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PHOTOGRAPHIC IRON-SILVER COLOR PROCESS

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The present invention relates to the photographic production of monochrome and plurichrome pictures by means of light sensitive ferric salt layers and is characterized by the fact that at one stage or another of the inherent procedure silver salts are brought into play resulting in the formation of silver images, the latter being afterwards transformed or converted into colored compounds or used to form colored compounds by way of accessory reactions. The iron salts are only intermediary means, while the color formations are truly based entirely on silver.

An object of the invention is to provide an inexpensive, simple, rapid and fool-proof method of color picture production, and especially one which is compatible with the conditions obtaining in processing laboratories handling moving picture film.

The various steps in the procedure and the sequence of their performance, as applied to color film production, form a new method of photographic color printing.

Having well in mind the fact that a pluricolor picture can only be obtained by a combination of several monochromes, and that the main application in view is, as stated, to moving picture film processing, quite a number of conditions arise which have to be fulfilled and which place considerable restrictions on the choice of sensitizers most appropriate for the purpose. A chosen sensitizer intended to be handled in film laboratory establishments must be:

(1) Easily compounded
(2) Simple in coating
(3) Of no critical temperature and atmospheric requirements
(4) Preservable without particular care
(5) Innocuous to underlaying, previously produced, colored pictures
(6) Call for treatments innocuous to previously produced color pictures
(7) Neither strongly acid nor thoroughly alkaline in itself nor in the treatments required
(8) Of great latitude in every direction

Only ferric salt sensitizers fulfill at one and the same time all these conditions, with the added advantage that the ultimate pictures obtained thereby are practically without any grain, or at least of an extreme fineness of grain compared to other multicolor pictures produced in any other way. Ferric salts require, it is true, a powerful source of light in exposure, but modern technical means are available that quite serve the purpose; and, furthermore, exposure can be effected during continuous travel of moving picture film and thus the exposure may be considered as a step in the processing sequence, just the same as coating, eliminating thereby separate operation exposure, so called printing.

Ferric salts are preferably used in water solutions, which can be compounded with suitable media as gelatine and other colloids, gums, viscose and any other suitable media, or can be applied plain to a support previously

coated with a colloid layer or composed of or surfaced with a porous water-absorbent or water-adsorbent substance, such as paper, fabrics, regenerated cellulose, spongy-texture rubber, suitable plastic compounds, natural and artificial resins, cellulosic esters, etc.

A silver salt may be applied to the layer after exposure. The ferrous ions that are formed, image wise, by light action on ferric salt layers, act as reducing agents—actually developers—of silver salts that may be applied to it in after-treatment.

On exposure, the layers so sensitized print-out in rich dark brown to black, and they only need a first rinse in water for 1 minute, then about 1 minute fixing in 15% hypo, then a 5 minute wash. The silver image so obtained is then treated in any of the known ways whereby color pictures can be obtained, namely by bleaching and color-development, oxidation and reduction processes, toning, dye toning, ozobrome, dye imbibition, and the like. One detailed example of such color conversion procedure will be given further on.

The following are examples of ferric salt sensitizers intended to be treated with a silver solution after exposure:

The simplest formula, for application to base surfaces or to surfaces previously treated with a substratum intended to cause permanent retention of a gelatine layer is:

Water	cc	100
Gelatine	gr	7
Ferric ammonium oxalate	gr	10

A more complex formula would be:

Water	cc	100
Gelatine	gr	10
Ferric ammonium oxalate	gr	15
Ammonium oxalate	gr	2.50
Ammonium chromate	gr	0.05

An example of a formula for use to impregnate—for instance, by immersion or by spraying—a water absorbent material or a gelatine coated surface, is similar to the above, with the difference that the given quantities of water are reduced in each case to 75 cc. and the gelatine is either entirely omitted or reduced to only 1 or 2 grammes. An all-round improved formula would be:

Water	cc	100
Ferric chloride	gr	3
Oxalic acid	gr	1.50
Ferric ammonium oxalate	gr	10
Sodium oxalate	gr	2
Ferric ammonium sulphate	gr	1

The ferric sulphate and the oxalic acid are for contrast. A small amount of gelatine, one to two percent of the water content, considerably enhances speed.

After exposure, in each case the material is immersed directly for 30 seconds up to 1 minute in a 1 to 2% silver nitrate solution in distilled water. An improved silver nitrate solution for the purpose is:

Water, distilled	cc	100
Silver nitrate	gr	2
Ammonia		Q.s.

(By q.s. is meant as much as required just to re-dissolve the brown precipitate that is at first formed.) Then add:

	Grams
Sodium sulphite	0.15
Borax	0.10

Immediately on application of the silver nitrate solution a vigorous image in a rich sepia to black is formed: rinse for 1 minute, then fix for 1 minute in 15 to 20% hypo solution, then wash for about 4 minutes.

The silver image so obtained is thereafter treated, as in previous cases, so as to yield a colored image in any known suitable way.

Reverting to general characteristics of ferric ion sensitizers, in repeated meticulous practices I have been able to ascertain three novel points of considerable relevance:

(1) Gelatine layers seem endowed of an infinite capacity to absorb and adsorb ferric ions time and again over and over repeatedly, almost endlessly. I have actually sensitized and resensitized the same piece of a fixed-out moving picture film as many as eight times, with the production of a good strong image in every case, resulting in as many as eight images on the same film area.

(2) The speed to light of a gelatine-ferric salt sensitive layer increases with increase in the saturation of ferric ions absorbed or adsorbed; hence, when a gelatine layer has been made the recipient already of one color image, there is physically a reduced quantity or area of impregnable colloid. This would cause a progressive reduction in speed of each impregnation, but can be compensated to a degree with increased saturation of ferric salts in the solution used to resensitize. In practice, and in the case of ferric ammonium oxalate, if in a first impregnation a 10 to 13% water solution of the salt is used to produce a first color image, in a second re-impregnation a 22% solution of the same salt may be used, and in a third impregnation the saturation may then be 30% and should be preferably added with up to 2% gelatine. Thus exposures may be equalized, standardized or corrected, as the case may be, having in mind also that the different elements of a set of color separation negatives may be of varied overall density so as to require adjustment.

(3) At each impregnation, the ferric salts permeate to any part of the layer in which impregnable colloid is still free or partly free for instance also, in part, underneath a previously formed image. Everywhere the ferric salts so penetrate an image is thereafter formed. Hence my resulting pluricolor images are not produced in stratifications but really are composed of effective mixture of images, which, in projection, focus all on the same plane. This constitutes a considerable advantage on any other present color process, mostly pluri layers. This together with the absence of any discernible grain makes my process outstanding in its superiority, despite the fact that it is much more economical.

These points of speed increase, compensation and standardization are not embodied in the following general examples, as they come of use only dependently on the particular qualities of the various negatives of a given separation set, while the following examples are only intended to give a clear full description of average working procedure.

Examples here follow the whole procedure, step by step, in extenso, for the production of a multicolor moving picture film.

Example I

Step 1.—A Celluloid film coated with plain gelatine (as may be obtained for instance, by fixing out and washing well a positive film acquired on the market) is immersed for 1 minute in a solution made up of distilled water 100 cc., and 15 gr. of ferric ammonium oxalate. Nothing else is strictly necessary. The film is then dried in a current of warm air, which takes only another minute.

Step 2.—Expose the coated film under the green filter negative of a color separation set to a strong light rich in ultra violet rays, which will require, according to the strength of the light unit and the density of the negative, from one to three seconds.

Step 3.—Immerse for thirty (30) seconds in a 2% silver nitrate solution with sufficient ammonia added to dissolve the brown precipitate first formed and then add 0.15 gr. of sodium sulphite and 0.10 gr. of borax. Rinse 1 minute, fix in 15 to 20% hypo 1 minute, wash 4 minutes.

Step 4.—Bleach 1 minute in a solution of 100 cc. of water, 7 gr. of potassium ferricyanide, and 7 gr. of potassium oxalate neutral. Wash 2 to 4 minutes.

Step 5.—Immerse in a color developer compounded as follows: 100 cc. of a sodium carbonate 2% water solution containing also 0.50% sodium sulphite: add to it 2 cc. of a 5% solution of diethyl-p-phenylene diamine hydrochloride in methyl alcohol, and 2 cc. of a 2% solution of p-nitro benzyl cyanide in equal parts of acetone and methyl alcohol. In 2 to 5 minutes the desired magenta image is formed. Wash 2 minutes, bleach 2 minutes in same bleacher of step 4, rinse, fix 2 minutes in 15% hypo, wash 4 minutes.

Step 6.—Wipe off surface moisture (no need to dry) then immerse again (the same material) in sensitizer exactly as in Step 1 and dry correspondingly.

Step 7.—Expose again the same material, so re-sensitized, with the magenta image in register with the red filter negative of the separation set.

Step 8.—Repeat exactly step 3.

Step 9.—Repeat exactly step 4.

Step 10.—Repeat step 5 with the only modification that, instead of the p-nitro benzyl cyanide solution mentioned, the same quantity (2 cc.) of a 5% solution of phenyl phenol sodium salt in methyl alcohol is employed. All operations as in the corresponding step. A cyan image results, on top of the magenta previously formed.

Step 11.—Repeat step 6.

Step 12.—Repeat step 7, using the blue filter negative of the separation set.

Step 13.—Repeat step 8 (=3).

Step 14.—Repeat step 9 (=4).

Step 15.—Repeat step 10 (=5) with the further modification that instead of the p-nitro compound and of the phenyl phenol salt the same quantity (2 cc.) of a 5% solution of acetoacetanilide in methyl alcohol is used. All operations as in the corresponding step. A final multicolor picture is thereby obtained.

Example II

A release positive unexposed film is printed in normal way under a green-filter negative of a separation set and developed fixed and washed in normal way as in black and white procedure. The silver image is bleached in a suitable bleacher, then washed, and then all the steps from 5 on are applied as in Example I.

Example III

A release positive unexposed film is printed in normal way under a green-filter negative of a separation set and then directly color-developed in magenta in a known way, freed from silver also in known way, and finally washed. Then all steps from 6 on are applied as in Example I.

Modifications in the order in which the images in the various colors are produced can be introduced as desired. Duplicator materials, i.e. coated with plain gelatin or with silver halide emulsions on both sides, can be utilized, with resultant shortening of the overall procedure inasmuch as sensitizing baths and other general baths would then operate at one and the same time on both sides, applicators being resorted to only when differentiation of agency (different color coupler) is demanded on each face.

Needless to say, considerable variations in quantities and kind of ferric salts are possible in all formulae.

From the above description it will be apparent to those skilled in the art that the objects of this invention can be accomplished in a number of specifically different ways and I do not, therefore, desire to be limited to the illustrations, but only as required by the appended claims.

What I claim is:

1. A process of producing colored picture film which comprises carrying out at least once the sequence of steps comprising: sensitizing a film with a solution consisting of water and ferric ammonium oxalate, exposing

the sensitized film to light rich in the spectral region of the ultraviolet through one of a set of color separation negatives, treating the exposed film with a solution of silver nitrate to produce a visible metallic silver image, bleaching said silver image into a silver salt image, redeveloping said silver salt image with a color developer in the presence of a coupler to produce a dye image and a silver image in situ therewith, and removing said silver image.

2. A process for producing colored picture film which comprises carrying out at least once the sequence of steps comprising: sensitizing a film with a solution consisting of water and a ferric ammonium double salt, exposing the sensitized film with light rich in the spectral region of the ultraviolet through one of a set of color separation negatives, treating the exposed film with a solution of a silver salt to produce a visible metallic silver image, bleaching said silver image into a silver salt image, redeveloping said silver salt image with a color developer in the presence of a coupler to produce a dye image and

a silver image in situ therewith, and removing the silver image.

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