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PROCESS FOR THE PRODUCTION OF PHOTOGRAPHIC IMAGES

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ABSTRACT OF THE DISCLOSURE

Positive photographic images consisting of a silver image and a vesicular image superimposed on the silver image are produced by imagewise exposure of a supported light-sensitive silver salt emulsion layer, photographic development in the presence of silver salt solvents while in contact with an image receiving layer, whereby the silver salt from the unexposed and undeveloped areas of the light-sensitive silver salt emulsion layer is transferred to the image receiving layer and reduced to form a silver image therein and treatment of the image receiving layer containing the said silver image with a compound which is decomposed by the image silver to form the vesicular image in accordance with the silver image.

The invention relates to a modification of the silver salt diffusion process for the production of photographic images, which consist of a silver image and a vesicle image superimposed on the silver image.

The production of vesicular images comprises light-scattering photographic materials containing a supported or self-supported layer having photolytic compounds dispersed therein, which upon exposure and development by heat treatment yield minute vesicles acting as light-scattering centers. The unexposed areas of the layer remain transparent. The vesicular image therefore appears dark in transmitted light but light when viewed in reflected light. The main disadvantage of vesicular photography is the low light sensitivity of the photographic compounds.

It is also known to produce photographic images which are composed of a silver image and a corresponding vesicular image by treating a silver image which has been produced in known manner with a compound which is decomposed by the silver image to form a vesicular image.

The particular advantage of this process is the high light sensitivity of the silver halide emulsion layers as compared with the poor light-sensitivity of the known materials used for the production of vesicular images.

In addition, a substantial increase in the density of the silver image produced in the photographic silver salt layers is achieved by this process by the superposition of the vesicular image. The process can therefore be carried out with layers which have a very low silver content, and the silver images produced which by themselves have insufficient density can be converted into images of normal density by superposition of the vesicular image.

It is among the objects of the invention to modify the process for the production of the combined vesicle and silver images in such a way that the silver image can be produced by the silver salt diffusion process.

We now have found a process for the production of photographic images consisting of a silver image and of a vesicle image superimposed on the silver image in a supported layer by treating the layer containing the image of finely divided silver with a compound which is decomposed by the silver image to produce a vesicle image, which comprises the steps of:

(a) imagewise exposure of a supported silver salt emulsion layer;

(b) development of the exposed layer in contact with an image-receiving layer in the presence of a solvent for the silver salt and reduction of the silver salt transferred from the unexposed and undeveloped parts of the silver salt emulsion layer into a silver image, and

(c) treatment of the image-receiving layer with a compound which is decomposed by the silver image in the image-receiving layer to form a vesicle image superimposed on the silver image.

In general the silver salt diffusion process steps of the process of the present invention are performed in known manner whereby, however, the details of the process steps and measures must, of course, be adapted to the subsequent step, i.e. the production of the vesicle image.

In the simplest method of carrying out the process according to the invention, the light-sensitive silver salt emulsion layer and the image-receiving layer are arranged on separate support. In this case, the silver salt diffusion process may be carried out under the usual conditions.

Since the vesicle image which is superimposed on the silver image has a high covering power, light-sensitive silver salt layers which have a relatively low silver salt content, in particular silver halide content, may be used. Suitable concentrations are in the region of about 0.1 to 0.3 g. of silver in the form of the silver salt per $m.^2$. Although the photographic development produces silver images of insufficient density which could not normally be used, the subsequent production of the vesicle image results in a combined image which has excellent covering power. When using such light-sensitive layers having low silver content, the concentration of the silver salt solvent must be lower than that normally applied in the silver salt diffusion process. Suitable solvent concentrations for the silver salt content indicated above are, for example, between 1 and 5 g. per l. of developer in the case of sodium thiosulfate.

For the process according to the invention, one may also use photographic materials which contain the light-sensitive layer and the image-receiving layer on a common support, whereby preferably the image-receiving layer is arranged on the support and the light-sensitive silver salt emulsion layer on the image-receiving layer. During processing of the exposed material, the silver salt emulsion layer may advantageously be washed off before the vesicle image is produced in the image-receiving layer. A suitable binding agent for such layers which can be washed off is e.g. unhardened or slightly hardened gelatin. An intermediate or separating layer, e.g. of alginates, may be arranged between the silver salt emulsion layer and the image-receiving layer. The binding agents and methods of procedure may be selected from those used in known processes.

The process becomes more complicated when the light-sensitive silver salt layer is arranged on the support and the receiving layer above it. When using this arrangement of layers one may, for example, first imagewise expose and briefly develop the material and then subject the developed material to ammonia vapour. A weakly covered positive silver image is then obtained in the image-receiving layer. Vesicle formation may then be effected e.g. by moistening the material with alcoholic hydrogen peroxide solution. Since the silver deposited in the receiving layer has a finer grain than the silver produced in the light-sensitive layer by reduction of the silver halide, it reacts more easily and more rapidly with hydrogen peroxide vapour. Moreover, this vapour first enters the receiving layer, with the result that the vesicles are formed only in this layer.

Processing may also be carried out by first developing with the usual developers used in the silver salt diffusion process, but these developers should preferably not contain potassium bromide. When using layers which have a low silver content it is sufficient to use a concentration of silver salt solvent of e.g. 1 to 5 g. of sodium thiosulfate per liter of developer bath. After development, the material is exposed to air for some time, which results in the formation of a visible yellow positive image consisting of finely divided silver in the image-receiving layer. The superimposed bubble image may then be produced e.g. by treatment with hydrogen peroxide at elevated temperature as will be described hereinafter. The optimum conditions for the process, such as concentration of active substances, moisture content of the layer temperature conditions, etc. can be determined by simple laboratory tests.

The receiving layers for the process according to the invention are advantageously layers which contain uniformly distributed development nuclei for the reduction of the transferred silver salt in suitable binders such as proteins, e.g. gelatin, albumin or casein, alginic acid or derivatives thereof, such as salts, esters or amides, starch or starch derivatives, cellulose or cellulose derivatives or synthetic film-forming substances. Suitable nuclei are known from the silver salt diffusion process, e.g. finely divided noble metals, in particular finely divided silver, or heavy metal sulfides or selenides such as silver sulfide and nickel sulfide, etc. If these nuclei catalyse the decomposition of the compound which forms the gas bubbles, care must be taken to ensure that their concentration is kept so low that no decomposition will take place. Otherwise, uniform fogging would occur due to formation of vesicles since the development nuclei are uniformly distributed in the layer. The concentration of the development nuclei may otherwise vary within wide limits. The optimum concentration depends on the nature of the nuclei and the conditions under which processing is carried out. Quantities of between 10^{-4} and 10^{-3} g./m.^{2} of receiving layer have been found to be sufficient.

Silver halide emulsion are preferably used as light-sensitive layers. Both silver chloride emulsions and silver bromide emulsions, as well as mixtures thereof which may contain up to about 10 mols percent of silver iodide are suitable. The emulsions may contain the silver halide in the form of fine or coarse grams e.g. in the case of ammonia emulsions. Suitable binders are e.g. gelatin or other synthetic or natural film-forming substances or mixtures thereof. Materials comprising such emulsion layers are processed in the usual manner.

The silver image obtained in the image-receiving layer is treated with a compound which is decomposed on the silver image to form gaseous products. Preferred are compounds which form oxygen upon decomposition for example hydrogen peroxide (H_2O_2). As to the vesicle forming reaction, we refer to Belgian Pat. No. 725,903 or U.S. application Ser. No. 748,420, now U.S. Pat. No. 3,650,755.

Treatment with the compound which forms vesicles, in particular hydrogen peroxide, can be performed in many different ways. For example, the image-receiving layer which contains the silver image may be covered with a fresh layer containing hydrogen peroxide, e.g. with a solution of polyvinyl chloride in butanone-(2) which contains hydrogen peroxide. After this layer has been applied, the material is dried and the bubbles are produced by heating. The image-receiving layer may also be treated with a hydrogen peroxide solution, e.g. an alcoholic solution of hydrogen peroxide.

The vesicle formation in the image-receiving layer is most advantageously achieved with hydrogen peroxide vapour. After about 30 seconds' treatment with saturated hydrogen peroxide vapour, the layer has taken up sufficient hydrogen peroxide. The treatment time depends, of course, on the treatment temperature and the concentration of the hydrogen peroxide vapour. Temperatures of 50° to 90° C. for example, are suitable.

According to a preferred embodiment, the image-receiving layer which contains the silver image is exposed to an atmosphere of water vapour at about 50° to 90° C. for about half a second to 5 seconds after the treatment with the hydrogen peroxide vapour. When this treatment with water vapour is carried out, the formation of the minute vesicles which proceeds relatively slowly with hydrogen peroxide treatment alone, then takes place very rapidly.

According to another preferred embodiment the image-receiving layer, bearing the silver image, is exposed to an alkaline water vapour atmosphere after the treatment with hydrogen peroxide. pH values of between 8 and 12 are suitable for this alkaline atmosphere. This can easily be achieved by adding small quantities of ammonia or vapours of volatile amines to the water vapour. The concentration of the alkaline additives is not critical. Quantities of between 0.1 and 5 volumes percent and preferably about 0.3 to 1 volume percent have generally been found sufficient.

The visible vesicles are formed by expansion of the originally formed gaseous reaction products. This is achieved by heating to temperatures of between 60 and 100° C. Formation of the vesicles is assisted by slightly softening the layer, e.g. by moistening it. This effect is achieved by the treatment with water vapour described above. The vesicles are very small. Minute vesicles are particularly advantageous since they form images of high density. Light-sensitive photographic materials which contain developer substances in the silver salt emulsion layer or in an auxiliary layer are also suitable for the process of the invention (see German application No. P–19–17–744). Since the final image, which consists of the silver image and the superimposed vesicle image, has a certain sensitivity to atmospheric moisture and aqueous baths, it is advisable to take suitable steps to stabilize it against moisture. Suitable methods are described in German applications Nos. P–18–15–143.4; P–19–00–540.1; or P–19–00–864.1.

EXAMPLE 1

A silver bromide gelatin emulsion of the following composition is applied to a support of polyethylene terephthalate:

20 ml. of a silver bromide gelatin emulsion which contains 5 mols percent of silver iodide based on the total silver halide content (silver halide content of 3% by weight gelatin content 6% by weight);
280 ml. of a 6% aqueous solution of a photographically inert gelatin;
5 ml. of a 7.5% aqueous solution of saponin;
1.5 ml. of a 30% aqueous solution of formaldehyde.

The silver halide emulsion layer is dried and overcoated by the following image-receiving layer:

200 ml. of a 4% aqueous solution of a photographically inert gelatin which contains about 3 mg. of colloidal silver sulfide;
4 ml. of a 7.5% aqueous solution of saponin;
0.5 ml. of a 30% aqueous solution of formaldehyde.

The material is dried. The two-layer material contains 0.2 g. of silver in the form of silver halide and about 10^{-4} g. of colloidal silver sulfide per m.^{2}.

The material is imagewise exposed and developed for one minute in a developer of the following composition:

3 g. of hydroquinone
1 g. of p-methylaminophenyl
13 g. of sodium sulfite sicc.
26 g. of sodium carbonate
1 g. of potassium bromide in 1 liter of water.

The developed layer is then subjected to an ammoniacal atmosphere for 30 seconds, washed for one minute and dried. A very weakly visible positive silver image is obtained.

Vesicle formation is effected by treating the layer with saturated hydrogen peroxide vapour at 70° C. for half a second.

A very powerful increase in density immediately occurs due to the formation of minute vesicles, the density in one area of the silver image, for example, being increased from 0.04 to 1.8 in focused light.

EXAMPLE 2

A casting solution of the following composition is applied to a support of cellulose triacetate to form a layer which contains development nuclei:

200 ml. of a 6% aqueous solution of a photographically inert gelatin containing about 10 mg. of colloidal silver selenide;
4 ml. of a 7.5% aqueous solution of saponin;
0.5 ml. of a 30% aqueous solution of formaldehyde.

The layer is dried and overcoated by silver halide emulsion of the following composition:

290 ml. of a 6% aqueous solution of a photographically inert gelatin;
10 ml. of a silver chloride gelatin emulsion (3% by weight of silver chloride-6% by weight of gelatin);
6.0 ml. of a 7.5% aqueous solution of saponin;
1.0 ml. of a 30% aqueous solution of formaldehyde.

The layer is dried. The two-layer material contains 0.1 g. of silver in the form of silver chloride and about 5×10^{-4} g. of colloidal silver selenide per m.^{2}.

The material is imagewise exposed and treated for 45 seconds with a developer solution of the following composition:

9 g. of hydroquinone
0.5 g. of 1-phenylpyrazolidone-3
120 g. of sodium sulfite sicc.
60 g. of sodium carbonate in 1 liter of water.

The material is then bathed for 20 seconds in 2% aqueous acetic acid, washed for one minute and dried. A hardly visible positive image is obtained. Vesicle formation takes place as in Example 1. A positive vesicle image of normal covering power having a density of 1.7 (in focused light) is obtained with a silver density of 0.05.

EXAMPLE 3

A photographic material consisting of a support of cellulose triacetate, a layer containing nuclei and above it a silver chloride gelatin emulsion layer as described in Example 2 is developed in the developer solution of Example 1 but which in addition contains 2 g. of sodium thiosulfate per liter as silver halide solvent. A hardly visible silver image is obtained. The process is then continued as described in Example 2. A positive vesicle image having a density of 1.5 (in focused light) is obtained with a silver density of 0.04.

EXAMPLE 4

The silver halide gelatin emulsion layer and the image-receiving layer containing nuclei described in Example 2 are each applied separately to separate cellulose triacetate supports. The emulsion layer contains 0.2 g. of silver (in the form of silver halide) and the nucleated layer contains about 8.10^{-4} of silver selenide per m.^{2}.

The light-sensitive silver halide emulsion layer is imagewise exposed and developed for 15 seconds in the developer described in Example 2. The emulsion layer still soaked with developer solution is then run through a pair of rollers while in contact with the dry image-receiving layer. After a contact time of 10 seconds, the layers are separated and the image-receiving layer is briefly dried. A barely visible positive silver image is found in the image-receiving layer. When this layer is dipped in 96% aqueous ethyl alcohol containing about 3% of hydrogen peroxide and maintained at a temperature of 60 to 70° C., a positive image having a density of 1.4 (in focused light) composed of the original weak silver image (density 0.04) and minute vesicles is formed after a few seconds.

We claim:

1. A process for the production of photographic images consisting of a silver image and an image superimposed on the silver image composed of visible vesicles, comprising the steps of
   (a) imagewise exposing a layer of an emulsion containing a silver salt having 0.1 to 0.3 g. of silver per square meter, said layer being on a support;
   (b) developing the exposed silver salt emulsion layer in the presence of a concentration of a thiosulfate as a silver salt solvent in the developer in an amount of between 1 and 5 g./l. and while in contact with an image-receiving layer containing uniformly distributed development nuclei for the silver salt;
   (c) treating the image-receiving layer containing a silver image with a compound which is decomposed by the silver image to form a superimposed image composed of visible vesicles.

2. The process of claim 1, wherein the light-sensitive silver salt emulsion layer and the image-receiving layer are arranged on separate supports and are brought into contact with each other before or during the development.

3. The process of claim 1, wherein the light-sensitive silver salt emulsion layer and the image-receiving layer are arranged on the same side of a common support.

4. The process of claim 3, wherein the image-receiving layer is arranged on the support and the light-sensitive silver salt emulsion layer is applied on to the image-receiving layer.

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