sulphate of Union Carbide and Carbon, New York, U.S.A.) and 50 g of N-vinylcarbazole were added in a high speed mixer. After intensively mixing for 8 min. the temperature of the mixture reached 72°C.

To the thus obtained mixture 50 g of carbon tetrabromide dissolved in 30 ml of ethylene glycol monomethylether, 2 ml of tricresyl phosphate and 1.5 g of a naphthalene sulphonate as dispersing agent were added. High speed mixing was continued for 2 min.

To the obtained dispersion 30 mg of 2-[p-(N,N-dimethylaminostyryl)quinoline was added together with 1 ml of a 5% aqueous solution of mucochloric acid and 20 ml of a 11.7% solution of saponine in a mixture of ethanol/water (1:4 by volume). Finally an amount of water was added so as to obtain 1000 g of coating composition. This coating composition was applied to barytacoated paper at 35°C and at a coverage of 120 g per sq.m.

Recording and processing

The photosensitive recording layer held in contact with a transparent printed text original was exposed for 5 sec. through said original with a 1000 W ultra-violet lamp held at a distance of 10 cm. A negative weak print-out image was formed.

The image-wise exposed recording material was then subjected to an overall exposure for 5 sec. with incandescent bulbs (together representing 1000 W) placed at a distance of 10 cm.

Thereupon the recording material was heated for 10 sec. at 150°C by contacting it with a hot glazing plate.

A contour line image of the printed text representing almost white contour lines on a grey background was obtained.

EXAMPLE 2

The preparation of the recording material was the same as described in Example 1.

Exposure and processing were the same as described in Example 1 with the proviso that the image-wise exposure proceeded with incandescent lamps (together representing 1000 W) placed at a distance of 10 cm and imagewise irradiating the recording layer for 50 sec.

The contour line image was of the same quality as that obtained in Example 1.

By shortening the image-wise exposure to a period of 10 sec and overall exposing for only 5 sec. a contour line image was obtained, wherein the width of the contour lines was reduced markedly.

EXAMPLE 3

Preparation of the recording material

To a photographic paper support a subbing layer was applied in a ratio of 45 g per sq.m from the following composition:

gelatin	30 g
11.7 % solution of saponine in a mixture of ethanol/water (1:4 by volume)	5 ml
5 % aqueous solution of a 50:50 mixture of the wetting agents having the following formulae:	
$H_{17}C_{18}-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_8\text{OH}$	
$H_{17}C_{18}-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_8\text{OCH}_3-\text{COOH}$	5 ml
water to	1000 g

The coating composition of the photosensitive layer was prepared as follows

64 g of gelatin were dissolved at 50°C in 240 ml of water and to this solution 1 ml of a 5% aqueous solution of the wetting agent TERGITOL 4 and 50 g of N-vinylcarbazole were added in a high speed mixer. After intensively mixing for 5 min. a solution of 50 g of carbon tetrabromide in 30 ml of ethylene glycol monomethyl ether was added together with 10 ml of a 15% aqueous

solution of a naphthalene sulphonate as a dispersing agent.

High-speed mixing was continued for 2 min. during which period of time the temperature reached 72°C.

The obtained dispersion was cooled down to 40°C and then mixed by low speed stirring with the following ingredients:

tricresyl phosphate (plasticizing agent)	3 ml	10
0.6 % solution of 2-(p-dimethylamino-styryl)-quinoline in ethylene glycol monomethyl ether	5 ml	
11.7 % solution of saponine in a mixture of ethanol/water (1:4 by volume)	20 ml	15
water to	1000 g	

After a deaeration period of 1 hour the recording layer composition was coated at 90 g per sq.m to the subbing layer.

Recording and processing

The light-sensitive recording layer held in contact with a transparent line original was exposed for 2 sec. through said original with a 1000 W ultra-violet lamp held at a distance of 10 cm. A negative blue print-out image was formed.

The image-wise exposed material was then overall exposed for 3 sec. to light of an incandescent lamp of 1000 W.

Thereupon the recording material was heated for 10 sec at 140°C and then overall exposed for 10 sec with an ultra-violet lamp of 1000 W placed at a distance of 10 cm.

The thus exposed recording layer was then held under a jet of water having a temperature of 30°C. This treatment resulted in a black contour line copy of the original on a white image background.

We claim:

1. A photographic process for producing a contour line or border image against a contrasting background comprising the steps of:

1. imagewise exposing a recording layer, containing particles of intimately mixed N-vinylcarbazole and carbon tetrabromide that are in effective contact with a styryl dye base and are dispersed in a hardenable hydrophilic colloid binder to actinic or ultraviolet light until a distinctly visible print-out image of a poly-N-vinylcarbazole dye is formed within said exposed areas, said print-out dye image being incidentally surrounded by a visible narrow

border image having a color different from that of said print-out image;

2. uniformly exposing the imagewise exposed layer to actinic light until coloration appears in the originally unexposed background areas and the coloration in the originally exposed image areas is intensified, said narrow border image being substantially unaffected by such uniform exposure; and

3. uniformly heating said material in the range of about 100°-150°C until the coloration of said border image is substantially weakened but without substantially weakening the coloration produced in the initial image and background areas, whereby said border image appears as a weakly colored image against a more strongly colored background.

2. The process of claim 1 wherein said recording layer is carried on a support of a coloration contrasting with the color of the weakened border image and including the further step of subjecting the layer after step (3) to a washing off step to remove all of the layer except said border image.

3. The process of claim 2 wherein said washing off step is with water.

4. The process of claim 2 wherein following said heating step (3) but before said washing off step, said layer is exposed to ultraviolet radiation to darken the coloration of said border image without rendering said border image susceptible to removal in said washing off step.

5. A photographic process according to claim 1, wherein the recording layer incorporates coloring matter in the form of at least one dye or colored pigment particles.

6. A photographic process according to claim 1, wherein the dye base is a 4-(p-dimethylaminostyryl)-quinoline or 2-(p-dimethylaminostyryl)-quinoline.

7. A photographic process according to claim 1, wherein the hydrophilic colloid binder is gelatin.

8. A process according to claim 1, wherein the recording layer contains N-vinylcarbazole and carbon tetrabromide in a molar range of 40:60 to 75:25.

9. A process according to claim 1, wherein the recording layer contains 60 parts by weight of hardenable hydrophilic colloid binder with respect to 100 parts by weight of the mixture of N-vinylcarbazole and carbon tetrabromide.

10. A process according to claim 1, wherein the molar ratio of dye base to photosensitive carbon tetrabromide is in the range of 0.0001 to 0.01.

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