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PROCESS FOR THE MANUFACTURE OF COLOR PHOTOGRAPHIC IMAGES

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A known process for the manufacture of color-photographic images and more specifically for the conversion of a negative silver image into a positive dye-image, consists in treating a film containing a silver image and diffusely dyed with an azo-dye in a dilute solution of a hydrohalic acid, whereby the dyestuff is bleached out at the places where silver is present. It is also known to produce diffusely dyed photographic layers or films by building up an azodyestuff from a diazo-compound and an azo-coupler within the layer or the emulsion used for its preparation such, for example, as is disclosed in my Letters Patent 2,071,688 dated February 23, 1937.

It has now been found that the building up of the azo-dye and the production of dye images in photographic layers containing a photographic silver image can be carried out more simply than heretofore known. This improved process is accomplished by treating a photographic layer containing a silver image and impregnated with an azo-coupler in an acid solution containing a diazo-compound. The acid solution employed has no destroying reaction with regard to the diazo-compound, although it does react with silver deposits of the images to oxidize the metal and substantially simultaneously to form a reducing substance which locally destroys the coupling properties of the diazo-compound by reduction at the points of the silver deposit. Upon completion of this treatment, the photographic layer is washed for a short time and then treated in an alkaline solution containing sufficient alkali, such for example, as sodium carbonate to insure an alkaline reaction. Coupling of the azo-coupler and the portion of the diazo-compound present which was not previously destroyed takes place in this alkaline solution to complete the formation of the dye images.

Various substances may be used to prepare the acid solution described above, among which are hydrohalic acids and other dye-destroying baths of acidic reaction which are described in my Letters Patent 2,020,775 dated November 12, 1935. Such acid solutions are used in a concentration at which coupling does not occur. A 3–12% hydrochloric acid or a 2–10% hydrobromic acid may be used for this purpose. The concentration of acid which has been found effective to prevent coupling of most of the diazo-compounds has a pH range in the vicinity of 2 to 3 although this concentration may be increased or decreased, especially if catalysts such as dimethyl-quinoxaline are added to the acid solution.

The formation of the azo dye and the production of the dye image in the manner described above results in several advantages which distinguishes the improved process from previously known methods. In the present process it is unnecessary to incorporate diazo-compounds in the photographic layers for which reason a greater selection of compounds may be employed owing to the fact that not all diazo-compounds are stable at room temperature. In addition, by carrying out the improved process outlined above, dye images can be obtained by the use of a lesser number of treating baths than heretofore used.

The following examples will further illustrate the manner in which the improved process may be carried out in practice.

Example I.—A light sensitive silver halide emulsion layer is treated for fifteen minutes in a bath containing 0.5 g. of β -naphthol and 0.5 g. caustic soda in 100 ccs. of water, washed, and dried. The layer is exposed, developed and fixed in the usual manner. Instead of impregnating the layer with the β -naphthol before the exposure, the impregnation may also be effected with the exposed and developed layer containing the silver image. The layer is thereupon treated for two minutes at +5° C. with a solution containing 5% hydrobromic acid and 1% diazotized α -naphthylamine. After a short washing the layer is immersed in a 2N aqueous sodium carbonate solution, washed again, treated in a copper chloride solution and fixed out. In this manner an insoluble magenta dye is formed in inverse proportion to the amount of silver present.

Example II.—Instead of using 5% hydrobromic acid in the above example, the following may be substituted:

Thio-urea	-----g--	2
Conc. sulfuric acid	-----cc--	2
Diazotized α -naphthylamine	-----g--	1
Water	-----cc--	100

The light sensitive silver halide emulsion layer containing the β -naphthol is treated as outlined in Example I and the same insoluble magenta dye is formed.

Example III.—Instead of using β -naphthol as set forth in Examples I and II above, 2-oxy-3-naphthoylanilide may be employed. Substitution of 2-oxy-3-naphthoylanilide in the above examples will result in an insoluble purple dye.

Example IV.—The light sensitive silver halide emulsion layer containing the β -naphthol as set forth in Examples I and II may be treated for

1½ minutes at 18° C. in 20 ccs. of 11% aqueous hydrochloric acid solution containing diazotized diamino-stilbene disulphonic acid. This bath may be prepared by dissolving 0.37 g. of diamino-stilbene sulphonic acid in 20 ccs. of aqueous hydrochloric acid and diazotising by the addition of 0.18 g. of sodium nitrite. After the washing, treatment in the sodium carbonate solution, washing, treating in copper chloride solution and fixing out as set forth in Example I, a violet dye is obtained at the places where no silver was present.

For developing the latent image obtained by the exposure of a silver halide emulsion layer containing a dye component soluble in alkaline solutions, e. g. a dye component containing phenolic, carboxylic acid or sulphonic acid groups, instead of the alkaline developer usually employed an acid or neutral developer is used. Thereby the bleeding out or diffusion of the dye component is prevented. In such cases in which the use of an organic acid or neutral developer leads to an undesired color development an inorganic acid or neutral developer may be employed. The following developer, for example, is suitable.

Solution 1: 100 grms. potassium oxalate dissolved in 400 ccs. of water.

Solution 2: 100 grms. ferrous sulphate and 1 gm. citric acid dissolved in 300 ccs. of water.

4 parts of solution 1 are mixed with 1 part of solution 2 for use.

Example V.—A film containing a silver image and impregnated with benzoylated H-acid, obtained by employing an 0.5% solution of benzoylated H-acid as described for β -naphthol in Example I, is treated for 3 minutes at 18° C. in an 11% aqueous hydrochloric acid containing diazotized 4-chlor-2-amino-diphenyl ether (Brunner, *Analyse der Azofarbstoffe*, Berlin 1929, page 113) a bath obtainable by diazotizing a solution of the chloramino-diphenyl ether in 11% hydrochloric acid by the addition of sodium nitrite. After this treatment the film is washed for a short time, immersed in a 2n sodium carbonate solution, washed again, treated in a copper chloride solution and fixed out. In this manner a magenta dye is obtained at the places where no silver was present.

Example VI.—A film containing a silver image and impregnated with β -naphthol as described in Example I, is treated 3 minutes at 18° C. in a solution prepared in the following manner. 11.9 grms. potassium bromide and 2.8 ccs. of conc. sulfuric acid are dissolved in water to form 100 ccs. 0.68 gm. "Diazolichtgelb 3 GL" (Schultz *Farbstofftabellen*, 7th ed., supplement I, page 87) are dissolved in 20 ccs. of this solution and then 0.18 gm. of sodium nitrite are added. After the treatment in this solution the film is washed for a short time, immersed in 2n sodium carbonate solution, washed again, treated in a copper chloride solution and fixed out. In this manner an orange dye is obtained at the places where no silver was present.

Example VII.—A film containing a silver image and impregnated with β -naphthol as described in Example I, is treated 3 minutes at 18° C. in a solution prepared in the following manner. 11.9 grms. potassium bromide and 2.8 ccs. of conc. sulfuric acid are dissolved in water to form 100 ccs. 0.57 gm. Primuline (Schultz, *Farbstofftabellen*, 7th ed., vol. I, No. 932) are dissolved in 20 ccs. of this solution and then 0.09 gm. sodium

nitrite are added. After the treatment in this solution the film is washed for a short time, immersed in 2n sodium nitrite solution, washed again, treated in a copper chloride solution and fixed out. In this manner a red-orange dye-image is obtained at the places where no silver was present.

The improved process described above is suitable to form multi-color images in a multilayer material having different dye coupling components and different silver part images in superimposed layers, such as described in Letters Patent 2,166,049 which issued to me July 11, 1939.

What is claimed is:

1. The process of producing a reversed dye-image from a photographic silver image within a developed photographic layer uniformly impregnated with an azo-dye coupler, which comprises treating said layer with a diazonium salt in an acid solution having an acid concentration which prevents coupling and which is indifferent to said salt but which is reactive with said silver to form a reaction product which locally destroys the coupling property of said salt by reduction, thereafter neutralising said acid within said layer sufficiently to cause said azo-coupler to combine with said diazonium compound and removing the silver from said layer.

2. The process of producing a reversed dye-image from a photographic silver image within a developed photographic layer uniformly impregnated with an azo-dye coupler, which comprises treating said layer with a diazonium salt in a hydrohalic acid solution which has a pH-value at which coupling does not occur but at which said solution reacts with the silver to produce a reaction product whereby the coupling property of the diazonium salt is locally destroyed at the points of silver deposit by reduction, thereafter neutralising said acid within said layer sufficiently to cause said azo-coupler to combine with said diazonium compound and removing the silver from said layer.

3. The process of producing a reversed dye-image from a photographic silver image within a developed photographic layer uniformly impregnated with an azo-dye coupler, which comprises treating said layer with a diazonium salt in a hydrobromic acid of about 5% strength, thereafter neutralising said acid within said layer sufficiently to cause said azo-coupler to combine with said diazonium compound and removing the silver from said layer.

4. The process of producing a reversed dye-image from a photographic silver image within a developed photographic layer uniformly impregnated with an azo-dye coupler, which comprises treating said layer with a diazonium salt in a hydrochloric acid of about 8% strength, thereafter neutralising said acid within said layer sufficiently to cause said azo-coupler to combine with said diazonium compound and removing the silver from said layer.

5. The process of producing a photographic dye-image which comprises exposing a photographic silver halide emulsion layer uniformly impregnated with an azo-dye coupler, developing said layer and treating said layer with a diazonium salt in a hydrohalic acid solution, which has a pH-value at which coupling does not occur but at which said solution reacts with the silver to produce a reaction product whereby the coupling property of the diazonium salt is locally destroyed at the points of silver deposit by reduction, thereafter neutralising said acid within

said layer sufficiently to cause said azo-coupler to combine with said diazonium compound and removing the silver from said layer.

6. The process of producing a photographic dye-image which comprises exposing a photographic silver halide emulsion layer uniformly impregnated with an azo-dye coupler which is soluble in alkaline developing solutions, developing said layer with a developer having neutral to acid character and treating said layer with a diazonium salt in a hydrohalic acid solution

which has a pH-value at which coupling does not occur but at which said solution reacts with the silver to produce a reaction product whereby the coupling property of the diazonium salt is locally destroyed at the points of silver deposit by reduction, thereafter neutralising said acid within said layer sufficiently to cause said azo-coupler to combine with said diazonium compound and removing the silver from said layer.

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