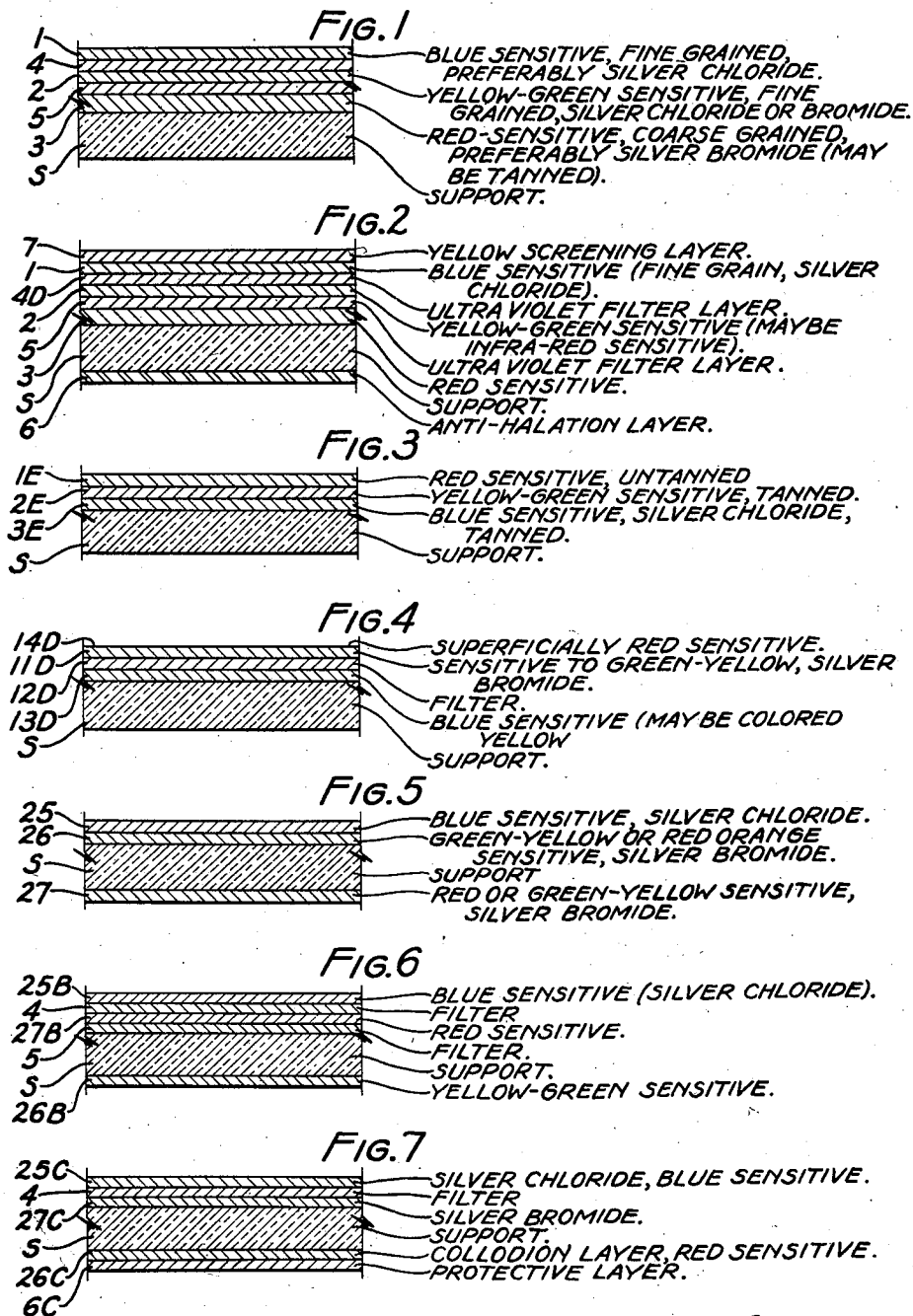


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MONOPACK FILM SENSITIZED WITH LAYERS  
CONTAINING DIFFERENT SILVER HALIDES  
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## MONOPACK FILM SENSITIZED WITH LAYERS CONTAINING DIFFERENT SILVER HALIDES

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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. This application is a division of my prior application Serial No. 139,759 filed April 29, 1937.

In the present invention the residual developable silver halide or that formed on the original latent image by general rehalogenation or rehalogenation of 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 differential diffusion of reagents into the layers is rendered unnecessary and the process is, therefore, 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.

Figs. 1, 2 and 3 show sections of film having three differentially color sensitized layers on one side of the support, the several figures illustrating different embodiments.

Fig. 4 shows in section an embodiment of film in which a single layer of emulsion is differentially color sensitized in different zones, in connection with other color sensitized layers.

Figs. 5, 6 and 7 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 dis-

tance 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.

In order to obtain a vigorous, well-graded blue image, which is of primary importance for the character of the color photograph, coating of the lower red-sensitive emulsion (for printing, also infrared-sensitive) of an average thickness of about 0.02 mm. using a highly sensitive emulsion of medium soft gradation, preferably sensitized only for red and orange, is recommended. Above this, a yellow and green-sensitive emulsion of medium sensitivity and a thickness of not more than 0.01 mm. is coated and over that a sensitized emulsion of also medium sensitivity and not color sensitive and a thickness of 0.005—0.01 mm. For this purpose, transparent, coarse-grain silver bromide emulsion can be used. Finest grain emulsions are, however, to be preferred, because their blue and blue-green sensitivity has been strongly increased by recent sensitizers so that the speed of all layers is of the same order.

The efficiency of these sensitizers can be materially increased by "ultrasensitization" and "hypersensitization" or according to the British Patent 385,545, and this is especially important if in the upper layer a pure silver chloride—or silver chloro-bromide gelatine emulsion is used, capable of being sensitized by the sensitizer of the British Patent 376,746 to ten times normal, and by ultrasensitization to 50 times normal, not much less by pinaflavol. If the finest-grain silver chloride emulsion is arranged in the middle, its sensitivity for yellow-green is already sufficiently high with the usual sensitizers, just as with silver bromide, and this is strongest if some ammonia or also soluble silver salts are added to the emulsion, as has been proposed for hyper- and ultra-sensitization. This increase in sensitivity is sufficient for exposures, if modern high-aperture optics are used.

The classical succession of the three layers can be changed, if a very sharp blue image is desired, by having the upper emulsion sensitive to blue-violet, the middle emulsion to red and orange (or infrared) and the lower emulsion to yellow and green; in which case they are developed lemon-yellow, green-blue and purple respectively. It is less desirable to arrange the layers so that the upper emulsion is redsensitive, the middle emulsion yellow-green sensitive and the lower emulsion blue sensitive, even if red sensitizers are produced today which in stronger concentration sensitize better for red than for blue (and this effect can still be increased by adding desensitizers for blue).

#### *Two-zone double layers*

Instead of obtaining differentially color sensitized strata by coating successive layers upon a common support, a somewhat similar resultant effect may be obtained by superficially treating a single previously sensitized layer so that it will, throughout a portion or zone have a sensitivity different from the remaining zone.

On Fig. 4 is shown a form in which an emulsion layer 11D sensitized by erythrosin, rhodamine B, certain thio-pseudo-cyanines etc. is coated on a non-color-sensitized silver halide gelatine- or collodion-emulsion layer 13D. A yellow filter 12D may be arranged between them or the lower layer itself may be colored yellow. The extreme portion 14D of the upper layer is then also sensitized for red with pinacyanol in dilute-alcoholic solution or with another sensitizer which under the proper conditions acts only superficially. The results are, of course, only approximate, because the upper layer 11D is sensitive throughout also for yellow-green. It is, therefore, recommended to eliminate a part of the yellow-green sensitizer by superficial action of alcohol or acetone and to then sensitize for red. Orange-red coloring of this layer acts also in that respect since in the superficial treated portion principally only the red, and towards the middle only the yellow-green rays, act during exposure through the back.

The upper or lower layer in any of these two zone double-layer forms may consist of silver chloride. Referring specifically to Fig. 4 a thin silver chloride gelatine- or collodion-emulsion 13D of normal or reduced silver content, highly sensitized for blue or blue and green with dyes, and preferably containing an easily decolorized yellow filter dye, is first coated on the film. This is followed by a silver bromide gelatine emulsion of normal or reduced thickness, containing erythrosin or other yellow-green sensitizers in the emulsion. Then it is best to allow a dilute alcoholic solution of pinacyanol or other high-colloidal red sensitizers to act on this layer, preferably after drying. This sensitizes the extreme outer portion of this layer also for red. A pure alcoholic solution of pinacyanol etc. or one diluted with 10-30% of water can also be allowed to act on the dry layer; or the swelled or hardened layer is sensitized with a pure alcoholic solution superficially applied with brushes, rollers or sprays. Exposure is made through the support.

#### *Coating of both sides of the film*

In the three-layer film shown in Fig. 5 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 collodion 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 suppression 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 temporarily mounted, if necessary, on permeable paper or aluminum foil; for larger images, thin Cellophane or transparent paper, possible 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-o-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 underexposure 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 oxidationstable 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 impenetrable 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 pre-treatment 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, because 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 the 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 re-

ducing 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.

5 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.

10 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.

15 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.

20 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.

40 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 pretreated 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.

75 (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-dimethylglyoxime 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 developable 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 sufficiently 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 types shown in Fig. 5, 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 pretreated 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. 6 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 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 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 rear surface, as in Figs. 5, 6 and 7, 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 films 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. 6 and 7, 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 emulsion 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.

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-aminodimethylaniline 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-chloro-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-aminophenol 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- $\beta$ -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 glycol 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 processes described before are mainly concerned with reversal color development and usually presuppose a general black development similar to the three-color redevelopment. The following methods are also, and this point should be especially noted, applicable directly or with suitable, often only slight, changes, to the reversal development of each part color image, and in this respect, they have the great advantage that developer- and oxidation-stable sensitizers are not absolutely required. In addition to this, they make immediate development in the corresponding color of each part image possible after exposure and without previous general black development. Unfortunately, the primary three-color development yields only a complementary-colored negative which in turn yields a correctly



colored positive only by printing in the same manner or by exposure-printing methods.

In three-color direct development, one can use only one single tanned layer or one protected by intermediate layers. This will usually be the red-sensitive silver bromide gelatine layer 3 adjacent to the support which may be so strongly tanned that it is not developed in the general black development, nor in the individual color development of the two other layers, but only after removal of the tanning. The upper layer consists of silver chloride or highly dispersed silver bromide, the middle layer of fine-grain or also coarse-grain silver bromide sensitized for green-yellow; strongly swelling gelatine is used for both. The silver chloride or highly dispersed silver bromide emulsion is developed first, then the middle silver bromide layer is developed in a more vigorous developer to the corresponding part color image, or these two layers are fixed alone, since thiosulfate cannot penetrate the lower tanned emulsion; on moderate duration of the fixing action; the last part image is now developed with a stronger alkaline color developer, if necessary, after preliminary detanning or removal of the retarding action of a filter layer between middle and lower emulsions.

A very fine-grain silver chloride gelatine emulsion or collodion emulsion can be first coated on the film, above it a silver bromide gelatine emulsion sensitized for green-yellow. Both or the middle layer are thoroughly hardened by formalin or better by the more recent tanning agents without after-action described in U. S. Patents 1,870,354 and 1,941,852, or only in zones as in German Patent 486,644. One can also coat an emulsion of silver chloride collodion sensitized in the same manner and above this the tanned silver bromide gelatine emulsion; or both lower layers consist of collodion, or also the silver halide is emulsified in another nonswelling colloid, as cellulose acetate, ethyl cellulose etc. This is covered by a soft red-sensitive silver bromide gelatine emulsion. The silver chloride emulsion can also be arranged in the middle. The normally compounded green-blue developer will only develop the untanned red-sensitive emulsion during the usual time of action. By prolonged action of a color developer acting only on silver chloride, the corresponding part image is obtained, and the corresponding part color image is developed from the silver bromide of the lower emulsion with a vigorous, perhaps ammoniacal color developer or one containing fixed alkali; the silver is finally removed with Farmer's reducer. Tanning of the emulsion can be entirely or partially removed before development by alkalies, oxalates, etc., and suitable substances may be added for this purpose to the color developer.

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 mid-

5 dle 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 ferrocyanide 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.

10 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.

15 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.

20 The emulsion situated alone on one side of the film can, according to the invention, consist of a red-sensitive collodion emulsion. If the middle layer on the other side consists of the same emulsion, the thickness of the cellulose acetate film and with it refraction can be considerably reduced. Part of the gelatine of the blue-sensitive emulsion can be substituted by colloids which are less inclined to swelling. Substances opposing swelling may also be added to the developing solutions, or one may moderately tan before development.

#### Three-color redevelopment

25 In previous methods of three-color reversal development and in direct three-color development, the silver halide contained in the layers serves for color development, either that containing the latent image or that remaining after usual black development. Another possibility is

30 to reconvert the metallic silver formed in the general black development with ordinary developers into silver halide, to convert to other compounds of silver developable under certain circumstances (silver ferrocyanide) and other metals and then develop by layers in color. It may also be advantageous in three-color reversal development to reduce the residual silver halide at any stage after removal of the primarily formed silver and to reconvert the metallic silver into silver chloride or silver bromide. In all these cases, the advantage is offered that the regenerated silver halide can be obtained in highly dispersed form, especially as a pseudomorpho after formation of intermediate silver ferrocyanide or during treatment of the metallic silver with bichloride of mercury or copper chloride, also with a mixture of both or of copper vitriol with potassium bromide. Any oxidizing agents are suitable for rehalogenation in the presence of potassium bromide or sodium chloride, as long as they do not tan. The silver chloride formed in this manner is very easily reduced, so that the color developers applicable in this case do not require any or only very weak alkali, or also the reduction takes place without exposure with formation of the colored image. This is especially important for the middle part image. If one has converted into silver chloride, two part images can be produced by colored development, the third, or middle layer, which is usually difficultly accessible to exposure is developed by toning or mordanting processes, by conversion of the silver chloride of this emulsion into silver ferrocyanide or better into the corresponding mordanting bodies and coloring, or directly into color substances, as colored ferrocyanide or red nickel dimethylglyoxime or other compounds mentioned later.

35 If properly compounded color developers are used acting differentially on silver chloride, one can, after general black development, convert directly into silver chloride or through silver ferrocyanide without preliminary fixing out of the silver bromide. Fixing takes place only at the end with Farmer's reducer. The color substances of the middle emulsion obtained by different methods than colored development must, of course, also be stable to potassium ferri- and ferro-cyanide or thiosulfate. It would be less advisable to convert the unused silver bromide into silver iodide which is also hard to reduce, and then to rehalogenate.

40 If both upper layers consist of sensitized silver chloride, the middle silver chloride layer can be developed in color with a developer acting only on silver chloride, after superficial colored development by controlled diffusion of the outer silver chloride layer; then the lower silver bromide layer can be independently developed.

45 In certain processes, the intermediate gelatine layers are relied on, in part, to prevent diffusion. The superficial effect on the upper layer created by this can be attained much more perfectly, if first the middle layer is treated so that it is excluded, and then forms, together with the two intermediate filter layers, a neutral zone of approximately triple thickness. After this "inactivation" of the middle silver halide layer, individual color development of the upper layer can then be accomplished by controlled diffusion of so many kinds that in the following only the most important ones can be explained:

50 In reversal development, the primarily reduced silver of all three silver bromide layers can be

removed or at least converted into silver ferrocyanide with potassium ferricyanide. Then the residual silver bromide of the middle layer can be exposed to yellow or red light and developed in color, provided that its color sensitivity has not been destroyed by developer and potassium ferricyanide. The residual silver bromide of the two other layers is now made developable with thiourea, stannous salt etc., or by re-exposure, and the upper part image is obtained by superficial action of a color developer by known methods of controlled diffusion, then in the usual manner the lower part image.

Similar results can be obtained with a triple layer having a silver bromide gelatine emulsion only in the middle; above and below, however, silver chloride emulsions, preferably with pure or colored or ultra-violet absorbing intermediate gelatine layers. Other colloids less permeable to water than gelatine can be used for the latter and also for the middle silver bromide layer. The middle silver bromide layer is especially desirable in two ways, as the following examples show:

The three layers are first submitted to a non-tanning developer yielding a black image in each, and this is bleached out in the usual way. Then, after selective exposure of the middle layer to light to which it is differentially sensitive, and development of this layer to an appropriate color, a color developer acting specifically on silver chloride is allowed to penetrate superficially, of course, deep enough to develop completely the latent color image of the upper layer. An effect on the lower silver chloride emulsion is eliminated with certainty, since the surface developer to reach the lowest layer has to penetrate two gelatine intermediate layers, in addition to the middle silver bromide emulsion layer. The lower part color image is then developed by prolonged action of another color developer specific for silver chloride.

Another method is to allow a properly compounded solution of potassium ferrocyanide to diffuse differentially and superficially after general ordinary development. This converts only the silver chloride of the upper layer into silver ferrocyanide, but certainly does not act on the residual silver chloride of the lower emulsion which latter is then directly developed in color. After reconversion of the silver ferrocyanide of the upper layer into silver chloride, this is reduced with a specific color developer, then the residual silver bromide of the middle layer after making it developable by thiourea etc. It is less desirable to develop the residual silver bromide of the middle layer first in color after corresponding pre-treatment and only to then reduce the silver ferrocyanide of the upper layer after conversion into silver chloride or directly with a vigorous color developer. The silver ferrocyanide of the upper layer could be converted into the corresponding part color image either directly or after colored development of one of the two other

part image, also by conversion into a colored ferrocyanide, etc., or into a mordanting body.

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, what I claim as new and desire to be secured by Letters Patent is:

1. A photographic element for use in color photography comprising a support having upon one surface thereof at least two superposed emulsion layers differentially sensitized for different colors, at least one of which layers is of silver chloride emulsion and at least one of which is of silver bromide emulsion, the silver chloride layer being of very fine grain and outermost, and the silver bromide layer being of coarse grain and beneath the silver chloride layer.

2. A photographic element for use in color photography comprising a support having upon one surface thereof at least two superposed emulsion layers differentially sensitized for different colors, at least one of which layers is of silver chloride emulsion and at least one of which is of silver bromide emulsion, the silver chloride layer being above the silver bromide layer, and the silver bromide layer being less pervious to water than the silver chloride layer.

3. A photographic element for use in color photography comprising a support having upon one surface thereof at least two superposed emulsion layers differentially sensitized for different colors, at least one of which layers is of silver chloride emulsion and at least one of which is of silver bromide emulsion, the silver chloride layer being of very fine grain and outermost, and the silver bromide layer being of coarse grain and beneath the silver chloride layer, and less pervious to water than the silver chloride layer.

4. A photographic element for use in color photography comprising a support having upon one surface thereof at least two superposed emulsion layers differentially sensitized for different colors, at least one of which layers is of silver chloride emulsion and at least one of which is of silver bromide emulsion, the silver chloride layer being of very fine grain and the silver bromide layer being of coarse grain, the speed of the several layers being of the same order.

5. A photographic element for use in color photography comprising a support having upon one surface thereof at least two superposed emulsion layers differentially sensitized for different colors, at least one of which layers is of silver chloride emulsion and at least one of which is of silver bromide emulsion, the silver chloride layer being above the silver bromide layer, and the silver bromide layer being less pervious to water than the silver chloride layer, the speed of the several layers being of the same order.

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