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FINE-GRAIN PHOTOGRAPHY

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This invention relates to photography and more particularly to the art of producing fine-grained photographic deposits.

A principal object of this invention is to provide fine-grained photographic images with exposed silver halide emulsions. A further object is to provide these images by means of a fine-grain color-forming developer. Another object is to provide these images by means of developing latent photographic images into fine-grained silver images in combination with dye images. Another object is to provide fine-grained silver-dye images for use in photographic printing. These and other objects will more plainly appear from the detailed specification of the invention hereinafter presented in exemplification and not in limitation thereof.

There are numerous prior suggestions for the restricted production of so-called fine-grained images. A substantial decrease in the graininess of an image was suggested by developing an exposed silver halid emulsion in a para-phenylene diamine developer, either alone or mixed with other developing agents such as metol, hydrochinon or glycin. However, it was then necessary to increase the exposure given the film to be developed in a para-phenylene diamine developer because this type of developer reduced the effective speed of the emulsion. Other prior suggestions for fine-grain development include: the addition of a silver halide solvent such as ammonium chloride to the developer; increasing the concentration of sodium sulfite for the purpose of increasing its solvent action on the silver halide to dissolve away some of the halide grain and thus reduce the size of the silver grain formed thereon; diluting the developer to increase the time of the solvent action of the sodium sulfite; the addition of thickeners such as sugar and glycerine to restrain the diffusion of developer through the emulsion layer and thus decrease the development velocity. These and other proposals have failed to supply a commercially satisfactory method for fine-grained development as they require either an increase in exposure or in time of development, and in addition they produced photographic images of unsatisfactory tonal gradation.

The present invention hereinafter described produces vastly improved fine-grained photographic images and on a commercial scale by developing the latent image of an exposed silver halide emulsion to a low contrast in a color-forming developer and retaining the dye image formed thereby to intensify the printing opacity of the silver image. Photographic images produced by the developers hereinafter described possess low contrast and are weak in their gradations when judged visually but due to the color of the dye image formed with the silver image, the printing contrast and graduations are normal.

As is well-known, the visual contrast of a photographic image is a measure of the differences in brilliancies between the lightest and darkest portions of the image as determined by some type of photometric measurement. On the other hand, however, photographic contrast is a measure of the differences in transmission between the lightest and darkest areas of the image as determined by its printing characteristics to another photographic emulsion. Since the emulsions employed for printing stocks are usually only blue sensitive, a photographic image which absorbs strongly in the blue region will appear much more dense to the printing emulsion than to the eye. Likewise, the gradations of a picture whose deposit is blue-absorbing will appear flat and of low contrast according to photometric measurements, yet will print strong and as having normal gradations. Thus, to obtain fine-grained images according to the present invention, the images are developed in color-forming or dye-forming developers which produce gradations of low visual contrasts but which have normal printing contrasts. In following this process of fine-grain development, the developing time, and temperature, are so chosen so that the contrast of the developed picture, as measured by the gamma of the characteristic curve of the emulsion, is approximately 0.35–0.55 for the silver portion of the image. At this low gamma, the graininess of the silver deposit is extremely fine, since development has not been prolonged sufficiently and is not of sufficiently high velocity to have allowed the individual silver grains to attain even a fraction of their normal size. By themselves, these deposits of silver would be too weak in opacity and of too low a contrast to print favorably, but since a dye image is formed in combination with the silver, the dye acts to intensify the printing opacity of the otherwise weak silver image. This dye can be chosen so that it will add either to both the visual and the printing opacity of the deposit that is neutral in color, or to only the printing opacity. In the latter case, since the positive printing emulsions are usually blue sensitive, the color-forming developer is so chosen as to produce a minus-blue dye which adds greatly to the printing opacity of the developed image. The present invention has proven to be particularly adaptable to the con-

tinuous commercial processing of cinematic negatives.

In a preferred form of this invention, a fast, coarse-grained silver halide emulsion, after exposure, is developed for 7–9 minutes, at 70° F. with occasional agitation, in the following developer:

Example 1

Diethyl-p-phenylenediamine hydrochloride	grams	3
Sodium carbonate, anhydrous	do	25
Sodium sulfite, anhydrous	do	5
Water to	liter	1

To which is added:

P-nitro-benzyl cyanide	grams	0.75
Phenacyl chloride	do	0.75
Alpha-naphthol	do	0.50
Ethyl alcohol	cubic centimeters	75

This developer produces a fine-grained silver deposit in combination with a practically neutral dye image which intensifies the otherwise low opacity of the silver image. After fixing, washing and drying, the image can be printed in a normal manner by passing light through the combination of silver and dye images onto a sensitive silver halide emulsion. The above type of neutral color forming developer is particularly advantageous when it is desired to print the developed image onto color sensitized printing stocks.

If, however, the printing stock is only blue sensitive, then a red color-forming developer can be used. A satisfactory formula is as follows:

Example 2

Dimethyl - p - phenylenediamine hydrochloride	grams	3
Sodium carbonate, anhydrous	do	25
Sodium sulfite, anhydrous	do	5
Water to	liter	1

To which is added:

P-nitro-benzyl cyanide	grams	2
Alpha-chlor-ethyl-aceto-acetate	do	2
Ethyl alcohol	cubic centimeters	25

Development time is 7–9 minutes at 70° F. The above developer produces a fine-grained deposit of silver in combination with a red dye which intensifies the printing opacity of the silver image since the red dye is tremendously absorptive of those rays to which the positive printing stock is sensitive.

For extremely fine-grained images, the following yellow-red color forming developer is satisfactory:

Example 3

Sodium carbonate, anhydrous	grams	25
Sodium sulfite, anhydrous	do	5
Thio-indoxyl carboxylic acid	do	2
Ortho-aminophenol	do	5
Pyrogallol	do	2
Water to	liter	1

Development time is 6–8 minutes at 70° F.

While the above examples describe preferred forms of the invention, other preferred modifications produce very satisfactory results. Thus, it may be desirable in some cases to divide the developing process into two stages, for example, an exposed film bearing a latent image is developed for five minutes at 70° F. in the following yellow color-forming developer:

Example 4

Diethyl - p - phenylenediamine hydrochloride	grams	3
Sodium carbonate, anhydrous	do	20
Sodium sulfite, anhydrous	do	5
Water to	liter	1

To which is added:

Benzoyl acetone	grams	1.0
Phenacyl chloride	do	.7
Ethyl alcohol	cubic centimeters	25

After this initial development in a yellow color forming development, a second or intensifying development can be given the exposed film. For this purpose a red or magenta color developer is satisfactory, a formula for which is as follows:

Example 5

Diethyl - p - phenylenediamine hydrochloride	grams	5
Sodium carbonate, anhydrous	do	35
Sodium sulfite, anhydrous	do	5
Water to	liter	1

To which is added:

Thio-indoxyl carboxylic acid	grams	2.0
P-nitrobenzyl cyanide	do	3.0
Ethyl alcohol	cubic centimeters	50

The film, already carrying weak silver and yellow dye images is developed 2–3 minutes at 70° F. in the above developer which acts to both intensify the opacity of the silver deposit and convert the yellow dye image to a red image. After the second or intensifying development, the film is fixed, washed and dried.

Another very satisfactory modification of the preferred form of this invention may comprise developing the latent image of a silver halide emulsion in a weak-non-color-forming developer to a gamma of 0.35 to 0.55, converting the silver image to a re-developable form and re-developing the film in either a minus blue or a red color forming developer. A suitable developer for producing the low gamma while, at the same time, one which brings up the shadow detail, is as follows:

Sodium sulfite, anhydrous	grams	100
2 - hydroxy - methyl-p-aminophenol sulfate	grams	10
Sodium carbonate, anhydrous	do	40
Water to	liter	1

At 70° F. a development of 4–5 minutes produces a low contrast, fine-grained silver image. The film is then fixed as usual, then washed and then the silver image is converted into the form of a re-developable salt of silver. A convenient method is to convert the silver into silver ferrocyanide by means of a solution of ferricyanide. A satisfactory bleach bath for this purpose is the following:

Potassium ferricyanide	grams	30
Ammonium hydroxide, concentrated	cubic centimeters	5
Water to	liter	1

After 1–2 minutes' treatment in this ferricyanide bleach, the film is washed well and re-developed in a yellow color-forming developer as described under Example 4 and followed by an intensifying development, a formula for which is given as Example 5. After being re-developed to a combination of low contrast silver image and red dye image, the film is washed and dried. The last-

described process, except for the initial development in the non-color-forming developer, can be conducted in full illumination.

It is evident from the foregoing that the invention herein described utilizes color-forming or dye-forming developers not for the immediate purpose of producing colored photographs, but as a novel means for providing improved well graded fine-grained images that can be readily reproduced onto silver halide emulsions. In reproducing by printing processes the images provided by this invention the printing light must pass through both the silver and the dye images, neither of which, by itself, would be of sufficient opacity, or of sufficient gradation, to make a satisfactory print. However, by passing the printing light through the novel combination of silver and dye image, the gradations as exposed onto the positive emulsion, are of sufficient contrast to provide extraordinarily fine-grained prints having extremely satisfactory gradations.

While a range of approximately 0.35–0.55 has been described as the preferred gamma range to which the silver image portion is to be developed, it has been observed that with some of the organic reducing agents used in color-forming developers, among which are p-phenylene diamine and its di-methyl derivative, the silver deposits are fine-grained even when developed to a higher gamma.

It is thus apparent that the present invention affords an improved means for providing properly graded and unusually fine grained images for faithfully rendering large scale enlargements either from miniature camera shots or on the cinema screen, either in black and white or in any color process employing color component records.

The present invention also affords a method of fine grain development two to three times faster than possible in the prior art, and thus affords a method that for the first time in the art may be used in continuous developing machines which are inherently not adaptable to any prolonged development time.

The foregoing specification sets forth preferred embodiments of the present invention in exemplification but not in limitation thereof and is intended to include all variations and modifications within the spirit and scope of the appended claims.

I claim:

1. A fine-grained photographic image of low silver opacity and of normal printing opacity comprising a combined silver and dye image said image being formed in situ with the silver image, the silver portion of said combined image being developed to a gamma not greater than approximately 0.5.

2. The method for producing a properly graded fine-grained photographic image that comprises developing a latent image in a silver halide emulsion to metallic silver to a gamma not greater than approximately 0.5 with a color-forming developer comprising a photographic developing agent and a dye coupling component to form a dye image in situ with the silver image and subsequently printing said combined silver and dye image onto another sensitized layer.

3. The method for producing a properly graded fine-grained photographic image that includes the steps of developing an exposed silver halide emulsion in a non-color-forming developer to the point where the gradations are evident but insufficient for photographic reproduction, converting the silver image into the form of a re-developable silver salt and re-developing the silver salt in a color-forming developer comprising an aromatic amino photographic developing agent and a dye coupling component to a gamma of approximately 0.30–0.50.

4. The method for producing a properly graded fine-grained photographic image that includes the steps of initiating development of an exposed silver halide emulsion by means of a non-color-forming developer, clearing the film of the developer and continuing the development in a color-forming developer comprising an aromatic amino photographic developing agent and a dye coupling component to a gamma of approximately 0.30–0.50 of the silver image portion.

5. The method for producing a properly graded fine-grained photographic image that includes the steps of initiating development of an exposed silver halide emulsion by means of a non-color-forming developer, clearing the film of the developer and continuing the development with a p-phenylene diamine developing solution containing a dye coupling component which will form a yellow-red color forming developer to a gamma of approximately 0.30–0.50.

6. The method for producing a properly graded fine-grained photographic image that includes the steps of developing an exposed silver halide emulsion in a non-color-forming developer to the point where the gradations are evident but insufficient for photographic reproduction, converting the silver image into the form of a re-developable silver salt and re-developing the silver salt in a color-forming developer to a gamma of approximately 0.30–0.50 of the silver image portion, said color-forming developer comprising a p-phenylene diamine developing agent and a dye coupling component capable of forming a dye image substantially transmissive in the yellow-red spectral region.

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