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PRODUCTION OF COLOR PHOTOGRAPHIC IMAGES

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Our present invention relates to the production of color photographic images.

In the production of color photographic images it is known to use photographic materials which contain differently sensitized silver halide emulsions in the form of several layers or of small particles on the support, one or all silver halide emulsions having incorporated therein dyestuff formers, which are fast to diffusion inasmuch as they do not wander from a silver halide emulsion layer or particle into the others and which are transformed into the image dyestuffs by treating with a special agent as, for instance, another dyestuff former. There have also been used silver halide emulsions which from the start contain the image dyestuffs. In this case the dyestuffs are removed at the places containing silver to form the color image as, for instance, by the silver dyestuff bleaching out process. Since in this process colored layers are employed, the photographic material cannot of course serve for exposure, but it is practically suited only as a copying material. This disadvantage is with all methods in which colored layers are used. In order to overcome this disadvantage it has already been proposed to use silver halide emulsion layers having dyestuff formers for the silver dyestuff bleaching out process and to form the dyestuffs in the layers after exposure or development and then to destroy the dyestuffs corresponding to the images according to the silver dyestuff bleaching out process. The method is of course disadvantageous inasmuch as the dyestuff must at first uniformly be produced in each layer and then be destroyed corresponding to the component silver images in one operation.

Furthermore there is a method in which the silver image is directly converted into an azo dyestuff image. In this case by the treatment with diazo solutions the silver image is transformed into a silver antidiazotate image which then forms dyestuff images with the azo coupling components already contained in the layers.

Moreover it has already been suggested to transform the silver image into an azo dyestuff image in such a manner, that the silver image is converted into a soluble nitrite compound and azo dyestuffs are formed by this nitrite compound from azo coupling components which were present in a water-insoluble condition in the silver halide emulsion. The addition of the insoluble azo dyestuff components to the gelatin emulsion is to be performed in such a way, that these water-insoluble components are precipitated from a solution in the gelatin. However,

it has always been observed that silver halide emulsion layers with such dyestuff formers precipitated in the gelatin are not suitable for the production of colored images since these precipitated dyestuff formers exhibit a too low reactivity and the transparency of the dyestuff images and hence the capability thereof of being projected an enlarged are considerably reduced by these dyestuff formers.

In accordance with the invention we have found that the above mentioned drawbacks of the methods hitherto known can be avoided in the photographic production of azo dyestuff images by producing an azo dyestuff in silver halide emulsions by azo dyestuff coupling from a diazotizable amine and a compound capable of azo coupling, at least one of these reactants already being in a non-diffusing form in the layer, at the places free from silver after development of the silver image and, if necessary, after fixing and then removing the image silver and, if necessary, the residual silver salts in a manner known per se.

It is surprising, that an azo dyestuff is formed at the points free from silver in a photographic layer, which contains an amine capable of being diazotized besides a silver image, after the treatment of the layer with a hydrochloric acid-nitrite solution and the solution of an azo coupling component not containing a salt of a heavy metal or any other additional compound. The course of this reaction is also complete when the photographic layers already contain an azo coupler in a condition fast to diffusion, for instance, a derivative of naphthol or of pyrazolone in which case it is immaterial whether or not the nitrite solution contains a salt of a heavy metal.

The following example illustrates this modification:

A silver halide emulsion layer containing α - hydroxy - β - naphthoyl-2-amino-3-palmityl-amino-toluidine-5-sulfonic acid as the azo coupler is exposed by means of a gray wedge. After development of the silver image and fixing the layer is bathed in a 1% solution of dehydrothio-toluidine-4-sulfonic acid for 20 minutes, shortly watered, then treated with a solution consisting of 8 cc of 1/1 normal sodium nitrite solution and 1000 cc of 1/25 normal hydrochloric acid, subsequently watered again for a short time, and finally treated in a 1/1 normal sodium acetate solution. A red dyestuff is produced thereby in the layer at the places free from silver and a reverse dyestuff image of the original silver image is obtained after the removal of the silver either

with a solution of potassium cyanide or with Farmer's Reducer. It is immaterial for the final effect whether or not the hydrochloric acid-nitrite solution still contains a salt of a heavy metal. Since the diazotizing solution does not surprisingly influence the non-diffusing azo coupling components being in the layer, for instance, naphthols or compounds having reactive methylene groups such as pyrazolones, it is possible to use for this process silver halide emulsion layers already containing azo couplers. The process can be applied to single layers as well as a multi-layer material. In the latter case several silver halide emulsion layers, which contain different azo dyestuff couplers and exhibit different spectral sensitivities to light, are arranged in superposition, if necessary together with filter layers on one or both sides of the support. Such material is suited to the exposure as well as the reproduction of multi-color images.

We have moreover found that also non-diffusing amines which are contained in the silver halide emulsion layers already before exposure can unobjectionably be diazotized also in the presence of azo coupling components.

This modification is illustrated by the following two examples:

(a) 2 g of the urea with the formula carbonyl-di-(p-aminobenzoyl-p-phenylene-diamino-sulfonic acid) are dissolved in 80 cc of water. The solution is mixed with a solution of 3 g of sodium α -hydroxy- β -naphthoyl-2-amino-3-palmityl-amino-toluidine-5-sulfonate in 30 cc of water. The mixture is cooled to 15° C, filtered and added to 300 cc of a silver halide emulsion. The layer cast therefrom is exposed, developed and fixed whereupon it is treated in a nitrite solution having the composition described in the above-mentioned example. After a short watering the layer is brought into a 1/1 normal sodium acetate solution whereby the dyestuff coupling is effected. After the removal of the silver with a usual bleaching bath or a potassium cyanide solution one obtains a red dyestuff image which represents a reverse image of the silver image at first formed. If an acetic acid solution is used for the diazotization instead of the hydrochloric acid solution, the dyestuff coupling is already effected in the diazotizing bath.

(b) 3 g of sodium α -hydroxy- β -naphthoyl-2-amino-3-palmityl-amino-toluidine-5-sulfonate are dissolved in 40 cc of water and a solution of sodium 4-methyl-octadecyl-amino-aniline-3-sulfonate in 20 cc of methanol and 40 cc of water is added thereto. The whole is mixed with 300 cc of a silver halide emulsion and then cast to form a layer. After exposure, development and fixing the layer is bathed in a solution consisting of 8 cc of 1/1 normal sodium nitrite solution, 1000 cc of 1/25 normal hydrochloric acid and 10 cc of 5% copper chloride solution for 3 minutes. After watering the layer is treated in a 1/1 normal sodium acetate solution whereby a red azo dyestuff is formed at the plates free from image. After the removal of the silver image one obtains a reverse dyestuff image of the silver image. The acetate bath as the coupling bath may be omitted if acetic acid is substituted for the hydrochloric acid in the diazotizing bath since in this case the coupling is already effected in the diazotizing bath. The gradation of the dyestuff image may essentially be influenced by varying the concentration of the salt of the heavy material in the diazotizing solution.

The process of the present invention substan-

tially differs from the processes hitherto known with formation of azo dyestuff in that in the present process the two components can from the start be incorporated in the layers. In the known processes, for instance, the antidiazotate process mentioned above there are used silver halide emulsion layers which contain only one dyestuff former. In a multi-layer material the three partial color images are produced from the different dyestuff formers contained in the layers by reacting them with another dyestuff former not being in the layers, for instance, antidiazotate in which case the coupling bath may simultaneously be used for removing the silver image by adding a silver dissolving agent, for instance, potassium cyanide or a bleaching and fixing agent such as Farmer's Reducer to the bath. In the process hitherto known it is therefore necessary to adjust the dyestuff formers added to the layers and the dyestuff former not contained in the multi-layer material in such a manner that solely by the latter dyestuff former a different dyestuff image is produced in each emulsion layer viz. a yellow, purple and blue-green partial color image in the correct color tones. It is to be understood that under these conditions the selection among the known dyestuff formers is very limited, for it is known to be very difficult to produce three dyestuffs, yellow, purple and blue-green with a single diazo compound and three different coupling components which must moreover satisfy certain photographic conditions.

In contrast with these methods both dyestuff formers can be added to the silver halide emulsion layers in the present process i. e. the azo component as well as the diazo component, the latter in the form of an amine capable of undergoing the diazo reaction. Thus it is possible to construct the desired dyestuff in each layer of the multi-layer material from components which yield not only the desired color but the most favorable tint.

According to the antidiazotate process hitherto known it was necessary, for instance, to produce the three partial color images, for instance, with tetrazotized diamidine as the general diazo component and with di-(acetoacetyl)-benzidifor the yellow image, with di-(2,3-hydroxynaphthoyl)-diamidine for the purple image and with stearyl-H-acid for the blue image, the azo components being incorporated in the single layers. By the present invention, however, each dyestuff is formed in the single layers from different azo components and different diazo components as, for instance, the yellow dyestuff from 1-phenyl-3-heptadecyl-5-pyrazolone-3'-sulfonic acid and the tetrazotized urea obtained with two mols of sodium p-aminobenzoyl-p-phenylene-diamine-sulfonate, the purple dyestuff from di-(2,3-hydroxynaphthoyl)-benzidine and the tetrazotized urea obtained with two mols of sodium p-aminobenzoyl-p-phenylenediamine sulfonate and the blue-green dyestuff from the tetrazotized octylether of dihydroxybenzidine and 8-stearyl-amino-naphthol-2,4-disulfonic acid. This possibility to add a diazo component as well as a coupling component to each layer represents a considerable advantage over the possibilities hitherto known, for it is nearly impossible to construct the three dyestuffs yellow, purple and blue-green from one diazo component and three different coupling components in such a manner that satisfactory partial color images are obtained. All these dyestuff formers mentioned above which are fast to diffusion are incor-

porated into the photographic multi-layer material already in the production thereof. It is of advantage already to add them to the emulsion before casting in the form of an aqueous, if necessary, alkaline solution which may contain an organic solvent, if necessary.

For the production of a multi-layer material the silver halide emulsion layers containing the amines capable of being diazotized and the azo coupling compounds are sensitized to different spectral ranges. If desired, the layers are combined with filter layers and anti-halation layers and arranged on one or both sides of a support.

In making a multi-color image it is furthermore possible to prepare one or two partial color images according to the present invention and the other partial color images according to another method. For instance, as mentioned above the red and yellow images may be produced in two layers which are on one side of the support whereas a Prussian blue image may be obtained in a third layer on the other side of the support by the toning process, this third layer advantageously serving for recording a sound track. The present process is especially suitable for the simultaneous production of sound track and image record when such azo dyestuffs are produced as are capable of being after-treated with a salt of a heavy metal as, for instance, derivatives of salicylic acid suitable for after-chroming. In this case one obtains dyestuffs which contain salts of a heavy metal and show an especially favorable capability of absorbing the light rays affecting the photo-cells.

It is not necessary that each of the three layers contains both azo dyestuff components already before exposure. For instance, it is possible that only two layers have incorporated therein the two dyestuff components whereas the third layer contains only one azo coupling component. This process is so carried out that the two azo dyestuff images are first produced in the two layers which contain both coupling components whereupon the third layer is bathed in the solution of a diazotizable amine as, for instance, dehydrothiitoluidine-sulfonic acid and after shortly watering is treated in an acid nitrite solution. After shortly watering the layer is brought into a 1/1 normal sodium acetate solution whereby the dyestuff is formed. After the removal of the partial silver images one obtains the desired multi-color image.

The examples mentioned above already show that there are numerous possibilities for the production of multi-color images according to the present invention. Moreover combinations of different modifications of the present process as well as for other processes are possible whereby numerous ways for reaching the desired color tones are given.

As diazo components all monovalent and bivalent diazotizable amines as, for instance, dehydrothiitoluidine, nitroaniline, benzidine and methyloctadecylstearylanyl sulfonic acid are suitable for the process of the present invention. As azo components all compounds capable of coupling such as phenols and amines are to be mentioned. These compounds may carry radicals effecting fastness to diffusion and water-solubilizing groups. Corresponding with the used diazo or azo components mono- or polyazo dyestuffs can be formed.

The dyestuff formers may be rendered fast to diffusion with respect to gelatin in different ways. For instance, molecular groups are disclosed in

Patent 2,179,238 dated November 7, 1939 and which impart to the dyestuff substantive properties with respect to cotton as, for instance, one or several diphenyl radicals, heterocyclic radicals or stilbene radicals may be introduced into the molecule of the dyestuff former. In U. S. Patents 2,178,612, 2,179,244, 2,186,719 dated November 7, 1939, U. S. Patents 2,186,732, 2,186,733, 2,186,734, 2,186,849, 2,186,851, 2,186,852 dated January 9, 1940, French Patent 844,637 and U. S. Patent Applications Ser. Nos. 284,250, 284,257, 284,258 filed July 13, 1939 327,628 filed April 3, 1940, 333,814 filed May 7, 1940, 335,144 filed May 14, 1940, 341,180 filed June 18, 1940, 360,662 filed October 10, 1940 and 362,592 filed October 24, 1940 there are disclosed further numerous possibilities of making dyestuff formers fast to diffusion with respect to gelatin. The radicals effecting fastness to diffusion include, for instance, long straight carbon chains, high molecular weight fatty derivatives or long-chain polymers as, for instance, polyethyleneimine and many polymerizates and mixed polymerizates of vinyl derivatives (also together with unsaturated acids such as maleic acid and crotonic acid). The dyestuff formers made non-diffusing in this way sometimes show the property of producing no real but only colloidal solutions. Also a certain difficult solubility in aqueous media can effect that the diffusion from the layers is prevented. Further diffusion-preventing means are the known precipitating salts.

The non-diffusing dyestuff formers may be incorporated into the silver halide emulsions in the presence of wetting or dispersing agents as described in U. S. Pat. 2,186,717 or in the presence of bile acids or salts thereof as described in U. S. Patent Application Ser. No. 401,676 filed July 9, 1941.

According to the invention diazo compounds may also be used in the present process which step leads to a further simplification and possibility of variation. In this instance the photographic layers which contain an azo component capable of coupling and conveniently in a difficultly diffusing condition are treated in the solution of a diazo compound, if necessary, in the presence of a salt of a heavy metal as, for instance, potassium ferricyanide, copper sulfate and sodium chloride or copper chloride. At the places free from silver an azo dyestuff is formed immediately.

As diazo solutions there are suited all solutions of diazotized amines which may contain a stabilizer for increasing the stability thereof. It is, however, also possible to incorporate these diazo compounds into the layers, the only slowly coupling stabilized forms of the diazonium compound and the diazotates being especially suitable. In this case the coupling is accomplished in a special bath, if required, with the addition of a salt of a heavy metal.

The following example illustrates this modification:

A silver halide emulsion layer which contains 1-phenyl-3-heptadecyl-5-pyrazolone-3'-sulfonic acid as a coupling component is exposed, developed, fixed and then treated in 100 cc of a 1% solution of p-nitrobenzene-diazoniumchloride which contains 1 cc of a 10% copperchloride solution. A yellow dyestuff image is formed at the places free from silver in a short time. As to the multi-color image a multi-layer material containing different dyestuff formers in the single layers, for instance, 1-phenyl-3-heptadecyl-5-

pyrazolone-3'-sulfonic acid for the yellow image, 2,3-hydroxynaphthoylbenzidide for the purple image and 8-stearyl-aminonaphthol-2,4-disulfonic acid for the blue image is treated after exposure and development of the partial silver images with a suitable diazo solution, for instance, with tetrazotized benzidine or dianinsidine whereby the reversed dyestuff images of the original partial silver images are produced.

This modification may also be combined with those already mentioned above in any way in which case it is also possible to produce some partial color images by means of a diazotizing reaction whereas a partial color image is produced by means of a diazo component already formed.

According to the present method the images may be produced by direct exposure or copying multi-color negatives or partial sensations and it is possible to work up the photographic material for exposure as well as copying according to the present process. The silver images at first produced may be obtained by simple or reverse development.

Dyestuff formers especially suitable for the process of the invention further include the following compounds: diaminobenzoyl compounds of the aminonaphthol-sulfonic acids and -carboxylic acids, naphthylaminosulfonic acids and -carboxylic acids, cresotic acids, diaminocarbazoledisulfonic acids, pyrazolones and the ureas of the aminobenzoyl compounds of the mentioned coupling components. Moreover the benzoyl-, benzyl- and benzilidene compounds of the diaminediphenyl-ureas, diaminodiphenylthio-ureas, diaminostilbenes, benzidines and similar compounds which may be substituted at any positions by any radicals capable of diazotizing or coupling, if desired, are of especial importance. Such compounds are, for instance, the urea from p-aminobenzoyl-p-aminobenzoyl-I-acid and the urea from p-aminobenzoyl-p-phenylenediamine-sulfonic acid. Furthermore as coupling components the following compounds are suited: aromatic hydrocarboxylic acidamides as, for instance, hydroxynaphthoic acidarylide, hydroxyanthracenecarboxylic acidarylide, hydroxycarbazolecarboxylic acidarylide, hydroxynaphthocarbazolecarboxylic acidarylide, amides of the ketocarboxylic acids as, for instance, terephthaloylacetic acidanilide, benzoylacetic acidbenzidide and amides of pyrazolenecarboxylic acids or acidamides of aminopyrazolone such as the condensation product from two mols of aminophenylmethylpyrazolone and diphenyldicarboxylic acid.

Moreover couplers heterocyclically substituted come into question for the present invention such as arylides of α -naphthindole-2-phenyl-7-hydroxycarboxylic acid and pyrazolones from 2-p-aminophenylthiazole. The heterocyclic radicals may simultaneously be combined with a further diffusion-preventing radical as, for instance, a diphenyl. Such compounds are, for instance, 1-(dehydrothiitoluidyl)-3-(diphenylcarbonylamino-phenyl)-5-pyrazolone, 4,4'-diphenyldicarbonyl-di-3-p-aminophenyl-1-(p-6'-methyl-2-benzoxazolephenyl)-5-pyrazolone. All these compounds show a certain affinity for gelatin owing to their special constitution so that they can be arranged in the multi-layer process on one or both sides of the support.

All these compounds which are dyestuff formers and have been made fast to diffusion with respect to gelatin by special substitution are suitable for the purposes of the present invention. These color couplers are especially valuable if they carry besides the diffusion-preventing radicals such substituents as increase the solubility of the color coupler in aqueous-organic solvents, if necessary, in the presence of an alkali or acid. Such compounds are, for instance, a color coupler containing an acid group and a diffusion-preventing amino group such as α -hydroxynaphthoyl-dodecylamide-4-sulfonic acid, 2,3-hydroxynaphthoic acidabietinylamide, 2,3-hydroxyanthracenecarboxylic acidoleylamide- ω -sulfonic acid or the esters or amides of color couplers containing hydroxy- or amino groups and diffusion-preventing substituents containing at least one acid group as, for instance, 1-stearyl-amino-8-naphthol-2,4-disulfonic acid, palmitylamino-phenylmethylpyrazolonesulfonic acid, undecanoylamino-benzoyl-acetylanthranilic acid, 2-laurylamino-8-naphthol-6-sulfonic acid, moreover compounds as, for instance, acetoacetylamino-4-methyloctadecylaniline-3-sulfonic acid, 4-acetoacetylamino-4-abietinylaminoaniline-3-sulfonic acid, abietinylamino-benzoylanthranilic acid, heptadecylphenylpyrazolonesulfonic acid and -carboxylic acid, condensation products from hydroxycarboxylic acids capable of coupling such as hydroxynaphthoic acid with polymers containing amino groups as, for instance, polyethyleneimine or from polymers containing carboxyl groups such as polymerization products from polymerized vinylalcohol and maleic acid with color couplers containing amino groups such as aminophenylmethylpyrazolone.

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