Patented Oct. 16, 1951

2,571,671

UNITED STATES PATENT OFFICE

2,571,671

PROCESS OF PRODUCING PHOTOGRAPHIC CONTRASTS

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No Drawing. Application February 8, 1947, Serial No. 727,310. In the Netherlands January 18, 1946

Section 1, Public Law 690, August 8, 1946.
Patent expires January 18, 1966

5 Claims. (Cl. 95—5)

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This invention relates to a method of producing photographic contrasts and more particularly to material sensitised by means of a photo-sensitive diazonium compound. It is particularly important for producing copies of sound-plus-picture films since it enables contrasts of different graduation to be obtained side by side on one and the same material.

It is known that photographic material sensitised by means of photo-sensitive diazonium compounds frequently yields contrasts the graduation of which leaves much to be desired. Thus, metallic images developed physically and obtained with the use of diazonium compounds and metal compounds reproducible in aqueous medium, such as mercurous salt, frequently have a gamma value of from 6 to 7, i. e., the maximum value of the gamma, that is to say the maximum value of the gradient of the characteristic curve of the material. Such a gamma value is very suitable for producing copies of sound recordings obtained by so-called variations in width and more particularly for copying sound tracks obtained by mechanical means (cf. French patent specification 817,850). This value is, however, far too high for producing copies of, for example, image negatives and sound recordings obtained by variations in depth.

This graduation may be decreased by variation of the composition of the liquid by means of which the photographic material is sensitised, or of the developer, but more particularly by variation of the time of development. If, however, it is desired thus to obtain a gamma value of about 2 or lower as is desired, for example, for copying image negatives, which themselves have in most cases been developed up to a gamma value of from 0.5 to 0.8, then the difficulty arises that the maximum blackening and the colour of the contrast leaves much to be desired. Furthermore, a short time of development, for example shorter than from 1 to 2 minutes, is objectionable since working in a reproducible manner is difficult in the case of short development times. Furthermore, the said means of reducing the gamma are not very appropriate for obtaining contrasts of different graduations side by side on one and the same piece of material.

Even if the graduation of a copy is reduced by placing a fine grate during copying between the image negative to be copied and the copying material (cf. French patent specification 848,531), then in many cases there arises the difficulty that sufficiently great reduction of the gamma is obtained at the expense of the maximum blackening. Furthermore, this method of reducing the gamma has the disadvantage that the copies obtained exhibit a grate structure and this may lead to annoyances, such as granular structure, in projecting the copy.

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Even when a so-called inner grate is used, which need not necessarily exhibit the disadvantage of an unduly coarse grate structure which is inherent in an outer grate, sufficient reduction of the gamma is not always possible. An inner grate is obtained by providing in the photographic material local variations in the concentration of the photo-sensitive substance by including in the material a substance dispersed colloidally (cf. French patent specification 841,911).

Furthermore, a method of controlling gradation by varying the wavelength of the photochemically active light has also been described (cf. French patent specification 697,340). A reduction of the gamma cannot always be obtained this way in practice.

The present invention relates to an entirely new method of gamma control by which it is possible, if desired in conjunction with other methods of influencing the gamma, to obtain control of the gamma value within very broad limits while retaining sufficient maximum blackening and avoiding grate structure.

In fact, in accordance with the invention it has been found that in the above-mentioned photographic material the gamma value is dependent on the moisture content of the material at the moment of exposure.

According to the invention, in the case of such a material having a moisture-dependent gamma value the gradation is controlled by adjustment of the moisture content of the material at the moment of the exposure. The term "material having a moisture-dependent gamma value" is defined as a material in which variation in the moisture content with otherwise unvaried conditions may bring about at least a variation in the relation 1:1 in the gradient of the portion of the characteristic curve exhibiting blackenings between 0.4 and 1.5. As a matter of course, for comparison tests this gradient should be measured with the same blackenings.

It should be noted that, in addition to and simultaneously with the method of gamma control according to the invention, other methods of influencing the gamma remain applicable. For the grate methods this is readily evident but this applies also to methods consisting in varying the composition of the developer and the sensitising liquid, the time of development and the wave-

length of the exposure. Combining the method according to the invention with one of the last-mentioned methods permits in many cases of obtaining a very generous variation of the gamma value while retaining sufficient maximum blackening and avoiding grate structure.

When the invention is used highly satisfactory results may be obtained in producing photographic contrasts and more particularly metallic images with the use of photographic material sensitised by means of a photo-sensitive diazonium compound.

This applies particularly to the production of photographic metal contrasts developed physically with the use of a photo-sensitive oxydiazonium compound and mercurous salt. Contrasts thus obtained are grainless, that is to say that the grains are smaller than 1 micron. If a film of regenerated cellulose which has been impregnated with a photo-sensitive oxydiazonium compound and mercurous salt is exposed in the dry state and subsequently developed physically to exhibit a neutral grey colour, a maximum gamma value of about 8 is readily obtained. Exposing the same material in the moist state results in a gamma value of from 1.5 to 2 while retaining sufficient maximum blackening and a neutral grey colour. The material is thus highly adapted, for example, for producing image positives adapted for projection.

The method according to the invention underlies the idea of preparing photographic material in which upon exposure, in addition to the reaction leading to the final photographic contrast, a competitive additional reaction occurs which is not contributive to the formation of the image, and of controlling the contrast by suppressing or facilitating one of the said reactions with respect to the other. According to the invention the means of suppressing or facilitating one of the reactions consists in adjusting the moisture content.

In producing metal contrasts by means of the above-mentioned mercuro-oxydiazonium-cellulose material the main reaction presumably consists in the formation of metallic mercury from the light-decomposition product of the diazonium compound and mercurous ions so that mercury-metal-germs are produced which may be developed. The additional reaction probably consists in the formation of colouring matter from the light-decomposition product having a diazonium compound which is not decomposed. When the moisture content is increased, the additional reaction is probably enhanced at the expense of the main reaction with the result that the contrast is weakened.

It should be noted that, such as, for example, with this mercuro-oxydiazonium-cellulose material, gamma control within sufficiently broad limits is possible only if the intensity of the exposure is not unduly great; the proper intensity may be readily determined empirically.

A very important advantage of the invention is that it enables contrasts of different graduations to be produced side by side on one and the same material by providing for the exposure required for the obtainment of contrasts of different graduation, to be effected at different states of humidity of the photo-sensitive material. Consequently, the invention is very important for producing copies of sound films, which exhibit images and sound recordings on one and the same film and which require different gradations for picture and sound. With the aid of photographic material as above referred to, consisting of a transparent carrier, for example of regenerated cellulose, treated with a photo-sensitive diazonium compound and mercurous salt, which material is developed physically subsequent to the exposure, it is possible, for example, to produce copies of sound film having an image of low gamma value and a sound recording of high gamma value. For this purpose the picture strip and the sound record are copied in different states of humidity of the material. The development of the exposed copy is preferably effected in one process. Copies thus obtained are inexpensive and of excellent quality.

The invention further permits of obtaining, in the case of a picture film, different gradations for successive series of images. It is possible, for example, with successive scenes to obtain the gradation which is most desirable for each scene by providing for a suitable state of humidity in copying.

A further application of the possibility of providing different gradations on one and the same material is, in the case of one image, to give different gradations to different portions. In copying a portrait or a landscape, for example, the background and the air respectively may be given different gradations.

The relationship between the moisture content of the photographic material and the gamma value obtained is dependent on various factors such as the nature of the carrier, the quantity of the photo-sensitive compound in the carrier, etc. This may, however, be determined empirically.

For obtaining reproducible results a reproducible adjustment of the moisture content is of great importance. A very reliable adjustment of the moisture content is obtained by bringing the material into a state of equilibrium with an atmosphere of appropriate humidity, which may be effected by leaving a film of regenerated cellulose, for example, for 24 hours in such an atmosphere.

It is, however, not necessary that the material be in a state of equilibrium with respect to its moisture content. It suffices if in the zone of the material in which the photochemical conversion takes place, the moisture content attains the value required in view of the desired gradation. This allows appreciably more rapid adjustment of the moisture content than if the attainment of a state of equilibrium is awaited. In many cases it will be desired to work, for example, with an increased moisture content, by which we mean a moisture content of the photo-chemically active part of the material which is greater than the moisture content which this part would have if it were in equilibrium with an atmosphere of a relative degree of humidity of 65% at 20° C. Treating in such a case the photo-sensitive material with water and subsequently drying to a small extent, or conversely introducing dry material into a moist atmosphere permits adjustment of the moisture content within a very short time to the increased value desired. It should be remembered that the essential point is the moisture content which the material possesses at the moment of the exposure. It has been found that in this way a reliable and reproducible control of the gamma value is quite possible. The gamma value obtained is not dependent on variations in the moisture content after the exposure.

In adjusting the moisture content, apart from the manner in which this is effected, the kind of

material is to be taken into account. If a photo-sensitive diazonium compound is included in paper or in gelatine, it is necessary for obtaining the same gamma value as with regenerated cellulose that the material be in equilibrium with an atmosphere of different humidity.

For obtaining a satisfactory result it is, of course, necessary that the material in which the photo-sensitive compound is included has the capacity of absorbing moisture. Highly satisfactory results are obtained with regenerated cellulose. It is not necessary that the whole of the carrier be capable of absorbing moisture. It suffices if that portion of the carrier in which the photo-chemically active compound is provided has the capacity of absorbing water. For example, a cellulose acetate which has been superficially saponified, or a carrier which is sensitive or not sensitive to moisture and which has applied to it a water-absorbing layer, for example of gelatine or an other albumin or albuminous product, in which the photo-sensitive compound is provided is very suitable. It is alternatively possible to utilize materials wholly or in part consisting of polycondensation products capable of being swollen, such as polyamides.

EXAMPLE I

Regenerated cellulose was impregnated with a solution of 0.4 n hydroxy-1, diazonium-2, methyl-6, benzene sulphonic acid-4, 0.1 n mercurous nitrate and 0.2 n nitric acid. The photo-sensitive material thus obtained was conditioned at 20° C. with a relative degree of humidity of 40% and 90% respectively by leaving it for a considerable time in an atmosphere of such humidity and temperature. The material in this state contained 10% and 28% by weight of water. Subsequently, the material was exposed for 15 seconds behind a sensitometer wedge by means of a Philips superhigh-pressure mercury lamp of 500 watts which was provided at a distance of 50 cms. from the photographic material. After the exposure a portion of the material was developed for 6 minutes and an other portion for 2 minutes at 20° C. in a solution consisting of 3% of metol (sulphate salt of p-methyl-aminophenol), 4% of tartaric acid and 0.4% of silver nitrate.

From the contrasts obtained the blackening curves were derived whereupon the gradations of the contrasts could be determined.

In Table 1 the values found for the maximum gamma as a function of the relative degree of humidity (R. H.) and the time of development are summarised.

Table 1

R. H.	Moisture content, in per cent by weight	Time of development, 6 minutes	Time of development, 2 minutes
Per cent			
40	10	7.0	4.8
90	28	4.2	2.4

EXAMPLE 2

Regenerated cellulose was impregnated with a solution of 0.4 n hydroxy-1, diazonium-2, methyl-6, benzene sulphonic acid-4, 0.1 n mercurous nitrate and 0.05 n nitric acid. After removal of the superficially adhering liquid and drying to differing moisture contents, exposure took place for 6 seconds under a sensitometer wedge by means of a Philips superhigh-pressure mercury lamp of 500 watts, which was provided at a distance of 20 cms. from the photo-sensitive material. Subsequently, development took place for 5 minutes at 20° C. by means of a solution consisting of 0.5% of metol, 1% of tartaric acid and 0.3% of silver nitrate. From the contrasts obtained the characteristic curves were obtained whereupon the gradations of the contrasts could be determined. The gradients g_1, g_2, g_3 of the chords of the characteristic curves were measured, which extend from a blackening exceeding by 0.05 the fog, to blackening 0.5 (g_1), from blackening 0.5 to 1.0 (g_2), and from blackening 1.0 to 1.5 (g_3).

In Table 2 the gradients found as a function of the moisture content are summarised, the total moisture content being stated. Although with regard to the moisture content the material was not in a state of equilibrium so that the moisture content stated was not wholly identical to that in the photo-chemically active zone, the moisture content specified is sufficient indication of the sequence of rising moisture content.

Table 2

Moisture content, in per cent by weight	g_1	g_2	g_3
18.3	1.9	3.8	4.5
21.3	1.8	3.1	3.1
24.3	1.2	2.1	2.3
28.0	1.1	1.8	1.9
30.7	1.0	1.6	2.0
32.8	0.9	1.5	1.7
34.5	0.8	1.4	1.6
37.0	0.7	1.2	1.6

EXAMPLE 3

Acetylcellulose which was superficially saponified on two sides over a thickness of 12 microns was sensitised by impregnation with a solution consisting of 0.1 n hydroxy-1, diazonium-2, methyl-6, benzene sulphonic acid-4, 0.05 n mercurous nitrate and 0.2 n nitric acid, conditioned at 20° C. in an atmosphere of a relative degree of humidity of 40% and 90% respectively, and subsequently exposed for 60 seconds behind a sensitometer wedge by means of a Philips superhigh-pressure mercury lamp of 500 watts arranged at a distance of 20 cms. The development took place for 4 minutes at 20° C. in a solution consisting of 0.5% of metol, 1% of tartaric acid and 0.2% of silver nitrate. The graduations found are stated in Table 3.

Table 3

R. H.	g_1	g_2	g_3
Per cent			
40	1.7	3.2	3.2
90	1.0	1.5	1.5

EXAMPLE 4

Regenerated cellulose was sensitised by means of a solution consisting of 0.1 n hydroxy-1, diazonium-2, methyl-6, benzene sulphonic acid-4, 0.02 n mercurous nitrate and 0.05 n nitric acid, conditioned at 20° C. in an atmosphere of a relative degree of humidity of 40% and 90% respectively, and subsequently exposed and developed in the manner described in Example 3.

Table 4 shows the values found for the graduations. The moisture content of the film as shown has been found by drying.

Table 4

R. H. at which conditioning tookplace	Moisture content, in per cent by weight	g_1	g_2	g_3
Per cent				
40	10	1.1	3.3	3.3
90	28	0.9	1.8	1.8

EXAMPLE 5

Regenerated cellulose was sensitised by impregnation with a solution consisting of 0.7% of diphenyldiazonium sulphate and 0.9% of silver nitrate, conditioned at 20° C. in an atmosphere of a relative degree of humidity of 40% and 75% respectively, and subsequently exposed for 3 minutes under a sensitometer wedge by means of a Philips superhigh-pressure mercury lamp of 500 watts provided at a distance of 10 cms.

Table 5 shows the gradients found as a function of the relative degree of humidity.

Table 5

R. H.	g_1	g_2	g_3
Per cent			
40	0.9	2.9	3.8
75	0.4	1.1	2.1

After the exposure, development took place for 2 minutes at 22° C. in a solution consisting of 2% of metol, 4% of tartaric acid and 0.4% of silver nitrate.

What we claim is:

1. In the process of producing photographic contrasts on a transparent cellulosic moisture absorbent carrier having a given initial moisture content and supporting a light-sensitive system containing a diazonium compound and a reducible mercurous salt, the steps comprising varying the moisture content of one portion of said carrier to an extent at which the resulting moisture content of said portion has a value of about 10 to 28% by weight of the carrier and corresponds to a state of equilibrium between said portion and an atmosphere having a relative humidity of about 40 to 90%, varying the moisture content of the second portion of the carrier to an extent at which the resultant moisture content of said second portion has a value different than the moisture content of said first portion and has a value of about 10 to 28% by weight of the carrier and corresponds to a state of equilibrium between said second portion and an atmosphere having a relative humidity of about 40 to 90%, and exposing said first and second portions containing the said moisture contents at the time of exposure to the action of light through a photographic negative with substantially the same intensity of illumintaion to form images on the respective portions of the carrier having different contrast values with respect to the image on the photographic negative.

2. In the process of producing photographic contrasts on a transparent cellulosic moisture absorbent carrier having a given initial moisture content and supporting a light-sensitive system containing a diazonium compound and a reducible mercurous salt, the steps comprising varying the moisture content of one portion of said carrier to an extent at which the resultant moisture content of said portion has a value of about 10 to 28% by weight of the carrier and corresponds to a state of equilibrium between said portion and an atmosphere having a relative humidity of about 40 to 90%, varying the moisture content of a second portion of the carrier to an extent at which the resultant moisture content of said second portion has a value different than the moisture content of said first portion and has a value of about 10 to 28% by weight of the carrier and corresponds to a state of equilibrium between said second portion and an atmosphere having a relative humidity of about 40 to 90%, exposing said first and second portions containing the said moisture contents at the time of exposure to the action of light through a photographic negative with substantially the same intensity of illumination to form a light-decomposition product on the respective portions of the carrier, and physically developing the respective portions of the carrier to produce images thereon having different contrast values with respect to the image on the photographic negative.

3. In the process of producing photographic contrasts on a superficially saponified cellulose acetate carrier having a given initial moisture content and supporting a light-sensitive system containing a diazonium compound and a reducible mercurous salt, the steps comprising varying the moisture content of one portion of said carrier to an extent at which the resultant moisture content of said portion has a value of about 10 to 28% by weight of the carrier and corresponds to a state of equilibrium between said portion and an atmosphere having a relative humidity of about 40 to 90%, varying the moisture content of a second portion of the carrier to an extent at which the resultant moisture content of said second portion has a value different than the moisture content of said first portion and has a value of about 10 to 28% by weight of the carrier and corresponds to a state of equilibrium between said second portion and an atmosphere having a relative humidity of about 40 to 90%, exposing said first and second portions containing the said amounts of moisture at the time of exposure to the action of light through a photographic negative with substantially the same intensity of illumination to form a light-decomposition product on the respective portions of the carrier, and physically developing the respective portions of the carrier to produce images thereon having different contrast values with respect to the image on the photographic negative.

4. In the process of producing photographic contrasts on a regenerated cellulose carrier having a given initial moisture content and supporting a light-sensitive system containing a diazonium compound and a reducible mercurous salt, the steps comprising varying the moisture content of one portion of said carrier to an extent at which the resultant moisture content of said portion has a value of about 10 to 28% by weight of the carrier and corresponds to a state of equilibrium between said portion and an atmosphere having a relative humidity of about 40 to 90%, varying the moisture content of a second portion of the carrier to an extent at which the resultant moisture content of said second portion has a value different than the

moisture content of said first portion and has a value of about 10 to 28% by weight of the carrier and corresponds to a state of equilibrium between said second portion and an atmosphere having a relative humidity of about 40 to 90%, exposing said first and second portions containing the said amounts of moisture at the time of exposure to the action of light through a photographic negative with substantially the same intensity of illumination to form a light-decomposition product on the respective portions of the carrier, and physically developing the respective portions of the carrier to produce images thereon having different contrast values with respect to the image on the photographic negative.

5. In the process of producing photographic contrasts on a transparent cellulosic moisture absorbent carrier supporting a light-sensitive system containing a diazonium compound and a reducible mercurous salt, the steps comprising varying the moisture content of a photographic record portion of said carrier to an extent at which the resultant moisture content of said photographic portion has a value of about 10 to 28% by weight of the carrier and corresponds to a state of equilibrium between said photographic portion and an atmosphere having a relative humidity of about 40 to 90%, varying the moisture content of a sound record portion of the carrier parallel to said film record portion to an extent at which the resultant moisture content of said sound portion has a value different than the moisture content of said photographic portion and has a value of about 10 to 28% by weight of the carrier and corresponds to a state of equilibrium between said sound portion and an atmosphere having a relative humidity of about 40 to 90%, and exposing said photographic and sound portions containing the said amounts of moisture at the time of exposure to the action of light through a negative having a photographic record and a sound record with

substantially the same intensity of illumination to form light-decomposition products on the respective portions of the carrier, and physically developing the respective portions to produce a photographic record, and a sound record having different contrast values with respect to the photographic record and sound record on the photographic negative.

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