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METHOD OF MAKING NEGATIVE PRINTS

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It is known to produce negative photographic prints by the use of materials, such as paper sensitized by means of diazonium compounds, the fixing operation being effected by rinsing out with water or by copying out by a second exposure the diazonium compound which has not been decomposed by light during the exposure.

The present invention has for its object to provide an improved method for obtaining negative photographic prints by "self-developing layers" sensitized by means of a diazonium compound.

The expression "self-developing layer" is to mean herein a layer whereon colored material is formed by the reaction of the light decomposition product of the diazonium compound, which decomposition product remains in the material and which, by reaction with the diazonium compound still present in the material, forms a colored compound.

According to present knowledge, the photochemical decomposition of a diazonium compound results in the formation of a corresponding phenol; the N_2X -group being replaced by the OH-group. This replacement may take place not only photochemically, but also otherwise, for instance, many diazonium salts yield by hydrolysis diazonium hydroxides which are so unstable as to lose nitrogen even at ordinary temperatures, whereby the OH-group takes the place of the N_2 -group.

When using, therefore, the last-mentioned sensitized materials, it might be expected that a "moderate actinic exposure" under a template, for instance, under a tracing, during which the portions under lines of the tracing receive practically no light and remain undecomposed, and whereas the portions under the transparent portions of the tracing receive sufficient light to cause the diazonium compound to partly decompose, would give no proper negative prints, this because of the following:

On the exposed portions the hydroxy-compound formation caused by photochemical decomposition would start to form colored material with the diazonium compound not yet decomposed, and on the nonexposed portions the diazonium compound would be hydrolyzed and decomposed and the resulting hydroxy-compound would also form colored material with the diazonium compound not yet decomposed. Such hydrolysis and corresponding decomposition is accelerated by the usual after-treatment in developing such prints, which consists in their exposure to a moist atmosphere, possibly with simultaneous heating of same.

Under the above conditions it can thus be ex-

pected that colored material will be formed both on the exposed and unexposed portions of the print, and that no satisfactory image can be obtained.

In this connection it may be mentioned that no satisfactory results could be expected even if the hydrolysis and the resulting decomposition of the diazonium compound were to be so accelerated that the hydroxy-compound thus formed, could not enter into a reaction with undecomposed diazonium compound to form colored material on the undesired portions, as such a rapid hydrolysis and decomposition of the diazonium compound would also prevent the light-decomposition product from entering into a reaction with the diazonium compound to form colored material on the desired portions.

However, we have found that under the given conditions the light decomposition product forms colored material with the diazonium compound much more rapidly than does the decomposition product obtained by hydrolysis.

We have furthermore found that the difference between the respective speeds of reaction of the light decomposition products and of the decomposition products obtained by hydrolysis to form colored material with the diazonium compound is such, that it is possible in the presence of sufficient moisture in the atmosphere—with the application of heat to accelerate the process if necessary—to decompose the diazonium compound without the formation in situ of colored material on portions of the light-sensitive layer which are not struck by light, whereas at the same time the presence of a plentiful supply of diazonium compound still present in situ in the layer will result in the formation of colored material by the light decomposition products formed at the exposed portions of the layer.

The present invention is based on the recognition of the above and consists of a method by means of which negative photographic prints are obtained with "self-developing" layers which are sensitized by means of a diazonium compound. Such layers, according to the invention, are subjected to a "moderate actinic exposure" and the fixing of the negative image is achieved by bringing about a decomposition by hydrolysis of the diazonium compound at such portions of the layer which are not struck by light, the decomposition being accompanied by the liberation of nitrogen.

By the term "moderate actinic exposure" is meant an exposure which, with the sensitized

material, lays the basis for the formation of a negative image.

As to the treatment by moisture, the subjecting of the actinically-exposed layer to the moisture normally present in the atmosphere as a rule suffices. The process, however, may be accelerated by insuring an ample supply of water vapor during the application of heat. Suitable methods to combine heat and moisture treatments are, for instance, to subject the photochemically-exposed layer to hot ironing under a damp cloth, or to pass it through heated calenders covered with damp cloth.

In many cases it suffices to pass the layer through a chamber having a high water vapor content, without applying heat at all.

Such diazonium compounds which readily hydrolyze and decompose are especially suitable to practice the invention. Especially good negatives are obtained if the sensitized layer also contains a copper salt.

In order to prevent hydrolysis and decomposition of the diazonium compound in the sensitized material before use, it is highly desirable to subject the sensitized material, for instance sensitized paper or linen, to intense drying, for instance, by drying it in a flow of gas which has been previously dried by means of P_2O_5 , or in a flow of gas from which the moisture has been frozen out by cooling the gas to a low temperature, and by providing means to preserve the intense dry state of the sensitized material during its storage.

In order that the invention may be clearly understood and readily carried into effect, some examples thereof will be given hereinafter.

Example I

A paper carrier is treated on one side with an aqueous solution of 2% of 1-hydroxy-2-diazonium benzene-4-sulphonic acid and 2.7% of $Cu(NO_3)_2 \cdot 6H_2O$ and is then exposed for 25 sec. under a positive drawing, for instance, under a tracing drawn on transparent linen, at a distance of 50 cms. from a 5 kilowatt incandescent lamp, so that the diazonium compound falling under the non-transparent portions of the drawing receives practically no light, whereas the remaining portions are subjected to a "moderate actinic exposure".

The exposed paper is developed and fixed by allowing it to remain for 3 days at ordinary temperatures in a chamber which is shut off from daylight and which is saturated with water vapor. Thereby a negative photographic print in, a dark-blue tinge is produced. On the non-exposed portions the sensitized material is decomposed and practically no formation of colored material takes place thereon.

Example II

The paper, after being sensitized and actinically exposed in accordance with Example I, is subjected in the dark for about half an hour at ordinary temperatures, to an atmosphere saturated with moisture; after this it is passed for 2 minutes under a damp cloth at a temperature of $100^\circ C$. The result is a brown-violet negative photographic print.

Example III

A paper carrier is coated on one side with a solution of 40 grams of 2-diazonium-1-hydroxy-5-methylbenzene-4-sulphonic acid and 100 grams

of $Cu(NO_3)_2 \cdot 6H_2O$ in 1 litre of water and then dried.

The so-sensitized paper is then exposed for 10 sec. under a drawing provided on transparent linen at a distance of 25 cms. from a 5 kilowatt incandescent lamp.

Subsequently the exposed paper is allowed to remain for 15 minutes in an oven heated to a temperature of $85^\circ C$. Into this oven air is blown which is saturated with water vapor at a temperature of $75^\circ C$. The result is a dark-blue negative photographic print.

As in this case, because of the high temperature, some formation of colored material also occurs at the non-exposed portions, the portions are slightly grey colored.

Example IV

The sensitized material of Example III, after being exposed as stated above, is kept for 24 hours in a dark medium, which at ordinary temperatures has been saturated with water vapor. Subsequently the material is subjected to hot-ironing for 2 minutes under a damp cloth at a temperature of $100^\circ C$. The result is a dark-blue negative photographic print.

Example V

A paper or linen carrier is coated on one side with a solution of 1% of 1-diazonium-2-hydroxynaphthalene-4-sulphonic acid (1 mol.) and 3.2% of $Na_2CO_3 \cdot 10H_2O$ (3 mols) in water and then dried in air. After a "moderate actinic exposure" under a tracing, the paper is exposed to air in the dark. After the self-development the diazonium compound remaining at those portions which have not been photochemically exposed, is decomposed by passing the material under a flat-iron having a temperature of about $120^\circ C$. so that a developed and fixed negative photographic print having a brown tinge is obtained.

While we have described our invention in connection with specific examples, we do not wish to be limited to same, but desire the appended claims to be construed as broadly as permissible in view of the prior art.

What we claim is:

1. In the process of producing negative photographic prints on a layer substantially free from moisture and sensitized with a diazonium compound which readily hydrolyzes to form an unstable diazonium hydroxide and couples with its light-decomposition product to form colored material at a considerably faster speed than it couples with the hydroxide, the steps of subjecting the layer to a moderate actinic exposure to decompose part of the diazonium compound on selected portions of the layer, and subjecting the exposed layer to moisture while preventing light-decomposition of the diazonium compound for sufficient time to develop and fix the negative image without the addition or removal of any substance other than nitrogen and to completely decompose the diazonium compound present at the unexposed portions of the layer.

2. In the process of producing negative photographic prints on a layer substantially free from moisture and sensitized with a diazonium compound which readily hydrolyzes to form an unstable diazonium hydroxide and couples with its light-decomposition product to form colored material at a much faster speed than it couples with the hydroxide, the steps of subjecting the layer to a moderate actinic exposure to decompose part of the diazonium compound at selected portions

2,095,408

3

of the layer, and applying water vapor to the exposed layer in the absence of actinic light for sufficient time to develop and fix the negative image without the addition or removal of any substance other than nitrogen and to completely decompose the diazonium compound present at the unexposed portions of the layer.

3. In the process of producing negative photographic prints on a layer substantially free from moisture and sensitized with a diazonium compound which readily hydrolyzes to form an unstable diazonium hydroxide and which couples with its light-decomposition product to form colored material at a much faster speed than it couples with the hydroxide, the steps of subjecting the layer to a moderate actinic exposure to decompose part of the diazonium compound at selected portions of the layer, and subjecting the exposed layer in the absence of actinic light to air saturated with water vapor for a sufficient time to produce colored material at the exposed portions and to completely decompose the diazonium compound at the unexposed portions.

4. In the process of producing negative photographic prints on a layer substantially free from moisture and sensitized with a diazonium compound which readily hydrolyzes to form an unstable diazonium hydroxide and which couples with its light-decomposition product to form colored material at a much faster speed than it couples with the hydroxide, the steps of subjecting the layer to a moderate actinic exposure to decompose part of the diazonium compound at selected portions of the layer, and applying heated water vapor to the exposed layer in the absence of actinic light for sufficient time to develop and fix the negative image without the addition or removal of any substance other than nitrogen and to completely decompose the diazonium compound present at the unexposed portions of the layer.

5. In the process of producing negative photographic prints on a layer substantially free from moisture and sensitized with a diazonium compound which readily hydrolyzes to form an unstable diazonium hydroxide and which couples with its light-decomposition product to form colored material at a much faster speed than it couples with the hydroxide, the steps of applying a copper salt to the layer, subjecting the layer to a moderate actinic exposure to decompose part of the diazonium compound at selected portions of the layer, and applying water vapor to the exposed layer in the absence of actinic light for sufficient time to develop and fix the negative image without the addition or removal of any substance other than nitrogen and to completely decompose the diazonium compound at the unexposed portions of the layer.

6. In the process of producing negative photographic prints, the steps of forming on a fibrous carrier a light-sensitive layer of a diazonium compound which readily hydrolyzes to form an unstable diazonium hydroxide and which couples with its light-decomposition product to form colored material at a much faster rate than it couples with the hydroxide, intensively drying the sensitized carrier, subjecting the dried carrier to a moderate actinic exposure to decompose part of the diazonium compound on selected portions of the layer, and applying water vapor to the carrier in the absence of actinic light for sufficient time to develop and fix the negative image without the addition or removal of any substance other than nitrogen and to completely decom-

pose the diazonium compound present on the unexposed portions of the layer.

7. In the process of producing negative photographic prints, the steps of forming upon a carrier a light-sensitive layer by applying thereto an aqueous solution of about 2% of 1-hydroxy-2-diazonium benzene-4-sulphonic acid and 2.7% of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, drying the carrier, subjecting the carrier to a moderate actinic exposure to decompose part of the diazonium compound at selected portions of the layer, and placing the exposed carrier in an atmosphere saturated with water vapor and free from actinic light for several days to develop and fix the negative image without the addition or removal of any substance other than nitrogen and to completely decompose the diazonium compound present on the unexposed portions of the layer.

8. In the process of producing negative photographic prints, the steps of forming upon a carrier a light-sensitive layer by applying thereto an aqueous solution of about 2% of 1-hydroxy-2-diazonium benzene-4-sulphonic acid and 2.7% of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, drying the carrier, subjecting the carrier to a moderate actinic exposure to decompose part of the diazonium compound at selected portions of the layer, and placing the exposed carrier in a darkened atmosphere saturated with water vapor for about one-half an hour and then beneath a dampened cloth for about two minutes at a temperature of about 100°C ., to thereby develop and fix the negative image without the addition or removal of any substance other than nitrogen and to completely decompose the diazonium compound present on the unexposed portions of the layer.

9. In the process of producing negative photographic prints, the steps of forming on a carrier a light-sensitive layer by applying thereto a solution of about 40 grams of 2-diazonium-1-hydroxy-5-methylbenzene-4-sulphonic acid and 100 grams of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1 litre of water, drying the so-treated carrier, subjecting the carrier to a moderate actinic exposure to decompose part of the diazonium compound at selected portions of the layer, and circulating over the exposed layer in the absence of actinic light for about 15 minutes air at a temperature of about 85°C . and saturated with water vapor at a temperature of about 75°C ., to thereby develop and fix the negative image without the addition or removal of any substance other than nitrogen and to completely decompose the diazonium compound present on the unexposed portion of the layer.

10. In the process of producing negative photographic prints, the steps of forming on a carrier a light-sensitive layer by applying thereto a solution of about 40 grams of 2-diazonium-1-hydroxy-5-methylbenzene-4-sulphonic acid and 100 grams of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1 litre of water, drying the carrier, subjecting the carrier to a moderate actinic exposure to decompose part of the diazonium compound at selected portions, and placing the layer for about 24 hours in a darkened atmosphere saturated with water vapor and at substantially room temperature, and then hot-ironing the carrier for about 2 minutes beneath a damp cloth at a temperature of about 100°C ., to thereby develop and fix the negative image without the addition or removal of any substance other than nitrogen and to completely decompose the diazonium compound on the unexposed portions of the layer.

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75