

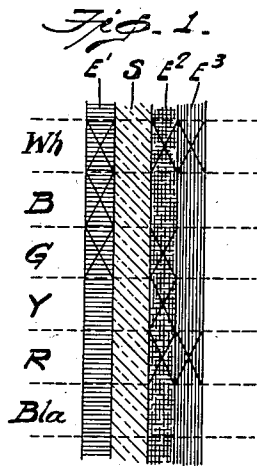
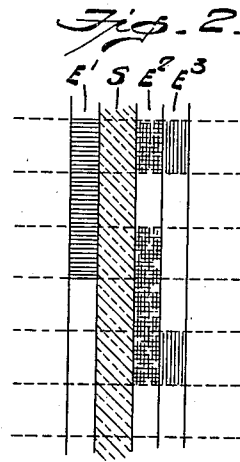
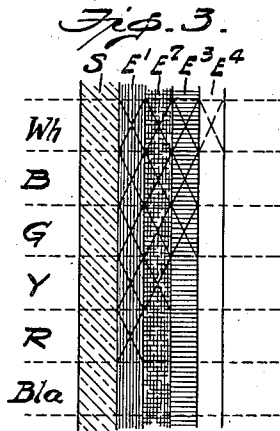
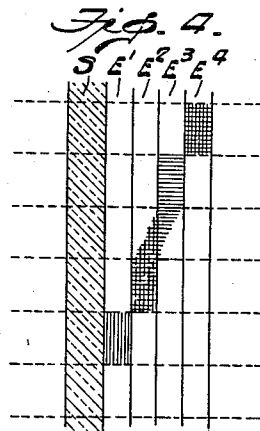
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PROCESS OF COLOR PHOTOGRAPHY

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PROCESS OF COLOR PHOTOGRAPHY

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1 Claim. (Cl. 95—2)

The invention consists in removing the color elements in the parts of a color photographic surface which have not been affected by light, any black silver formed by development being removed wholly or in part either simultaneously with, or subsequently to, the other removal.

In accordance with the invention color elements may be combined with light-sensitive layers or emulsions in various ways and forms, namely:

(a) The light-sensitive layers or emulsions themselves may contain color media diffused throughout or dissolved in them; by color media I mean either substances actually colored or potential colors, that is to say substances, colored or otherwise, which will change or acquire or produce a color on suitable treatment.

(b) The light-sensitive layers or emulsions may contain in suspension finely subdivided or grain-like particles of one color or of more than one color, whether such particles are actually themselves light-sensitive or not.

(c) The light-sensitive layers may contain a color medium diffused or dissolved throughout as in (a) and particles of one or more other colors suspended in them as in (b).

(d) The light-sensitive layers or emulsions are provided with a separate layer containing diffused color media or suspended color particles under or over them, or both.

Photographic materials provided with color elements in any of these forms are, after exposure in a camera, and simultaneously with or subsequent to, development or fixing or both, treated in a way designed to remove the color particles which have not been affected by light or the color media or particles immediately adjacent, over or under the parts which have not been affected by light, the light-sensitive elements themselves affected by light being afterwards or simultaneously removed wholly or in part.

The object is attained by hardening in a known manner, simultaneously with, or subsequently to, development, the gelatine corresponding with the exposed parts, and then dissolving by means of hot water, acids or alkalis the gelatine parts left unhardened, when also the color media or particles there present will be removed together with the gelatine, or those lying beneath in separate layer will be left unprotected and may be removed as in the preceding case. Potential colors can also be made to produce or change their colors as in the previous case.

In some cases, however, it is not necessary to

remove the gelatine itself, its hardening being sufficient to retain in, over or under the parts that are hardened color media, particles or potential colors; because such hardening prevents or considerably retards the penetration of agents, whether simply water or appropriate solvents, which may be applied to dissolve out of the softer parts, such color media, particles or potential colors.

One material or a set of materials coated on one surface or on both surfaces, or one on one surface and another on both surfaces, with color particles or media or both, or different colors intermixed, or having different color media or particles, or both, distributed in the surfaces, provide means for attaining color photography and cinematography, in the manner described.

As instances of some color particles which can be used as hereinbefore mentioned I will name colored salts of silver, such as silver erythrosinate, silver ferricyanide or silver chromate; colored salts of mercury or of mercury and silver; other metallic colored salts, such as nickel dimethylglyoxime or copper benzoin-oxime; colored sulphides and oxides; the special sulphide of copper known as copper-indigo; ceruleum; cobalt blue; Thénard blue; other mineral colors; metallic resinates and the like, especially those which are likely to combine more or less completely with, or to be adsorbed by silver halides. Colored particles can also be made from animal or vegetable coloring matters, such as by precipitating with alcohol aqueous solutions of water-soluble dyes and dextrin or gum arabic, or both, or by precipitating with water alcoholic solutions of spirit-soluble dyes with or without such gums or resins as dammar, gualicum or mastic.

Color elements to be applied as diffused coloration in any suitable medium or in the sensitive layer itself may be furnished by solutions in appropriate solvents of coloring matters or dyes suitably selected from among those, the composition of which is not such as to destroy or hamper the sensitiveness and permanence or capacity for development of light-sensitive compounds and at the same time are not themselves destroyed or affected in any unrequired way by the chemicals usually used in photographic treatments. For instance, for red, pure carmine in ammonia solution, erythrosine, iodo-eosin, all quinoline colors and several of the alizarine derivatives; for yellow also alizarine and quinoline colors, tartrazine, carthamine and many others; for blue, compounds derived from logwood and indigotin, indigo carmine, alizarine blue and sev-

eral more; besides others already mentioned as suitable for colored particles.

Potential colors, in the meaning previously explained, may be furnished by any compound, salt, extract or other substance which may be made to yield a color reaction or preferably a colored precipitate of the required hue. For instance a nickel salt which may be treated subsequently with dimethylglyoxime or other reagent, or vice versa; a copper salt which may be treated subsequently with benzoin-oxime, or vice versa; benzidine; logwood extract; ferric salts; α - and β -naphthylamine; leuco-compounds; uranium salts and many others.

The invention may be carried out in a number of ways, which may be grouped in a few classes according to the kind of color medium used, many variations being also possible in each group or class. The color elements chosen, other than potential ones, are whenever possible selected with a view to their acting also selectively as light filters of the colors to be reproduced. In several instances the selective filtration due to the color-elements is improved by, or even depends solely upon, the arrangement of several superimposed layers, as will be more clearly defined in some of the examples which now follow and are to be considered as types and several varieties of each type.

The accompanying drawing represents cross sections through supports coated with various materials and are drawn to an exaggerated scale.

Class A.—Embodiments wherein color media are diffused or suspended throughout several layers of sensitive emulsions coated on both sides of a thin, transparent support.

Example 1.—A thin film of celluloid or other transparent cellulose material S (Fig. 1) is coated on one side with an ordinary emulsion E1, rather slow in comparison with that used for the coatings which are to be applied on the other side, and thinned by addition of 40–50 per cent. of its volume of a saturated solution, in aqueous gelatine of 7 per cent. strength, of the dye, mainly used as indicator, known under the name of Brilliant cresyl blue. The addition of this dye to an emulsion will reduce the speed of the emulsion, which must be taken into account. In a slightly alkaline medium, such as a silver bromide emulsion, the dye mentioned is yellow, and remains yellow until an acid bath is applied, in which it changes to a good blue. The other side of the film is coated firstly with an ordinary fast silver bromide emulsion E2, thinned by addition of 30–50 per cent. of its volume of an aqueous solution of plain gelatin in which, while it is hot, there is dissolved as much tartrazine and quinoline yellow as it can dissolve; this emulsion is rendered ortho-chromatic by the addition of the usual sensitizers for yellow and green. Over this layer there is coated a second layer E3, which is an ordinary silver bromide emulsion thinned by addition of 40–60 per cent. of its volume of a saturated solution of erythrosine in water containing also 7 per cent. of gelatin; this emulsion is made red-sensitive by addition of the usual sensitizers for the red end of the spectrum, and is the fastest of all the emulsions used in this instance. The usual hardening agents may be added to the present emulsions. The material is exposed in a camera with the surface bearing the single layer E1 facing the lens. On exposure, the layer E1, being an ordinary emulsion, is affected only by white and blue rays and by the blue components of the green rays,

while E2 is affected by white rays, green rays and yellow rays; should this E2 be also red-sensitive, which would do no harm, it would be affected also by red rays. Blue rays would not affect this emulsion because they would be absorbed by the yellow color of the E1 emulsion. The layer E3 will be affected by white rays and red rays only, because the blue rays will not reach it, and to yellow rays it is not sensitive. The crossed parts in Fig. 1 show where the layers are affected by the light rays, indicated at the left hand of the figure, where Wh stands for white rays, B for blue rays, G for green rays, Y for yellow rays, R for red rays and Bla for black or no rays whatever. The treatment to be applied to this material is development in any of the usual ways, and then the application of such a bath as is already known to have the effect of hardening the gelatine of an emulsion in the parts wherein black silver has been developed. Developers are also known which, in one single treatment, produce both the development of the exposed parts and at the same time the hardening thereof. The preferred prescription is the following, made in two stock portions.—

Solution 1

Metol	3 grams
Hydroquinone	4 grams
Sodium sulphite (anhydrous)	4 grams
Water to make	1000 cc.

Solution 2

Sodium hydroxide	12 grams
Water up to	1000 cc.

Equal parts of the first and the second solution are mixed for actual use. After this bath the material is transferred to a bath of warm water, or to a cold bath of an acid, wherein all the gelatine parts of the emulsions which have not been affected by light, the silver halide remaining therein and the colorations also contained therein, are all dissolved and there remains a negative picture in black which retains a color picture in itself, see Fig. 2. It is now sufficient to transfer the picture to a bath, made according to any of the known prescriptions, for the purpose of reducing and dissolving black silver, such as acid permanganate, acid persulphate or hypo-ferricyanide, the picture being kept in the bath until the color picture is plainly visible. The black silver can be removed entirely, or, preferably, can be removed only partly, according to taste, it being always advisable to leave a little of the black silver so as to soften the brilliancy of the colors. In the acid reducing bath or in a subsequent acid bath the dye in E1, where it remains, is changed to blue.

The picture obtained in this way is a peculiar one, inasmuch as it is a negative insofar as the blacks and the whites are concerned, but is a positive insofar as the colors are concerned, although the luminosity of the latter is inverted; that is to say in this negative, whilst the blacks will appear white and the whites will appear black, a pale blue will be represented in a darker shade of blue and vice versa, and so for all colors. Of course, in printing on a material of similar characteristics the black and whites and the luminosity of the colors are again inverted and thus a correct positive picture is obtained.

Class B.—Embodiments wherein color media are diffused or suspended throughout several layers of sensitive emulsion, coated on one side only

of a support, potential colors being most suitable for use in this class.

Example 2.—A transparent support S (Fig. 3) which may be celluloid, other cellulose film, glass, paper or the like, is coated firstly with an emulsion E1 which is panchromatic and contains such an agent, preferably colorless, as will give a red color or red precipitate on suitable treatment, for instance either a nickel salt or dimethylglyoxime or α -benzildioxime. The nickel salt may be dissolved throughout the emulsion or suspended therein, for instance in the form of a carbonate or a phosphate. This layer of emulsion, as indeed all other layers, may be extremely thin so that all the layers taken together are hardly any thicker than a single ordinary emulsion, because the function of those layers is simply to retain colorations or the agents therefor. Over the first layer there is applied a second layer of emulsion E2, faster than the preceding one and ortho-chromatic and containing, in suspension or diffusion, an agent which will give a yellow coloration or precipitate with a suitable reagent; for instance ammonium molybdate, which will give a yellow precipitate on treatment with a phosphate; or a cobalt salt which will give a yellow compound with an alkali nitrite; or a uranium salt which will give a yellow precipitate with an alkali carbonate. Over this layer there is coated again a third layer of emulsion E3 which this time is only an ordinary one and is faster still than the preceding emulsions. This layer contains, in suspension or diffusion, an agent which will give a blue coloration or precipitate under suitable treatment; for instance a solution of benzidine, which will give blue on treatment with potassium ferricyanide or other color developer; or a solution of logwood extract or hamatoxylin, which will give a blue precipitate with ferric salt or some other salt. Over this emulsion there is coated still another layer E4 of the same ordinary emulsion, that is of the same speed as E3, but specially intended for producing a contrast. This last layer contains a mixture of all the agents already used in the previous emulsions. The material so composed is to be exposed in an ordinary camera, preferably through the support side, that is with the glass or celluloid facing the lens. In Fig. 3 the crossed parts in each emulsion represent the parts which would be affected by light rays indicated to the left hand of the figure. There must be noted the gradations of the affected parts, which gradations are produced by the resistance to the penetration of the rays offered by the several layers, and by the different color sensitiveness of the layers themselves. A compensating filter or an *esculin* filter may be used in the lens. After exposure the material is developed and hardened, preferably in the developer bath described in Example 1, the hardening being applied for the purpose of retaining in the hardened parts the various agents embodied in the emulsions. Actual removal of the gelatine in the unhardened parts is optional, as the various agents can be so embodied as to be washed away by water, or by suitable agents, applied afterwards, or simultaneously. In most cases, however, the soda of the bath recommended as developer is sufficient to extract and dissolve all the agents mentioned, from the parts of the gelatine that are not hardened. After this operation all the various reagents mentioned, which are for the purpose of developing the colorations, are applied either in the form of a

bath, or by application by a brush, or by cotton wool. These reagents may be mixed together or used separately. It is preferable first to apply the various reagents in a solution in which they are all dissolved together, and afterwards to apply separately any one which may be required to enhance a particular color everywhere in the picture, or only locally in parts thereof. Fig. 4 shows the parts where the color reaction would be obtained; for it must be observed that, although all the parts which are crossed in Fig. 3 have been hardened, the color reaction can only happen where each layer is left uncovered by the superimposed layers. The emulsion E4 containing all agents, will yield black where the agents are left. This emulsion could also be used without any agent, relying for black on leaving some reduced silver, which is present at that point in the largest quantity. It is now sufficient to remove wholly or partially the black silver to obtain a clear view of the color picture, which is a negative in the blacks and whites and a positive in the colors. The removal of the silver may occur before, or simultaneously with, the development of the colors.

By inverting the order of the layers given in this example and their relative speed, the material could be used for exposure from the coated side, in which case the colors could be developed in the parts left soft, soon after, or together with, development and hardening.

Example 3.—As an instance of how any typical example may be varied I will outline an embodiment wherein some of the characteristics of Example 2 are combined with some of the characteristics of Example 1. A support is coated with a first layer of a red-sensitive emulsion containing an agent for red as mentioned in the preceding example; then with an ortho-chromatic emulsion, containing an agent for yellow as mentioned in Example 2, and lastly with an emulsion exactly like the E1 of Example 1. Treatment to be applied is development and hardening of the exposed parts, and then development of the colors in the parts hardened; this treatment will only act on the first two emulsions because the last one has no potential color and only changes its yellow color to blue in an acid bath. Such a material would yield a picture that is a negative in the blacks and whites and a positive in the colors.

Various other sequences of layers and ways of grouping are possible with potential colors; for instance in Example 2 emulsion E4, Fig. 3, can be made the slowest and emulsion E1 the fastest, exposure of the material being made with the coated side facing the lens. This variation would be specially suitable for coating papers intended to be exposed with the coated side against a first picture, obtained by camera exposure of material prescribed in Example 2.

Instead of potential colors, such colored particles may be used in the form of salts suspended in the emulsion, as may be dissolved by any appropriate agent, in which case it is not necessary to remove the gelatine. When this is the case, either with suspended potential colors or diffused potential colors, or again with suspended actual colors which are soluble, it is preferable to add to the gelatine emulsion containing them, some dextrin solution or gum arabic solution or glycerine, with the intent of leaving a certain extra porosity in the emulsion, so as to facilitate the extraction of agents, or color media, from it. In the case of potential colors the colorations may be developed, in a suitable arrangement of layers and dis-

tribution of agents, in the parts of the gelatine that are left soft, and not, as in Example 2, in the hard parts; in this case dextrin or gum arabic or glycerine need not be added to the emulsions.

Variation to Class B

One most important variation is also possible when potential colors are concerned. This consists in coating a support, such as paper or the like, with the reagents that are required to produce the colors in a material, such as for instance that described in Example 2. The reagents may be applied to the support in a suitable medium, for instance gelatine, gum arabic, dextrin or the like. Paper or other support bearing on its surface the various necessary reagents all mixed together, may be dried and kept for use when necessary. I will call this a positive reactive paper. The potential color photographic material, for instance that described in Example 2, is developed and hardened in the developed parts as described, and then the agents or potential colors contained therein are dissolved from the soft parts of the gelatine; no actual development of colors is applied. A sheet of the positive reactive paper is brought in contact with a material made as described in Example 2 while the latter is in a wet or damp state, the contact being maintained, preferably under pressure, for a short time, with the result that the color reaction will then occur between the material of Example 3 and the paper, and the color picture will appear on the latter. Thus prints may be obtained simply by contact, without using light-sensitive layers or resorting to exposure to light or any other treatment, except perhaps the washing in plain water of the positive reactive paper for the purpose of dissolving any reagents left therein. Only a limited number of copies could in this way be obtained from one picture, according to the quantity of agents incorporated in the layers of the material of Example 2, or of any other

example, in accordance with this invention, suitable for the purpose.

It should be added that, generally, the addition of the various color media slows down to the required degree a fast emulsion, so that it would be advisable, when practising any of the examples given, to start from a single emulsion and to divide it into so many parts as are the layers to be coated on a support, and then to make to each part of the necessary additions.

Also it must be kept in mind that the color media must not necessarily be incorporated in the emulsions; they may be applied as separate coatings between or over or under the relative layers of emulsion, when it will be found that they interfere less than otherwise with the sensitiveness and selectiveness of the emulsions, especially if alcohol is used as a medium for the separate coating of color media.

Finally, whenever, in any embodiment of the present invention, several layers of emulsion and color media are to be applied on a single support, separate supports may be used, instead, for any or each of the separate layers of emulsion or color media, and the various supports, so coated, may be used all together in the form of a pack, or in any other suitable way, and they may be separately subjected to the necessary treatments.

Having now fully described the nature of the said invention and the best means I know of carrying the same into practical effect, I claim:—

A process of color photography which consists in coating a surface with at least one photo-sensitive layer containing potential colors, then exposing the coated surface to the action of light, then removing potential colors from those parts which have not been affected by light, and then applying the surface to a support containing at least one agent adapted to develop the colors required from the potential colors remaining on the surface.

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