United States Patent

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[54] METHOD OF PRODUCING PHOTOGRAPHIC IMAGES BY RAPID PROCESSING

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[51] **Int. Cl.** **G03c 5/30,** G03c 1/78, G03c 1/06

[58] **Field of Search** ..... 96/87, 67, 66, 48 QP, 95, 50

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[57] **ABSTRACT**

Significant improvement in gradation, relative speed, and maximum density is obtained in a method of rapidly photographically developing an imagewise exposed light-sensitive photographic material comprising a hydrophobic film support and a rapidly developable silver halide emulsion layer wherein the silver halide consists of at least about 90 percent silver chloride, is developed with an aqueous processing solution in the presence of a photographic developing agent for a time of less than 15 seconds, provided at least one water permeable layer formed essentially of a hydrophilic colloid is interposed between the film support and the emulsion layer and in direct contact with the emulsion layer, the total weight of such water permeable layers being at least about 2 grams per square meter up to about 8 gm/sq. m. Preferably the colloid is proteinaceous and preferably the developed photographic material is passed in succession through stabilizing, fixing, and rinsing baths, remaining in contact with each less than about 15 seconds. An optimum time of contact for each processing step is about 2–8 seconds.

12 Claims, No Drawings

METHOD OF PRODUCING PHOTOGRAPHIC IMAGES BY RAPID PROCESSING

The present invention relates to rapid processing of photographic light-sensitive material comprising a hydrophobic supporting member and a rapidly developable silver halide emulsion layer applied thereto.

It has now been found that in carrying out said processing a considerable increase of the gradation and of the maximum density of the image produced as well as a sensitivity gain of the reproduction system involved can be obtained by applying a hydrophilic water-permeable intermediate layer having a weight comprised between 2 and 8 g. per sq./m. between the silver halide emulsion layer and the hydrophobic supporting member. This intermediate layer is very different from a usual hydrophilic colloid subbing layer having a weight of about 0.5 g. per sq./m. The presence of such a subbing layer does not result in obtaining the favorable effects of the present invention referred to above as will be shown by means of a comparison described in the specific example given hereinafter.

Thus, the present invention relates to a method of producing photographic images by rapid processing an image-wise exposed photographic material comprising a hydrophobic supporting member and a rapidly developable silver halide emulsion layer, wherein a hydrophilic water-permeable intermediate layer having a weight comprised between 2 and 8 g. per sq./m. is present between the silver halide emulsion layer and the hydrophobic supporting member.

The present invention is limited to rapid processing. This means that each of the processing steps wherein an aqueous processing liquid is applied takes less than 15 seconds at ambient temperature. These processing steps always include a developing step. Additional processing steps and their order of application are, of course, dependent on the kind of the reproduction system involved. Additional processing steps of frequent occurrence are a development stopping step, a stabilizing step, a fixing step, a bleaching step and a rinsing step.

The present invention is further limited to the use of a rapidly developable silver halide emulsion layer. An emulsion layer of this type is characterized in that the latent image produced on image-wise exposure is fully developed within 10 seconds upon contact of the developing liquid with the image-wise exposed silver halide grains. Increasing the development energy by applying generally known techniques such as raising the temperature and the pH value of the developer and enlarging the concentration of the active ingredients of the developer, does not substantially affect the development rate of rapidly developable silver halide emulsion layers. Rapidly developable silver halide emulsions generally are pure silver chloride emulsions, or silver chlorobromide, silver chloroiodide or silver chloro-bromo-iodide emulsions having at least 90 mole percent of silver chloride. Emulsions of the rapidly developable type generally are fine-grain emulsions having an average silver halide grain size of between 1 and 3 microns.

The favorable effects of the method of the present invention probably can be explained in that the presence of the intermediate layer permits the aqueous processing liquid(s) to reach the silver halide grains of the emulsion layer more quickly, whereby a better processing will be achieved in the short time available.

A thinner intermediate layer having a weight of less than 2 g. per sq./m. does not result in obtaining the favorable effects of the present invention, as has already been mentioned above and will be shown in the specific example. A thicker intermediate layer having a weight of more than 8 g. per sq./m. results in a less good adherence of the silver halide emulsion layer to the hydrophobic supporting member.

The hydrophilic water-permeable intermediate layer generally is a layer comprising a hydrophilic colloid binder. Suitable binders are proteinaceous colloids, e.g., gelatin and casein. The hydrophilic colloid layer may be applied according to whatever suitable coating technique. According the present invention it is even possible to apply two or even more hydrophilic water-permeable intermediate layers, which may

be of the same or of a different type, provided that the total weight of all the intermediate layers is comprised between the 2 and 8 g., limit per sq./m. required according to the present invention. The hydrophilic colloid binder may be hardened to some extent whereby the effects of the present invention often become still more pronounced, and also the physical properties of the intermediate layer are improved. The hardener has to be chosen with regard to the nature of the hydrophilic colloid binder. It is also possible to apply latent hardeners, which are effective only in an alkaline medium, and even to use a hydrophilic colloid binder having latent hardening properties per se, i.e., a binder which is hardened when brought in an alkaline medium, e.g., the developing medium. The hydrophilic water-permeable intermediate layer may comprise additional usual ingredients, e.g., latices, softening agents, antihalation dyes, developing agents, preservatives for developing agents, development accelerators, stabilizing agents, fog-inhibiting agents, etc.

The hydrophobic supporting member of the photographic material for use in carrying out the method of the present invention may be whatever hydrophobic support having sufficient mechanical strength. So a paper support having been provided at the emulsion side only or on both sides with a hydrophobic layer may be used. However, preferably a hydrophobic film support will be used, e.g., a support of a cellulose ester, e.g., cellulose triacetate, or a polyester support, e.g., a biaxially stretched polyethylene terephthalate support. The hydrophobic supporting member may be nontransparent, translucent or transparent, but preferably is transparent, since the copies produced according to the method of the present invention are preferably used as intermediates for making reproductions according to the transmitted light method. The hydrophobic supporting member may be provided with one or more layers at the rear side and one or more subbing layers at the front side before the hydrophilic water-permeable intermediate layer is applied. This or these layer(s) may comprise dyestuffs or pigments, a matting agent providing surface roughness, and/or substance or substances providing antistatic properties.

The silver halide emulsion layer applied on top of the hydrophilic water-permeable intermediate layer is a rapidly developable silver halide emulsion layer. Although it is a preferred embodiment of the present invention to apply the emulsion layer only on one side of the hydrophobic supporting member, it is also possible to apply an emulsion layer on both sides of the support provided the latter is a transparent support. It is also possible to have present two or more silver halide emulsion layers on each other, dependent on the kind of the reproduction system. The silver halide emulsion layer may comprise all kinds of ingredients usual in the art, e.g., developing compounds such as hydroquinone, a 3-pyrazolidinone developing compound and a p-amino-phenol developing compound or mixtures of at least two of these three types of developing compounds, further preservatives for developing compounds, development accelerators, stabilizing agents, fog-inhibitors, sensitizers, color couplers, hardeners, softening agents, latices, matting agents, coating aids, etc. On top of the photographic material a protective layer may be provided as generally known in the art.

In carrying out the method of the present invention, each of the processing steps wherein an aqueous processing liquid is applied takes less than 15 seconds at ambient temperature and preferably lasts from 2 to 8 seconds. This processing time is the period of time elapsing from the beginning of a processing step to the end of this step, i.e., when a stop-treatment or another processing step starts. This period of time mostly is somewhat longer than the period of time during which the processing liquid is really applied, except for the rinsing step which has to be considered as being finished when no further amount of aqueous rinsing liquid is supplied anymore.

Preferably the method of the present invention is carried out in an automatic compact processing apparatus, in which the photographic material may be guided automatically and at

a constant speed from one processing unit to the other in such a way that the processing time in each processing unit does not last longer than 15 seconds and preferably only lasts from 2 to 8 seconds. The processing liquids may be applied according to whatever technique conveniently known in the art, e.g., by dipping the photographic material in the processing liquid, o by applying this liquid by means of a licking roller, by spraying, or from a pod which is ruptured at the moment the processing liquid will be spread all over the photographic material. In carrying out the method of the present invention in an automatic processing unit it is also possible to keep the photographic material motionless and to apply the successive processing liquids automatically. The exposure unit may form part of the processing apparatus or may be mounted separately.

Although the method of the present invention may be applied in whatever type of photographic black and white or color reproduction system in which a photographic material is used comprising a hydrophobic supporting member and a rapidly developable silver halide emulsion layer, it is, however, preferably used in producing black and white images according to the so-called four-bath stabilization process, which comprises the successive processing steps of developing, stabilizing, fixing and rinsing the image-wise exposed photographic silver halide material. This process as well as suitable photographic materials for use in carrying out this process will be described in detail in the further part of the description

In carrying out this preferred embodiment of the method of the present invention, a light-sensitive material is used comprising a rapidly developable silver halide emulsion layer on top of a hydrophobic support member and further comprising a hydrophilic water-permeable layer having a weight of from 2 to 8 g. per sq./m. between the emulsion layer and the hydrophobic support member.

The silver halide emulsion layer preferably is a silver chloride, a silver chloro-bromide, a silver chloro-iodide, or a silver chloro-bromo-iodide emulsion layer, silver halide emulsions with a rather strong gradation for the reproduction of line work are preferably used, although silver halide emulsions having a softer gradation and being suited for the reproduction of continuous tone originals may be used too. Silver halide emulsions of the type normally used for the registration of an X-ray pattern or a pattern of a radioactive radiation are suitable too. In carrying out this preferred embodiment of the present invention it may be advantageous for some applications to employ a silver halide emulsion layer of such a type that the contrast of the developed image depends on the wavelength of the light that is used for the image-wise exposure. For more particulars on silver halide emulsions of this type reference is made to the published Dutch Patent application No. 6,805,450 filed Apr. 18, 1968 by Gevaert-Agfa N.V.

The silver halide emulsion layer, preferably being a gelatino silver halide emulsion layer, is applied to a support of a preferably transparent hydrophobic synthetic polymeric material. Generally the support has to be provided with one or more suitable subbing layer(s) for ensuring a good adherence of the light-sensitive silver halide emulsion layer to the support sheet. Between the occasionally subbed support and the silver halide emulsion layer a hydrophilic water-permeable intermediate layer is present having a weight of from 2 to 8 g., per sq./m. and having been described detailedly above. The light-sensitive material preferably comprises an amount of silver halide equivalent to from about 1 to about 20 g. of silver nitrate per sq./m.

The light-sensitive material may comprise one or more usual auxiliary layers such as an antihalation layer, an antistatic layer, a protective layer, etc. The light-sensitive material may further comprise any kind of usual ingredients and coating aids. Into the silver halide emulsion layer and/or into another water-permeable layer preferably one or more developing substances are incorporated. Developing substances that have proved to be especially suitable for the purpose of this preferred embodiment are hydroquinones and 3-pyrazolidinone developing compounds. These types of developing compounds are generally known in the art and thus need no further explanation. Preferably both types of developing compounds are incorporated into the light-sensitive material together. Mostly hydroquinone and/or an alkylated hydroquinone is applied in an amount of from about 200 mg. to about 3 g. per sq./m., and the 3-pyrazolidinone developing compound in an amount of from about 50 to about 800 mg. per sq./m. The hydroquinone developing compound is mostly incorporated into the silver halide emulsion layer itself, whereas the 3-pyrazolidinone developing substance preferably is incorporated into the silver halide emulsion layer and/or into a layer on top of the silver halide emulsion layer. In carrying out the specific embodiment of the present invention now described, it is even preferable to incorporate the total amount of developing substance(s) into the light-sensitive material. Normally also preservatives for the developing substances present are incorporated into the light-sensitive material. As suitable preservatives may be mentioned water-soluble organic and inorganic bisulphites such as formaldehyde-bisulphite and potassium metabisulphite. Other usual ingredients and coating aids for one or more water-permeable layers of the light-sensitive material are stabilizers, sensitizers (chemical and/or optical), hardeners, softening agents, development accelerators, antistaining agents, latices, dispersing agents, etc.

Depending on the kind of the original, of the ray pattern and of the light-sensitive material used, the image-wise exposure of the light-sensitive material can occur by transmitted light or in reflex, in contact or not, in a camera with lenses, outside of a camera by means of a common lamp or of a fluorescent lamp or in a cassette provided with reinforcing screens. When the silver halide emulsion layer is of the type of which the contrast depends on the wave length of the light used for the image-wise exposure (see the published Dutch Patent application No. 6,805,450 filed Apr. 18, 1968 by Gevaert-Agfa N.V. referred to above), said wave length can be chosen according to the kind of the original and of the desired contrast of the print. The exposure station may be coupled to the processing station but it may also be separate therefrom.

According to this specific embodiment of the present invention the image-wise exposed light-sensitive material may be transported automatically and at a substantially constant speed for processing e.g., by means of rollers and guide ways. First it may be transported through a developing or activating station. Such a station may consist of a tray containing the developing or activating liquid through which the light-sensitive material is transported, in other words the light-sensitive material may be wetted by dipping. The developing or activating liquid can also be applied by means of a lick-roller taking up said liquid on its surface and applying it uniformly to the whole emulsion side of the light-sensitive material. The developing or activating liquid may also be comprised in a kind of bottle from which again and again an accurately measured amount is supplied to the light-sensitive material, e.g., by spraying or by uniform spreading. Further, the developing or activating liquid may be contained in a pod, which is embodied in the light-sensitive material or is applied hereto later on, and which at the development stage is ruptured, whereupon the content is uniformly spread over the part of the photographic material to be developed. The term developing or activating station thus is very broad and encompasses any way of carrying out the development of the light-sensitive material. Also the stabilizing station as well as all further treating stations have to be taken in their broad sense. For a detailed description of different suitable practical embodiments for these processing stations reference is made to the detailed description given hereabove with respect to the developing or activating station. As to the processing time in each of the processing stations, reference may be made to the detailed description given hereinbefore.

The development applied in carrying out this preferred embodiment of the method of the present invention preferably is

an energetic surface development. The high energy is required in order to allow the development to proceed quickly and may be obtained by properly alkalizing the developing or activating liquid (pH 10-12) and/or by using (a) high-energy developing substance(s) or a combination of developing substances, which as a consequence of their superadditive action is very energetic, such as a combination of a hydroquinone and a 3-pyrazolidinone developing substance as already referred to above. The concentration of the alkaline substance(s) and developing substance(s) in the developing liquid is generally known in the art and needs no further explanation. Suitable alkaline substances for the developing or activating liquid are sodium hydroxide, sodium carbonate, trisodium phosphate and rather strong organic alkaline substances. The developing or activating liquid further may comprise usual ingredients such as preservatives, compounds releasing halide ions, toning agents and thickeners, whereby a developing or activating paste may be obtained.

As already indicated above, it is a preferred embodiment to incorporate at least part and preferably even the total amount of developing substance(s) into the light-sensitive material. In this way the developer may be reduced to a mere aqueous alkaline liquid, which is substantially free from developing substance(s) and consequently is better keepable. Such an alkaline liquid is also called an activator. However, even if an energetic development is carried out along the lines set out in this paragraph, the gradation, the maximum density as well as the sensitivity will be considerably lower if no hydrophilic water-permeable intermediate layer according to the instant invention is present, as will clearly appear from the specific example given hereinafter.

The stabilizing liquid for carrying out the next processing step is an aqueous liquid containing a suitable stabilizing agent. By "stabilizing" agent any compound is understood that is capable of converting light-sensitive silver halide grains in substantially light-intensitive complexes, which are water-insoluble or substantially water-soluble, but in the latter case they are usually not or not completely removed from the developed and stabilized silver halide emulsion layer by normal washing. Suitable stabilizing agents of the class that forms water-insoluble light-intensitive complexes with silver halide grains are compounds belonging to the class of compounds represented by the formula RSH, wherein R is an aliphatic, aromatic, or heterocyclic radical. Compounds of this class include thioglycolic acid, monothiohydroquinone, thiosalicylic acid, etc. Suitable stabilizing agents that form substantially water-soluble complexes with silver halide are thiosemicarbazide, acetylthiourea, sulphonated thioureas, sulphonated thiosemicarbazides, allylthiourea and water-soluble thiocyanates. The water-soluble thiocyanates are the best suited compounds for the purpose of the present embodiment. Especially potassium and ammonium thiocyanate are very suitable. The stabilizing solution is an aqueous solution comprising preferably of from about 20 to about 300 g. of stabilizing agent per litre. Preferably this solution has slightly been acidified. The stabilizing solution may furthermore contain any usual ingredients such as a preservative for the image produced etc.

After its treatment in the stabilizing station the light-sensitive material is treated in a normal fixing station. The treatment in a fixing station comprises a treatment with an aqueous fixer, i.e., an aqueous solution of a compound forming with silver halide water-soluble complexes, which are removed from the developed silver halide emulsion layer rather easily and completely by normal washing. Suitable fixing agents are the water-soluble thiosulphates, especially ammonium thiosulphate and sodium thiosulphate. The fixing agent is mostly present in an amount of from 50 to 300 g. per litre of fixer. Just as the stabilizing solution the fixer in most cases is slightly acidic. It may comprise some further ingredients such as sulphites and bisulphites.

Finally the light-sensitive material is rinsed in order to eliminate the silver halide complexes formed. Mostly this is done by means of water, preferably common tap water to which a calcium-sequestering compound as been added, e.g., the trisodium salt of ethylenediamine-tetraacetic acid, demineralized or distilled water, which may contain wetting agents. Rinsing can proceed according to any usual technique.

For the treatment in the various processing stations the image-wise exposed silver halide material is preferably transported automatically and at a substantially constant rate. During this transport the successive processing steps are carried out. In addition the four essential processing steps, other pretreatments, intermediate treatments or after-treatments may be applied in carrying out this embodiment of the present invention. So a development-stopping treatment may be inserted. It is often advantageous to eliminate the surplus liquid in one or more of the processing steps, e.g., by means of a doctor knife or a pair of pressure rollers between which the light-sensitive material is led. After rinsing, the light-sensitive material may be dried yet, e.g., by means of a device blowing hot air, or by bringing the material in contact with a heated plate. In most cases, however, no additional treatments are carried out and the total processing remains limited to the essential processing steps described above. The four processing stations may be arranged separately but mostly are grouped in a compact unit wherein the light-sensitive material is automatically carried from one unit to another at a constant speed. Preferably the units just consist of a tray containing the liquid through which the light-sensitive material is transported.

The photographic copies obtained according to this specific embodiment of the present invention have excellent keeping qualities and are not tacky. They are very suited as intermediates for producing contact copies by the transmitted light method.

The method of the present invention and the favorable results obtained are now illustrated by the following specific example.

EXAMPLE

A cellulose triacetate film support was provided in order with a gelatine-cellulose nitrate subbing layer, a gelatin intermediate layer having a dry weight of 4.0 g. per sg./m., and a gelatino silver halide emulsion layer containing hydroquinone and 1-phenyl-3-pyrazolidinone. The silver halide emulsion used was a rapidly developable silver chloro-bromo-iodide (98 mole percent chloride—1.8 mole percent bromide—0.2 mole percent iodide) emulsion, having an average grain size of about 1.8 micron and a gelatin silver nitrate ratio of 0.75. It was applied in such a way that per sq./m. 2 g. of hydroquinone, 0.3 g. of 1-phenyl-3-pyrazolidinone and an amount of silver halide equivalent to 5.0 g. of silver nitrate were present. On top of the silver halide emulsion layer a gelatin antistress layer was applied in a proportion of 1.5 g. of gelatin per sq./m.

The light-sensitive material thus obtained was image-wise exposed to a line original, whereafter it was guided in a compact automatic processing unit at a constant speed in order through the following 4 processing liquids at room temperature:

1. an activator liquid

sodium hydroxide	30 g.
sodium sulfite	50 g.
potassium bromide	2 g.
water to make	1,000 cc.

2. a stabilizing liquid:

ammonium thiocyanate	250 g.
sodium metabisulfite	20 g.
water to make	1,000 cc.
sulfuric acid in order to bring the pH to 4.5	

3. a fixer:

sodium thiosulfate	200 g.
potassium metabilsulfite	25 g.
water to make	1,000 cc.

4. a rinsing liquid consisting of demineralized water.

The total processing time amounted to 16 seconds (i.e., 4 seconds for each of the processing liquids).

By proceeding according to the method of the present invention as described above a permanent and nontacky copy (copy A) was obtained. The photographic characteristics are listed in the table below.

By proceeding in an analogous manner with the only difference, however, that the gelatin intermediate layer was replaced by a thin gelatin subbing layer having a dry weight of 0.5 g. per sq./m. a lower sensitivity, gradation and maximum density were obtained as clearly appearing from the table below (copy B).

TABLE

	gradation (γ)	relative speed	maximum density	fog
copy A	4.42	126	3.86	0.05
copy B	3.26	100	3.46	0.04

We claim:

1. In a rapid method of producing photographic images in which an imagewise exposed light-sensitive photographic material comprising a hydrophobic film support and a rapidly developable silver halide emulsion layer wherein the silver halide consists of at least about 90 percent silver chloride, is contacted with an aqueous solution in the presence of a photographic developing agent for silver halide for a time of less than 15 seconds to develop a photographic image therein, the improvement wherein said photographic material includes at least one water permeable layer consisting essentially of a hydrophilic colloid interposed between said film support and said silver halide emulsion layer an in direct contact with said emulsion layer, the total weight of such water-permeable layers being about 2–8 g./sq. m.

2. Method according to claim 1, wherein rapid processing comprises the successive processing steps of developing said developed photographic material is passed through stabilizing, fixing and rinsing baths in succession, said material remaining in contact with each bath less than 15 sec.

3. Method according to claim 2, wherein said successive processing steps are carried out at ambient temperature.

4. Method according to claim 3, wherein each processing step lasts from 2 to 8 seconds.

5. Method according to claim 2, wherein a water-soluble thiocyanate is used as the stabilizing agent in the stabilizing processing step.

6. Method according to claim 2, wherein the hydrophobic supporting member is a hydrophobic transparent film support.

7. Method according to claim 2, wherein the hydrophilic intermediate layer is a gelatin layer.

8. Method according to claim 2, wherein the average silver halide grain size of said emulsion is between 1 and 3 microns.

9. Method according to claim 2, wherein the light-sensitive photographic material contains a photographic developing agent in effective contact with the silver halide emulsion layer.

10. Method according to claim 9, wherein said developing substances are hydroquinone and a 3-pyrazolidinone developing substance.

11. Method according to claim 9, wherein the total amount of photographic developing agent is present in the photographic material and the exposed photographic material is developed by contact with an alkaline processing liquid substantially free from photographic developing agent.

12. The method of claim 1 wherein said hydrophilic colloid is a proteinaceous hydrophilic colloid.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,637,389 Dated January 25, 1972

Inventor(s) Emiel Alexander HOFMAN

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

Column 8, Claim 2, lines 4 & 5, cancel "rapid processing comprises the successive processing steps of developing".

Column 8, Claim 10, line 26, change "substances" to -- agents --.

Signed and sealed this 3rd day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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