Dec. 31, 1940. K. SCHINZEL 2,226,639

COLOR PHOTOGRAPHY

Filed April 29, 1937

FIG. 1

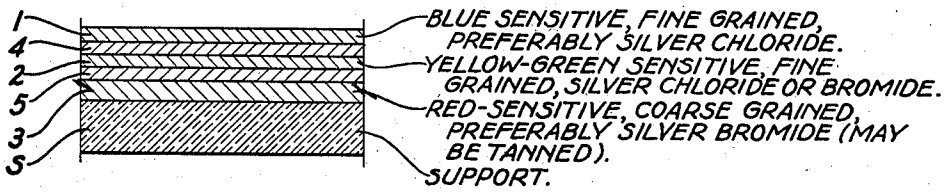


FIG. 2

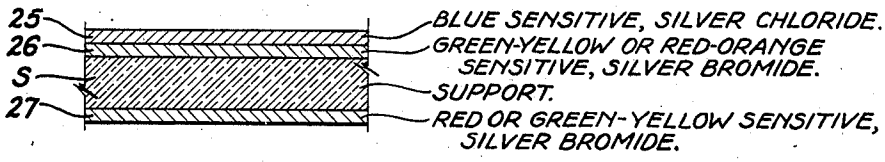


FIG. 3

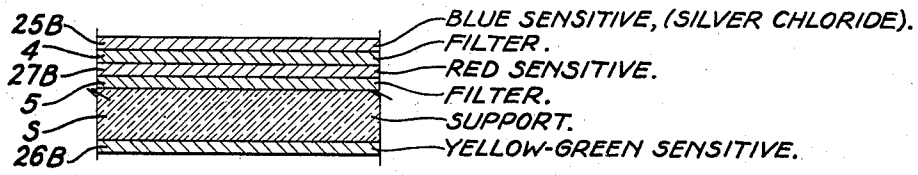
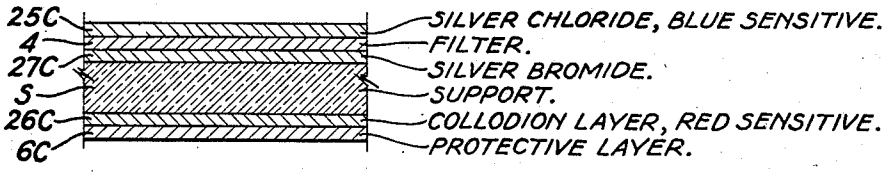


FIG. 4



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COLOR PHOTOGRAPHY

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5 Claims. (Cl. 95—2)

This invention relates to color photography and particularly to processes of the type known as "monopack", that is, involving the use of differentially color sensitive layers permanently superposed on a single support.

As will be hereinafter described, in a triple layer, and similarly in double layers, the making of natural color images by colored development of the silver halide which is present in the image, or is reconverted and optically treated, is possible; that is, the making of true color images by use of the residual silver halide after the usual black development, or of complementary color images, if the three latent part images obtained in the exposure, or the three silver halide images obtained after general development and fixation, are after rehalogenation independently developed to the corresponding part images.

In the present invention the residual developable silver halide or that formed on the original latent image by general rehalogenation or each layer is immediately developed to the corresponding final part image, unless other coloring methods are applied for one of the layers. Progress has been made by the present invention since by it diffusion of the reagent into the layers is free from the uncertainties of penetration and since production of entirely or almost true color photographs optically has been made possible without uncertainty and complicated developing machines, and this with the purest vat dyes.

Reference will be made from time to time, throughout this specification to the accompanying drawing which shows enlarged sections of photographic film embodying certain of my inventions or useful in my improved processes and in which the same reference characters indicate the same elements.

Fig. 1 shows a section of film having three differentially color sensitized layers on one side of the support.

Figs. 2, 3 and 4 show in section different embodiments having differentially color sensitized layers on the opposite surfaces.

The three-layer material

Referring to Fig. 1, the support S carries the differentially sensitized layers 1, 2 and 3, the upper layer 1 is generally blue-sensitive, the middle layer 2 yellow and green sensitive and the lower layer 3 red sensitive. In order to limit diffusion to a minimum, it is advisable to make the two upper layers as thin as possible, about 0.005–0.01 mm., requiring the use of very fine-grain emulsions, relatively poor in silver, for three-color reversal development. In case filter layers 4 and 5 are interposed, strongly swelling gelatine may be used for these, so that the individual layers are separated by the proper distance from each other during the chemical reactions. These filter layers are kept so thin, 0.01 mm. or less, that harmful diffusion is not increased, even if they should swell, to ten times their size. The lower layer can have the normal thickness of 0.02 mm., for reversal development 0.01–0.015 mm., so that the total thickness of the three layers is 0.025–0.240 mm. While the two upper layers require developers which deposit especially productive and intensive dyes on the image, less intensity is required for the lower layer, since this layer may contain considerably more silver halide than the upper and also middle layers. A similar intensity balance of the separation images is often obtained by addition of sulfite to the reversal developer for the lower layer, while this is omitted for the other layers.

Coating of both sides of the film

In the three-layer film shown in Fig. 2 the red or yellow-green sensitive silver halide emulsion layer 27 can be situated alone on the back of the support, the others on the front. In the two-zone-double layers, the blue-sensitive layer may be in front and the layer which is sensitive to red and yellow-green by zones on the back side of the film. In these films coated on both sides, the support may be very thin, if the motion picture camera is of the continuous moving film type and development is done under such conditions which prevent strong swelling of the preferably moderately tanned gelatine layers. This is attained by addition of alcohol or salts preventing swelling, such as sodium carbonate, sodium sulfate etc. to the different baths, also by the use of developers containing much alcohol, if the dye generated is insoluble in it. In the three-layer plate, the lower layer, and in films coated on both sides, the middle layer, can consist of silver halide collodium emulsion or an emulsion of silver halide in any other non-aqueous vehicle. In layers coated on different sides of the film, some may consist of silver halide collodion emulsion. In order to keep the pores of the collodion layer 26C open, a protective layer 6C, which may be of gelatine, dextrine, gum arabic etc. is coated over it serving at the same time as supression or anti-halation protection. Thin films of cellulose acetate, Cellophane or synthetic colloids, lacquered on both sides, if necessary, serve as support. A very thin film, emulsion-coated on both sides, is tem-

porarily mounted, if necessary, on permeable paper or aluminum foil; for larger images, thin Cellophane or transparent paper, possibly glued on stronger paper, may also be used.

Three-color reversal development

After exposure or printing exposure, the superimposed latent images are developed to the three black separation silver images by an ordinary, non-tanning, preferably neutral developer, as ferrous oxalate, amidol, diamido- -cresol etc. Most other organic developers in solutions containing sodium carbonate are also suitable, since they do not noticeably harm the color sensitivity, and this can be at least partially restored by the proper reagents. There is no emulsion for which the use of the so-called compensation developers for correction of the almost unavoidable differences in exposure of the individual separation emulsion is more recommended than for the triple layer.

In order to avoid the undesirable effect of local under-exposure in the lower layers, it is best to bathe all three layers first in a solution of the non-acting developer substance of a considerably stronger concentration than usual, and then to develop in solutions of sodium carbonate, ammonia or weak alkalies. Simple concentrated developing solutions can be allowed to diffuse with as low temperature as permissible and the development process started or accelerated by warming to room temperature or above. The same holds true for other reversal solutions.

Further treatment may be carried out in different ways and depends upon whether filter layers are provided, or the sensitization is oxidation-stable or only developer-stable, or whether the upper layer consists of silver chloride etc. The greatest difficulty is to make the residual silver halide of the middle layer developable without influencing the other two existing part images.

Usually, such sensitizers are selected, and this is assumed in the following examples, as are stable, at least to a neutral black developer and to the first weakly alkaline color developer. A special advantage of the invention, however, is the fact that sensitization does not even have to withstand the ordinary general development, if the middle layer is surrounded by two filters which are empenetrable to blue or ultra-violet light which latter makes the residual silver halide of the upper and middle layer developable, while the production of the middle part image is done, even without the action of light, by chemical pretreatment with weak reducing agents or with the use of energetically acting color developers. It is, of course, assumed that both filter dyes are stable to the developer and are destroyed only later by acids, bases, oxidation or reduction. The lost color sensitivity can be restored by resensitization which, however, complicates the process.

It must not be omitted to mention that the character of the reversal images can be changed to a certain degree by a very careful general exposure or additional exposure through color filters of all or some of the layers.

The following examples illustrate the practical application of the principles of three-color reversal development as explained in the preceding paragraphs, reference being made particularly to Fig. 1 by way of example.

In the absence of filter layers and with sensitization of the lower layer 3 exclusively for red or also orange or infrared, the initially reduced silver could be, as also in other cases, converted into silver ferrocyanide which is no more developable or only extremely slowly so with suitable color developers, or into highly dispersed silver iodide, or into any other colorless silver salts which is insoluble, and difficultly reduced, preferably soluble in hypo, and decomposed by alkali or acid or the metallic silver can be completely dissolved by oxidizing agents and washed out. Here and in analogous cases discussed later it is sufficient, if at least the highly dispersed silver of the upper layer 1 and, totally or partially also the fine-grain silver of the middle layer 2 is converted in this manner. Waiting is then not necessary, (and this is a characterizing point of the present invention), until also the coarser negative silver of the lower layer 3 is converted or dissolved, since exposure of the residual silver halide of the middle layer 2 is best done from above. The residual silver halide of the middle layer 2 is then exposed to yellow or green light from either side and developed purple. After this, the silver halide of the lower layer 3 is exposed to red light through the support S and developed green-blue. Finally, the residual silver halide of the upper layer 1 is exposed to blue or ultra-violet light and developed yellow. A variant of this procedure would be to re-expose the lower layer 3 first to red light and develop green-blue, then re-expose the middle layer to yellow light from above, etc. In all these variants it is assumed that the sensitizers of the middle and lower layers are stable to mild oxidizing agents acting on metallic silver. This condition can best be fulfilled by the presence of highly dispersed silver, as it exists in the highly sensitized grainless or very fine-grain silver halide emulsions of the upper or also middle layer. The color sensitivity can, however, be partially restored by dilute solutions of sulfite, bisulfite, hydrazine sulfate etc., unless addition of these agents with bleaching of the dye already formed does not take place.

The lower layer 3 can also be exposed to red light directly after primary general development and its residual silver halide developed green-blue, and only then all silver which was previously reduced, or at least the highly dispersed silver of the upper layer (or partially, also, the fine-grain silver of the middle layer), removed or preferably converted into silver ferrocyanide or the compounds mentioned above. The middle layer alone 2 is then exposed to yellow light from above and developed purple, then the upper layer is exposed to blue light and developed yellow. The exposure of the middle layer 2 to green light from below, or to blue light from below in the case of a yellow filter layer 4 between the top two layers, can be less satisfactorily accomplished by exposing in either case after preliminary reduction of the green blue dye formed in the lower layer 3 to its easily re-oxidized insoluble leuco-forms. Reduction of the residual silver halide of the upper layer 1 may be effected here, as in similar cases, by alkaline solution of the leuco-forms of various yellow vat dyes, best under exclusion of atmospheric oxygen to prevent fog. Oxidation stability of the red sensitizer, which may here be also sensitive to yellow, is no more required, which represents a very great advantage compared to the method of execution previously described, becaues the choice of proper red sensitizers is much less limited, and many may be used which excel by complete insolubility or inability to diffuse. Under certain circumstances, even oxidation-stability of the sensitizer

of the middle layer is unnecessary, as proven by the following examples:

The residual silver halide of the middle layer 2 can be exposed also to blue light through the support S, if sufficient blue sensitivity of the upper layer 1 was obtained by high sensitization which is then lost during conversion by oxidation of the primarily reduced silver, since here the undesirable effect of the very little sensitive upper layer is not feared. The hardly noticeable different conditioned by the lower blue (or purple) image can be corrected by creating a blue (or purple) indo-phenol or azo-methine dye in addition to the silver in the first general development which, however, in contrast to the final image dye of the lower layer (indigo, Russig's dye, seleno indigo etc.) is easily split by acid. After making the residual silver halide of the middle layer 2 developable with blue light through this lower layer now uniformly colored, the intermediate dye of the lower layer is destroyed. This may also be done after completion of the three-color image, if also final yellow dye of the upper part image is stable to acid.

As a further example, the middle layer 2 is exposed to yellow light from either side and developed purple, then the upper layer 1 is exposed to blue light and developed yellow, finally the lower layer 3 to blue, white or red light and developed green-blue after removal or conversion of the primarily reduced silver, if there is a yellow filter layer 4 between the middle and upper layer or if the latter is colored yellow and the yellow-green sensitizer alone is oxidation-stable. The lower layer 3 can also first be exposed to red light and developed green-blue, then the upper layer 1 to blue light and developed yellow, or in reverse order; after short action of potassium ferricyanide or suitable solvents on the newly reduced, highly dispersed silver of the upper layer, the middle layer 2 is made developable with yellow light and developed to the purple part image. It would be less correct to expose to red light the residual silver halide of the lower layer 3 after general black development and to develop green-blue, that of the upper layer to blue and to develop yellow, or in reverse order, and then only to convert all silver, or at least that of the upper layer, into silver ferrocyanide or to dissolve it, and finally to expose the middle layer 2 to yellow and to develop purple.

The stability of the green-yellow sensitizer to oxidation is not absolutely necessary for the middle layer 2, if at least the yellow filter layer 4 which also absorbs ultra-violet, or yellow coloring of the upper layer is present, so that in the triple layer, according to the present invention, one can entirely dispense with oxidation-stable sensitizers and pay more attention to prevention of diffusion of sensitizers from one layer to the other. The lower layer 3 is exposed to red light after general black development and is developed green-blue and treated further according to one of the following methods:

It would be simplest to expose the middle layer to ultra-violet light through the lower uniformly blackened layer and through the green-blue dye not absorbing ultra-violet or to infrared light, if it was also sensitized for this in addition to green-yellow, and to develop purple. This requires long exposure, however, since the lower layer absorbs most of the light. Even in exposure of the upper layer to blue light, because the primarily reduced silver prevents a complete exposure through the depth of the upper layer, some residual silver halide will be left and developed in the color of the middle layer, if this is developed later. By the use of ultra-violet light for exposure of the residual silver halide of the upper layer this evil is eliminated, according to the invention. The same effect is gained with soft X-rays, if the upper part image is produced last.

It is, however, better first to expose the upper layer to ultra-violet light and develop a yellow image. Alternatively it may be treated briefly with a 1 to 2% solution of potassium ferricyanide or with a silver solvent converting or dissolving only the highly dispersed silver of the upper layer entirely or partially into white silver ferrocyanide, without allowing this to take place in the other two layers. The residual silver halide of the upper layer is then converted into a yellow image. The lowest layer is then exposed to red light and developed to blue-green. If two filter layers 4 and 5 are provided a yellow and a red or orange one, or two yellow layers, exposure of the residual silver halide of the lower layer can be done even with blue light. The middle purple part image is then obtained by one of the following methods:

(a) The residual silver halide of the middle layer is made developable by pre-treatment with about 0.02% solution of thiourea, thiosinamine etc., or analogously acting sulfur derivatives, or with a 0.001% solution of zinc chloride, by means of arsenite, hypophosphite, thallo salt, triamido phenol, masking dyes, especially in the presence of heavy metal salts or other suitable agents, which may also be added to the corresponding color developers; it is then developed purple, and finally all silver removed or fixed out. The pre-treatment may be omitted, if a color developer is chosen which acts so vigorously on addition of ammonia or alkali, or also alcohol and acetone, preferably without air, that the residual silver halide of the middle layer is reduced without exposure after prolonged treatment. This is especially true for a silver chloride emulsion layer which, unexposed, is sufficiently stable to the color developers containing soda which is necessary for the two outer layers. The residual silver bromide of the middle layer is, however, reduced without pre-treatment or exposure by most leuco-vat dyes in alkaline solution or one containing alcohol or acetone with precipitation of the dye on the image. Residues of the latent images in the other two layers can be destroyed previously by the action of mild oxidizing agents, as potassium ferricyanide and ammonia etc.

(b) All previously reduced silver is removed entirely or for the largest part, combining with it possibly the destruction of filter dyes by oxidation or acid, or converting into ferrocyanide etc., exposing the residual silver halide of the middle layer from both sides to white, or better, ultra-violet light or to soft X-rays and developing purple, and finally, removing the silver and fixing out, if necessary, both of which are possible with Farmer's reducer. The residual silver bromide can also be reduced to black silver with vigorous ordinary developer or with any organic or inorganic reducing agent; this is then converted into very easily oxidizable highly dispersed silver chloride by bichloride of mercury with the color developers even without exposure.

(c) The residual silver halide of the middle layer is at once made developable by exposure from above or from both sides to ultra-violet light or better soft X-rays, and the corresponding part image is developed. This is possible, because very fine-grain and not cohering reduced

silver is very transparent to ultra-violet light. The silver is then removed.

(*d*) The residual silver bromide of the middle layer is converted into silver iodide or one of its complex salts, if necessary, after removal of the metallic silver, and this is colored purple or green-blue by mordanting dyes. The metallic silver is removed now or earlier and fixed, if necessary. The dyes are made insoluble before removal of the mordanting agent by proper precipitants, phosphotungstate etc. If the middle layer consists of silver chloride, its residue can be converted into silver ferrocyanide, and further into red nickel-dimethylglyoxime or into yellow titanium ferrocyanide which latter yields a green-blue image with blue basic dyes. The silver ferrocyanide originating from the silver chloride, can also be converted into other suitable non-tanning mordanting bodies which are colored purple or green-blue by basic dyes and may be removed after insolubilization of the dyes in order to attain greater transparency.

Since silver bromide must withstand four developments, three of them with color developers containing sulfite-free sodium carbonate or alkali, in order to obtain vigorous part images, fog is difficult to avoid. It is, therefore, recommended to use an upper or middle silver chloride layer, especially with film coated on both sides, where the film itself or a coated filter layer can contain colorless substances absorbing ultra-violet and the red-sensitive silver halide layer is alone on one side, because silver chloride is colored, even if it is not exposed, and still more so unexposed silver bromide. Colored development of the original residual silver chloride can be even entirely dispensed with, since it is easily converted into silver ferrocyanide and this into colored substances, or easily colored mordanting bodies. One is not dependent upon the easy reducing ability of silver chloride at all, if the residual silver chloride is only temporarily converted into silver ferrocyanide after first general black development, according to the invention. After colored development of the two other layers, it is reconverted into silver chloride or silver bromide, or less desirably, into silver iodide, which can also be effected by addition of potassium bromide, etc. to the last color developer. The residual silver ferrocyanide could also be reduced with a vigorous color developer directly, or with formation of the color image from silver iodide which is readily obtained from the residual silver chloride.

It is possible to utilize the differential development properties of silver chloride and bromide to form an image in the silver chloride only. Since silver chloride develops more rapidly than silver bromide, a strongly differential action is obtained particularly when the chloride layer is uppermost. In this case development is ordinarily not carried to completion but is stopped when a usable, even if incompletely developed image, is obtained prior to any substantial development of an image in the layer containing silver bromide. In such cases other expedients found useful in differential development may also be employed such as the use of retardants or hardening the lower layer.

The later undesired further development of the exposed but undeveloped residue may be avoided by converting the chloride to another salt.

The silver chloride layer only may be developed to a black silver image followed immediately with development of the residual silver chloride with a weak color developer which does not rapidly attack the exposed silver bromide. The residual silver chloride may also be directly or indirectly converted into a colored substance or a mordanting body, as described in detail later. Only then, the two silver bromide layers are simultaneously developed in an ordinary developer, and finally, the residual silver halide of the same developed in succession to the corresponding color, first, after corresponding exposure, the layer which was situated away from the objective, then the other one, after pre-treatment with thiourea, stannous salt etc. or with a vigorous color developer.

All this also holds true for a middle silver chloride layer and is especially favorable with films coated on both sides.

A middle silver chloride layer permits in this manner, independent development of all three part images, even when no filter layer or only one is present and sensitization is not even stable to an ordinary black developer. Several such processes will be outlined. (*a*) The latent image of the middle silver chloride layer is first developed alone with a weak ordinary developer, and then, with a color developer which is only strong enough to reduce the residual unexposed silver chloride, but not the exposed or unexposed silver bromide, the middle part image is developed. For this purpose, the silver chloride of this layer could be pre-treated with solutions of very mild reducing agents or compounds containing sulfur which make the residual silver chloride of the middle layer developable, but not the unexposed silver bromide. Since the middle layer is entirely blackened by metallic silver, the two other layers can be independently exposed to blue light after ordinary development, and their residual silver bromide can be individually developed in color.

(*b*) Furthermore, the residual silver chloride of the middle layer can be converted into silver ferrocyanide after usual black development, the latent images of the other two layers developed in an ordinary developer, the silver ferrocyanide of the middle layer reconverted into silver chloride and this silver chloride and the residual silver bromide of one or both layers made developable by exposure, chemical pre-treatment or in any other manner. Now the middle color image is developed with a specific silver chloride developer and the residual silver bromide transformed into the inert state by mild oxidizing agents, as for the destruction of chemical fog, then, by a bath of sulfite, bisulfite, hydrazine- or hydroxylamine salt it is made sufficiently light-sensitive and each silver bromide layer individually exposed and developed in color. The silver ferrocyanide obtained from the residual silver chloride is in itself sufficiently dense to allow the residual, highly sensitive silver bromide of the lower layer to be given a short exposure; a better procedure is to convert with lead chloride or thorium salt into the corresponding ferrocyanides and to convert the newly obtained silver chloride into silver ferrocyanide. All silver ferrocyanide could also be converted into lead chromate which acts like a yellow filter in the individual exposures of the two outer silver bromide layers and is removed at the end. All this holds especially true, if the very fine-grain silver bromide of the upper layer has lost its high sensitivity which it had acquired through high sensitization. The silver ferrocyanide of

the middle layer or the zinc ferrocyanide obtained from it with zinc chloride or zinc bromide may serve as an excellent mordanting substance for coloring with yellow basic dyes, resulting in a middle yellow-black filter. The two latent silver bromide images can now be developed under certain conditions, unless this has been done before, and the residual silver bromide of each layer individually exposed and developed in color.

(c) After simultaneous development of all three latent images, the residual silver chloride of the middle layer is converted into silver ferrocyanide and this into yellow titanium ferrocyanide or into any other non-tanning colored insoluble ferrocyanide, or also through nickel ferrocyanide into nickel-dimethylglycoxime or other insoluble colored and easily split complex compounds which act as middle light filters in the exposure of the residual silver bromide of the two outer layers. The insoluble ferrocyanides are split by sodium carbonate or alkali, the complex salts mostly by acids. The silver chloride formed can be reconverted into silver ferrocyanide which is practically insensitive to light, or it is converted with bromine salts, since silver bromide formed in this way is only very slightly sensitive to light in comparison with the silver bromide of the lower layer. After colored development of the two outer layers, silver halide may be regenerated from the silver ferrocyanide of the middle layer and this made developable by thiourea, stannous salt, masking dyes etc. or by intensive exposure to ultra-violet or X-rays, and developed in color or converted, similar to the original silver ferrocyanide, with a vigorous color developer directly into the part color image. Finally, all silver and the insoluble ferrocyanides are removed and the filter dyes washed out.

(d) All three layers can be developed simultaneously and the residual silver chloride converted into silver ferrocyanide and this reconverted into silver chloride which becomes very highly dispersed and easily developable, so that the middle part image is developed by a color developer without exposure. The other part color images are then developed from the residual silver bromide of the two outer layers. The residual silver halide of all three layers can be made developable simultaneously by ultra-violet or X-rays, by pre-treatment with thiourea etc., and the silver chloride of the middle layer developed in color, so that a homogeneous color filter is created in the middle. The latent developing ability of the residual silver bromide is now destroyed by the action of mild oxidizing reagents, p-phenylenediamine and acid etc., sufficient general sensitivity created by a bath of sulfite, bisulfite, hydrazine salt, hydroxylamine etc. or by optical sensitizers in preferably weak ammoniacal solution, and the two outer emulsions individually exposed and developed in color. If the middle emulsion is still sufficiently yellow-green or red-sensitive after ordinary development of the silver chloride, it is exposed to the proper light and the residual silver chloride developed in color, so that a homogeneous silver filter also results. The latent images are then developed in the two outer silver bromide emulsions, and finally, their residual silver bromide individually exposed and developed to the corresponding part color images. The same holds true, if the sensitizers mentioned do not survive the first general development, but if the middle emulsion contains in addition a resistant infrared sensitizer, so that the residual silver chloride of the middle emulsion can be made developable by infrared rays for which the two outer silver bromide emulsions are absolutely insensitive and which is not harmful to the latent images contained in them. Since a yellow filter between the upper and middle emulsions is indispensable for nature photography, all reduced silver can be removed after general black development of all three emulsions, and then the middle and lower emulsions simultaneously exposed to blue light, first the residual silver chloride, and then the residual silver bromide developed in color, and finally, the part color image developed in the upper silver bromide emulsion; or vice-versa. The silver is removed at the end.

(e) If an upper or middle silver chloride emulsion exists it is possible to convert the residual silver chloride into silver ferrocyanide, and only then proceed to general black development of the two silver bromide emulsions. Without preliminary removal of the metallic silver bromide, the lower (or in reverse order for exposure through the back; of the upper) red-sensitive emulsion is exposed to red rays (if a green-sensitive emulsion to green rays) and developed in the approximately complementary color. The residual silver bromide of the middle emulsion is then made developable with thiocarbamide etc. and the corresponding part color image developed. Finally, the silver ferrocyanide of the blue-sensitive emulsion is converted into silver halide by sodium chloride or potassium bromide, which may also be added to the color developer, made devolopable by light or repeated treatment with thiocarbamide and developed to the corresponding part color image. All silver is then removed simultaneously. The reconverted silver chloride is highly dispersed and is reduced by correspondingly vigorous color developers, also without exposure, similar to that obtained by treatment of metallic silver with bichloride of mercury. The silver ferrocyanide itself is also reduced by sufficently alkaline developers, especially leuco-vat dyes. A great advantage here is that the sensitizer for the emulsion which is most remote during exposure does not have to be oxidation-stable. An infrared sensitizer which is stable to the developer and mild oxidizing agents can also be added to this emulsion or to the silver chloride emulsion. The residual silver halide of this emulsion can be made developable through infrared light, even if the original sensitizer has become ineffective. Any other sensitizer could, however, be added to the lower emulsion in addition to that for red, for which the middle emulsion is insensitive. An infrared sensitizer which is stable to the developer, can generally be added to the lower emulsion in addition to the red sensitizer. After general primary development, the residual silver bromide of this emulsion is first exposed to infrared rays and developed in color, the other two emulsions can then be made developable with thiourea etc., and first the silver chloride, then the silver bromide emulsion developed in color. In printing, the lower emulsion can be sensitized exclusively for infrared, the middle for red, orange, yellow or green, and the residual silver halide made developable with this light.

The use of silver chloride is especially advantageous with films coated on both sides of the type shown in Fig. 2, on one side with an outer blue-sensitive silver chloride emulsion 25 and an inner silver bromide emulsion 26 sensitized for

green-yellow or red-orange on one side and with a silver bromide emulsion 27 sensitive to red or yellow-green on the other side. After general black development and perhaps removal or conversion of the reduced silver and also repeated exposure of all residual silver halide, each side is developed independently from the other. First, the residual silver chloride of the double-emulsion-coated side is developed in color, then the silver bromide of the middle emulsion or middle zone below, finally the silver bromide emulsion on the other side, or vice-versa, followed by removal of all reduced silver. Instead of a second exposure, it may also be pre-treated with thiourea stannous salt, masking dyes etc., or the reduced silver is removed entirely or for the greatest part and both sides exposed to ultra-violet rays.

If the red-sensitive emulsion 27B is in the middle, as in Fig. 3 with color filters 4 and 5 on one or both sides, if desired, the previous developing procedures can be applied here, if they are correspondingly changed. The following examples may serve as an example: If no filters are present, the middle emulsion is exposed to red light after removal or conversion of the primarily reduced silver and developed green-blue, the lower 26B to yellow and the upper 25B to blue light, etc. The lower emulsion can also be exposed to yellow light directly after black development and developed purple, then all silver converted into silver ferrocyanide or removed. This is followed by exposure of the middle emulsion from above or below the red light and green-blue development, then exposure of the upper emulsion to blue and development of the yellow part image. In the event of an upper yellow filter, the upper emulsion can be made developable immediately after black development in order to obtain the yellow part image; the middle emulsion is then made developable by thiourea etc. or after removal or conversion of all reduced silver by exposure to white light from both sides. If yellow filters 4 and 5 or ultra-violet-absorbing filter layers are arranged on both sides of the middle emulsion, the two outer emulsions are made developable with blue or ultra-violet light, and the middle emulsion in the manner just described. If the silver chloride emulsion is on top, one can expose to yellow light from the back, after general development, and the lower purple image can be produced. The upper and middle emulsions are then made developable directly by thiourea, etc., or, after preliminary removal or conversion of the reduced silver of at least this emulsion, by exposure to white or blue light from above. The yellow part image is then produced in the upper emulsion with a color developer which acts only on silver chloride, then the green-blue part image in the middle emulsion with a vigorous developer.

In films coated on both sides, all previous and subsequent methods of three-color reversal development and redevelopment, as well as of the primary three-color development and combination processes can be made much simpler, as can be seen from following examples. According to the invention, the most favorable results are obtained, when the blue-sensitive and the middle emulsions are on the same side of the film and the red- or yellow-green-sensitive one on the backside, as in Figs. 2, 3 and 4, because one-sided color-development can be accomplished by many perfected methods without changing the latent image or the residual silver halide of the other side. For nature photography, triple-layer film can be used, coated on the side not carrying the silver chloride emulsion 25C, with a layer 6C which at first retards development, as alcohol-soluble lacquer, benzyl ether cellulose, a stearine layer soluble in the alkaline color developer etc., in order to be able to accomplish one-sided development with greater certainty. After completion of the part color image or images on one side, the temporary coating is removed and the colored development of the other side completed. Since the double-emulsion side contains the yellow filter 4 between the two emulsions 25C and 27C, the residual silver halide of the blue-sensitive emulsion can be made developable with blue light after general black development and developed to the yellow part image; then both other emulsions are made developable with thiourea etc. and one after the other developed independently in colors. If the double-layer consists of a silver chloride and silver bromide emulsion as in Figs. 3 and 4, the residual silver halide of all three layers can be made developable by this pre-treatment. The silver and chloride emulsion alone is first developed in color, then the two other silver bromide emulsions independent of each other. The procedure is analogous in the two-zone double-layer, if the emulsion which is not sensitized by zones is alone on one side of the film. After general development, the outer zone of the other emusion is exposed to blue light, developed in color, then the zone underneath made developable with thiourea etc., and the next part color image developed in it; or the residual silver halide of the emulsion adjacent to the support is immediately developed in color with a vigorous developer, then the other side developed in color.

In addition, it may be mentioned that sometimes the reverse order of the silver halide emulsions, the blue-sensitive layer at the bottom, is especially advantageous in exposure through the back. A triple layer may be used in which the layer coated on the support consists of a highly-blue-sensitized silver bromide or silver chloride collodion emulsion, the middle layer of moderately hardened yellow-green-sensitive silver bromide gelatine emulsion and the upper layer of a soft-red-sensitive silver bromide gelatine emulsion. A yellow filter 4 is provided between the blue-sensitive and the middle emulsions. The red senstizer sensitizes exclusively for red, and at the most, for orange and is stable to the usual developers. After development of the residual silver bromide of the upper emulsion with red light to the green-blue part image, the lower emulsion is exposed through the back to blue light and developed yellow. Then all previously reduced silver is removed, the residual silver halide of the middle layer exposed to blue from above. This need not be yellow-sensitive, since the blue part image has no density to the blue light.

Specific action of a developer on silver chloride does not depend on its chemical constitution alone. but even more on the working conditions. P-aminophenol, p-dichloraminophenol, p-amino-dimethylaniline develop silver chloride even as free bases or their salts in the presence of bicarbonate, amidol and diaminoresorcin can be weakly acidified without losing their developing power for silver chloride. Pyrogalloldimethylether in alkaline solution works much more rapidly on silver chloride than on silver bromide and yields also much stronger brown-red images after removal of the silver with Farmer's solution, p-chlor-o-amino-vic.m.-xylenol in aqueous sodium carbonate solution yields strong lemon-yellow images with silver chloride emulsions, while silver

bromide even in alkaline solution develops much slower to very much weaker color images. Often the developing power is intensified by the presence of a coupling component or this power is even created by it: p-amino-phenol and dichlor-p-aminophenol do not develop the latent image on silver bromide gelatine emulsions, but do develop in a solution with m-toluylenediamine, which in itself is, of course, no developer. When using its salts in the presence of bicarbonate, a blue dye image is formed which is only slightly water-stable. Even p-amino-dimethylaniline plus bicarbonate does not develop silver bromide. In the presence of 3-nitro-phenylmethylpyrazolone, however, a brick-red image is slowly produced, but much more quickly on silver chloride gelatine emulsion. Also coupling developers containing sodium carbonate can act selectively to a certain degree: p-aminodimethylaniline and phenyl-J-acid Ciba yield very strong blue-green images in sodium carbonate solution on silver chloride emulsion, much weaker images on silver bromide emulsions. Similar differences exist in coupling with carbonyl-J-acid, forming dark grass-green images. 7-amino-α-naphthol couples in alkaline solution with p-aminodimethylaniline to a dark-green dye; but the images are intense only on silver chloride emulsion, while silver bromide, under the same conditions, yields only very weak dye images. The addition of NaCl or KBr also affects the selectivity. If one is not absolutely dependent on developer solutions prepared with alkali, if the developer and the possible coupling component are also soluble in water, or as most of the acid methylene compounds, in very weak alkalies (bicarbonate, borax, secondary sodium phosphate, ammonium carbonate, sodium glycocoll etc.), one is at liberty to make the simple and coupling color developers mentioned above specific for silver chloride by section and quantity of alkali. As the examples show, the working conditions can be changed in many ways for this purpose, so that it is unnecessary to give general rules. It must be decided rather in each individual case by the nature of the experiment, with which weak alkali, with which component or with which concentration and duration of the developer the best selectivity for silver chloride can be obtained.

Three-color direct development

The individual emulsions can also be separated by intermediate layers impermeable to the developer, especially the upper one from the two others. These layers can consist of gelatine, collodion, cellulose acetate or any other suitable colloid, in order to make possible the independent direct colored or reversal colored development. After completion of the upper part color image, the tanning of the gelatine is removed or the collodion etc. made permeable to aqueous solutions by alcohol, acetone etc. followed by development of the colored part images in the two lower layers according to previous methods; this is especially simple, if one of the two layers consists of silver chloride. The intermediate layers may contain substances which close the pores and these can be removed by acids, alkalies or complex forming compounds.

A further possibility of differentiation can be based on the different dispersity of the reduced silver. One develops with an ordinary developer and fixes, then converts into silver chloride or silver ferrocyanide whereby only in the upper layer a conversion product is obtained from the highly dispersed reduced silver; this is colored developed or used for mordanting after further conversion into copper ferrocyanide or zinc ferrocyanide etc. The silver halide formed from the more coarse-grained negative silver of the middle layer is obtained by prolonged action of potassium ferrocyanide and potassium bromide or sodium chloride is then developed in color, also the one formed on the other side of the film. All three emulsions can also be situated on the same side of the film, if a filter layer is inserted between the two coarse-grain emulsions; or two highly dispersed silver bromide emulsions with a yellow filter between them on the lower coarse-grain emulsion. After development and fixing, the metallic silver of all three emulsions is converted into silver ferrocyanide by prolonged action of potassium ferricyanide, and the two upper emulsions containing highly dispersed silver ferrocyanide are converted into a similar silver halide by short bathing in potassium bromide or sodium chloride, lead chloride solutions etc. The upper layer is then exposed to blue light and developed in color, then the middle layer from the back and developed to the corresponding part color image; the lower emulsion is finally developed immediately with a vigorous color developer after intense exposure of the silver ferrocyanide; or it is first converted into silver chloride which can be developed also without exposure. It is assumed that the original yellow-green sensitizer survives all these operations and also sensitizes the regenerated silver halide. The primarily reduced silver of all three layers can also be converted at once into silver halide, the lower and middle layers simultaneously exposed through the back to blue light and the highly dispersed silver halide of the middle layer, then the coarser one of the lower layer developed in color, finally the upper layer exposed to blue light from above and developed in color. Reversely, one could also make first the upper layer developable with blue light and develop in color, then expose the two others through the back to blue light and treat further as above. No color sensitivity of the middle layer is required. A blue-sensitive silver chloride emulsion could be coated at the bottom, a highly dispersed yellow-green-sensitive silver bromide emulsion in the middle, and a coarse-grain red-sensitive emulsion at the top, all untanned. After exposure, the silver chloride is converted into silver ferrocyanide by potassium ferrocyanide without attacking the latent images; then the highly dispersed silver bromide is developed in color, followed by the coarse-grain silver bromide. Finally, the silver ferrocyanide is reconverted into silver chloride or silver bromide and this developed in color. The latent developable state is not lost during these operations. The silver is then removed with Farmer's reducer. If the emulsions are coated in reverse order and also the blue-sensitized silver chloride emulsion is highly dispersed, this can be developed directly after exposure with a very weak color developer. The highly dispersed silver bromide of the middle emulsion is now developed in color with a stronger developer and then the coarse-grain silver bromide with a color developer of normal composition. All three emulsions could also be first developed as usual, the residual silver chloride then converted into silver ferrocyanide, then the residual highly dispersed silver bromide developed in color and finally the coarse-grain silver bromide. The last part color image is obtained after reconversion of the silver ferro-

cyanide into silver halide or directly with a vigorous color developer. Then the silver is removed. This is also satisfactory for three silver bromide emulsions, if the lower coarse-grain emulsion alone is tanned; the middle emulsion can then contain coarser silver bromide and the upper one highly dispersed silver bromide. In direct or reversal color development, the (residual) highly dispersed silver bromide is first developed in color, then the middle emulsion and, finally, the lower tanned emulsion. The silver is then removed.

If an upper silver chloride and a middle silver bromide emulsion is on one side of the film, the last silver bromide layer on the other side, only the silver chloride emulsion is first developed after exposure with a proper weak color developer. The residual silver chloride is converted into silver bromide or silver ferrocyanide which can also be effected by corresponding additions to the color developer; then the silver bromide layer, and independently the emulsions of the other side, are developed to the corresponding part color images, followed by removal of the silver in Farmer's solution. A yellow filter is inserted between the upper and middle emulsions, the middle layer is sensitive for yellow-green, the lower for red alone. The middle layer adjacent to the support consists of silver chloride gelatine emulsion or collodion emulsion.

On one side of the film, a middle hardened silver bromide gelatine or collodion emulsion may be coated and above it a non-hardened gelatine emulsion containing highly dispersed silver bromide. Often it is even sufficient to coat a gelatine emulsion containing highly dispersed silver bromide on a non-hardened normal negative emulsion. The upper and lower layers are individually developed, most of the silver halide fixed out and the middle tanned layer developed for a longer time into the corresponding color, possibly after detanning, and finally, the silver is removed. Such a triple layer could, of course, also be used for three-color reversal development.

I consider all of the embodiments of film and processes for treating them disclosed herein, and whether specifically claimed or not, generically and specifically a part of my invention and I desire to secure by Letters Patent of the United States protection on all the novel subject matter herein disclosed.

Having thus described my invention, I claim:

1. In a process of color photography that comprises forming color component images in separate layers on one side of the same photographic element, said layers comprising silver bromide and silver chloride, respectively, the steps of submitting said element to a developer having a higher reduction potential for silver chloride, and which acts on silver chloride more rapidly than on silver bromide, until a silver image is formed in the silver chloride layer and stopping the developing action before a useful image is formed in the silver bromide layer.

2. In a process of color photography that comprises forming color component images in separate layers on one side of the same photographic element, said layers comprising silver bromide and silver chloride, respectively, the steps of submitting said element to a developer having a higher reduction potential for silver chloride, and which acts on silver chloride more rapidly than on silver bromide, until a silver image is formed in the silver chloride layer and stopping the developing action before a useful image is formed in the silver bromide layer, treating the element to render undevelopable any exposed but undeveloped silver chloride particles and then separately developing an image in the silver bromide layer.

3. A process of color photography that comprises forming color component latent images in separate layers on one side of the same photographic element, said layers comprising silver bromide and silver chloride respectively, submitting said element to a developer yielding a silver and dye image and having a higher reduction potential for silver chloride than for silver bromide, and therefore acting more rapidly on silver chloride than on silver bromide, until a useful image is formed in the silver chloride layer, and then submitting said element to a developer yielding a silver and dye image of different color than the one first developed until a useful image is formed in the silver bromide layer.

4. A process of color photography that comprises forming color component latent images in separate layers on one side of the same photographic element, said layers comprising silver bromide and silver chloride respectively, submitting said element to a developer yielding a silver and dye image and having a higher reduction potential for silver chloride than for silver bromide, and therefore acting more rapidly on silver chloride than on silver bromide, until a useful image is formed in the silver chloride layer, and then submitting said element to a developer yielding a silver and dye image of different color than the one first developed until a useful image is formed in the silver bromide layer, and removing the silver from all layers, leaving only differently colored dye images.

5. A process of color photography that comprises forming color component latent images in separate layers on one side of the same photographic element, one of said layers containing silver halide particles of much smaller size than the other, submitting the element to a developer having a higher reduction potential for fine grain silver halide than for coarse grain silver halide, and therefore acting more rapidly on fine than on coarse particles, until a useful image is formed in the fine-grained layer, and stopping said developing action before a useful image is formed in the coarse grained layer.

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