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LIGHT SENSITIVE COLOR ELEMENT

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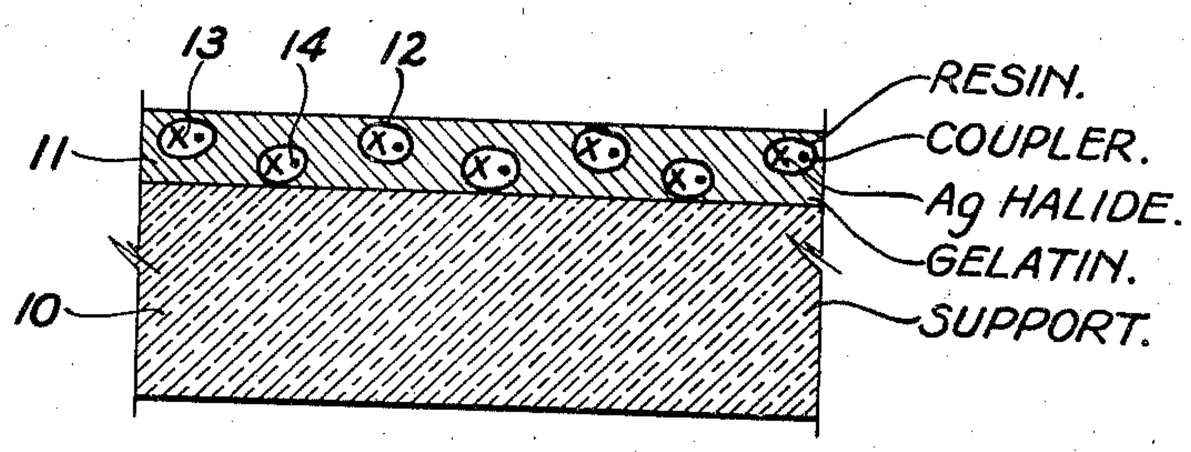

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LIGHT SENSITIVE COLOR ELEMENT

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This invention relates to color photography and particularly to sensitive photographic elements having color forming components incorporated therein. Many processes have been proposed for recording different color aspects in a photographic element for the purpose of producing natural color photographic records. These include multi-layer processes as well as mixed grain processes in which a single photographic layer records the different color sensations. Most of these processes, particularly those of the mixed grain type, have been found impractical because of the difficulty of separately recording the different color aspects.

In my application Serial No. 223,115, filed October 3, 1938 I have described a method dealing with the physical association of color formers and resins, these ingredients of the photographic layer being dissolved in a common volatile solvent and then dispersed in an emulsion. The resins served to restrain the solubility of the color formers and of the resulting dyes. I have referred to this means as the "localization" of color reactions.

It is an object of the present invention to provide an improved method for the formation of colored photographic images. A further object is to provide a method for the formation of colored photographic images by means of dye components or color formers rendered insoluble in sensitive photographic layers.

The present invention differs from that of my prior application in what I call "insulation" of the sensitive grains. By this means the individual photochemical properties of each of the differently sensitized grains are preserved with the possibility of singling out any group of light elements for treatment without acting on the others. This involves a consideration of the speed or sensitivity of the grains, the ability of the grains to produce a colored image, and the means for selecting from the incident rays, those to which the grain is to respond. This method differs from that of my prior application in that the color forming means and the sensitive agent are contained in a single grain whereas in the method of my prior application the color forming means was localized in the emulsion containing the sensitive salt.

The accompanying drawing illustrates in section view a photographic element formed according to my invention:

The object of my present invention is achieved by precipitating silver halide in the presence of a synthetic or natural resin, gum, or gum-resin, or similar substance, preferably of water-repellent properties, in such a way that the silver salt is formed within or in close physical association with the resin, which is the insulator of the grain so formed: a point of importance is that adjuncts, such as coloring matters, other metal salts, color sensitizers, color formers and similar salts or compounds may be made to be also present at the time of precipitation, so that they too form part of the grain: in certain cases, specially if soluble in alcohol or other volatile solvent, some adjuncts may be admixed soon after precipitation with the result that they also come to be closely associated with, or superimposed to, the grain.

In the further details that follow, I will use the word resin in general, or mention a particular resin, but it is understood that whenever only resin is mentioned or a particular resin is named, artificial or natural, any other such should be assumed to be indicated for alternative substitution, if necessary with other solvents than any mentioned.

Natural resins available may be colored and colorless. Colored ones may be usefully employed for layers and grains in which a light filter is desired: for instance amber, dragon's blood, gum ammoniacum, oxidised guaiacum, shellac, gum gutte, gum kino. Some of these lose readily their color, as it may be desired, in treatments. Instances of colorless ones are benzoin, mastic, colophony, sandarac, dammar, and others. The latter may be colored, if desired, with alcohol soluble dyes, preferably such as may be readily decolorised in treatments.

A variety of solvents are available, such as ethyl, amyl, and methyl alcohols, acetone, ether, benzene, chloroform, petroleum spirits, turpentine and other oils, amyl acetate, xylene, ethyl acetate, carbon disulphide, and even acetic acid.

In the case of synthetic resins and their solvents, the choice is still greater, as a large number have been made available in the rapid growth of the industry in the last few years. Such resins may be condensation products of formaldehyde or phenol alcohols with phenols, oxy-, aryloxy or alkyloxy-carboxylic acids or phenoxy fatty acids; also such synthetic resins as may further be treated with halogen fatty acids or the condensation products of phenols or phenol carboxylic acids with aliphatic, aromatic or heterocyclic aldehydes or thionyl chloride; polyvinyl esters or acetals, polyvinyl alcohol blended with polybasic acids, alkyd resins, polystyrene resins; including also mixtures of resins with rubber

latex and synthetic rubbers such as polymerised butandiene and polymerised chlorobutandiene, and also mixtures of synthetic resins with organic acid ester and with a cellulose, and other like or similar mixtures, compositions: finally and for instance those synthetic resin products trademarked under the registered names of Diakon, Paralac, Formvar, Alvar, Gelva, Victron, Glyptal and others. What I have said as to coloring matters relatively to natural resins also applies in the case of synthetic products.

Various methods may be followed in the formation of the insulated light sensitive elements, all of which more or less include known procedure by which light sensitive salts are formed. Some of the methods will be instanced further on.

In general it must be said that the insulated elements may be produced all alike of a type, or of different types. Grains of a type may be used to produce uniform layers for general or particular purposes. Layers each of a uniform type, but the type varying in each layer, may be used in multilayer materials, in bi- and tri-packs, and in sets of materials for color photography by superimposition of separate records. Different types of grains can be mixed to form a layer of the "mixed grain" type.

To produce different types of elements, or grains, the latter are to be differentiated in their characteristics in their formation, as will be more precisely described further on. In general I will now say that they can be differentiated: either by modifying manner of formation, for instance modifying speed of sensitivity to light, contrast and resolving power, by suitable additions, choice of colloid used, or by varying mode and time of mixing, temperature, ripening: or by introducing in the elements what I call differentiating adjuncts. By the expression "differentiating adjuncts" I mean to indicate the particular agents, such as color formers, metal salts, sensitisers and coloring matters which are required to obtain that any particular type of grain be impressed predominantly by colored rays which do not so impress other types of grains and to obtain that it be capable of being processed to yield an image of a color different from the color that other types of grain can be made to produce, so that these two characteristics of each grain may be utilised to serve the purposes of color photography.

In particular, as to types of formation:

1. In the simplest form, resins are the only medium employed. Two separate alcoholic solutions are made, one of an alcohol-soluble halide, such as chloride or bromide of ammonium, lithium, zinc, strontium, calcium, gold barium, the other of silver nitrate in equivalent quantity by specific weight. In either or both is also dissolved a quantity of resin equal for instance to about from one to three grams for every five grams of silver nitrate. Citric, tartaric or phosphoric acid and other adjuncts generally employed in the making of cellulosic and collodion emulsions may be employed in either solution, and the customary known manner of mixing, temperature, and the like observed. A color former may be incorporated, for instance from gr. 0.10 to 0.20 of alpha naphthol or of 1 phenyl 3 methyl 5 pyrazolone for every five grams of silver nitrate. Color sensitisers, coloring matters, and the like, may also be added at the time of mixing or afterwards, and also such plasticizers as may be desired, such as castor oil, glycerine, amyl acetate, triacetin, tricresyl phosphate and the like. Uniform layers of this type can be made also by coating on a support first a solution of an halide and resin in volatile solvent or in alkali and then applying over it a solution of silver nitrate, which may then be in water and may contain an acid, preferably organic, to destroy any alkalinity present. Adjuncts, as specified, in either solution.

A mixed grain emulsion of the same type may be made by forming two or three separate emulsions in the same way, with resins of different solubility; each emulsion containing a resin in a solvent in which the other or others are not soluble or are sparingly soluble. Silver nitrate may not then be soluble in the solvent required by the resin, but alcohol can always be added to other volatile solvents, thus silver nitrate would in such cases be dissolved in alcohol and added to the solution of the resin in its proper solvent. For instance, in the case of natural resins, one lot of emulsion may be made with benzoin or shellac in alcohol or with dragon's blood in ethyl acetate, a second lot with sandarac in acetone, and a third with mastic or dammar in benzene. To each, differentiating adjuncts can be added, as previously explained. Xylene can also be used as one of the solvents. Synthetic resins, as some of those already mentioned, and modern solvents as are available, hydrocarbons, alcohols, aldehydes, offer infinite possibilities.

Mixed single layers, multilayer materials and tripacks produced in this form would be slow and could be used only for positive making or for copying. Uniform single layers can be made in sets, on such supports as regenerated cellulose and thin Celluloid, for three-color photography by superimposition of separate color records: after the latter have been processed, dried, and assembled in register they can be made to permanently adhere to each other simply by application of controlled heat, the resins in the layers acting as adhesive.

2. Other formations of insulated elements provide for the presence of a colloid such as gelatin. The simplest way is to form silver halide in resin, medium, with the other adjuncts if desired, as initially described in the first formation, and then disperse and suspend such a resin emulsion in gelatin by pouring it in very fine stream in a solution of the colloid while the latter is energetically and rapidly stirred.

But for insulated elements of good speed to light gelatin is necessary to be present at the time of precipitation, or formation, of the elements.

Two solutions are still employed: one of gelatin and a halide, or mixture of halides or/and organic acids or salts thereof as usually employed in the formation of silver salt emulsions; the other an alcoholic solution of silver nitrate and resin, with addition, if necessary, of other solvents that may be required by the resin, and acids, if desired, specially organic. The silver salt in this solution is in the quantity necessary to produce light sensitive salts on admixture to the other solution, with or without the customary excess of salts in the latter. Manner and time of mixing, temperature, digestion, stirring, additions of ammonia and of general sensitisers, of extra halides, of extra gelatin, ripening, setting, washing to be carried out as in the recognised art of emulsion making. Differentiating adjuncts, as indicated, may be added to either of the solutions before or after mixing or when melting for coating.

For a mixed grain emulsion, a coloring dye to act as filter, if used, should preferably be soluble in the alcohol or other solvent together with the resin-silver nitrate solution. It should, of course, be of such a kind as will not harm in any way the properties of the silver salts and as can be easily discolorised in treatments. Colored metal salts or organic compounds thereof may be utilised for the purpose.

Alternatively, alcohol-soluble halides may be employed with a resin in appropriate solvent as one of the solution, while silver nitrate and gelatin would then be in the other solution, preferably, in this case, with addition of ammonia g. s. in the silver-gelatin solution: the latter may also be divided in two lots, one with and the other without ammonia, to produce an emulsion of a determined degree of contrast: or else the silver nitrate only may be in two lots: one present in the gelatin, the other added to it after addition of the halides and resin solution.

Mixed grain emulsions are formed out of two or three lots of emulsions, each of which must then contain at least one differentiating adjunct, preferably added to one of the main solutions before precipitation of the sensitive salt. It is an essential point that the various lots of emulsions that are to be used to make a mixed grain emulsion should be each separately well washed before melting and mixing them.

Emulsions produced in any of these forms just described may be made very fast indeed, equal in speed to any other known, and will always result of very good contrast, higher than can be obtained in usual ways of precipitation of silver halide.

3. In a third form use is made of three solutions: one of pure gelatin in water, a second of halides or/and organic acids and/or salts thereof in alcohol or water, and a third of silver nitrate and resin in alcohol and resin's solvent: the latter two solutions may be inverted, that is halides and/or other salts may be in the solution containing the resin, and silver nitrate in separate water solution. Mixing is made preferably by pouring contemporarily the two last mentioned solutions in fine stream in the gelatin solution, but, if desired, the solutions may be poured in the gelatin one after the other, or intermittently first a part of one, then a part of the other, and then again a part of the first, and so on. All other details, manner of finishing the emulsion, additions, inclusion of differentiating adjuncts and the like as mentioned in preceding cases and as known.

4. Still another form consists in making two main solutions only as in any previous example and then mixing them as they are or in plain water. A thickening agent such as small amount of glycerine, sugar, arabic gum may be present in the water. After precipitation, the grains obtained are washed and, if desired, dried. They may be emulsified or dispersed afterwards in any suitable colloid or other binding medium, including Celluloid, regenerated cellulose and the like. Suitable additions may be made to any of the solutions before precipitation, or to the water in which the latter occurs, or to the binding medium in which the precipitates are afterwards suspended dispersed or emulsified.

5. Emulsions in collodion or celloidine or other cellulosic product, or in a solution of another resin may be obtained by adding a suitable solution of any of these substances to either or both of two main part solutions made in suitable solvents, or by substituting a solution of the desired medium for the gelatin in any of the other described forms, mutatis mutandis.

6. Other known methods of emulsion making, in so far as applicable, may be followed for the production of the insulated light sensitive elements contemplated in this invention. For instance, it may be desired to avoid too large use of volatile solvents. Sodium or potassium or other water-soluble resinate may then be used, for instance, together with a solution of halide salts, so as to produce with silver salt or/and other metal salt at the same time silver halide and insoluble metal resinate closely associated one with the other.

Again, an alkaline solution of a resin may be employed on the one hand, and silver with an acid, preferably organic, on the other hand: or else an acid is added soon after precipitation, so as to reconstitute the resin. Suitable adjuncts always as desired.

Further and generally on the subject of mixed grain emulsion, it must be considered that, besides a differentiating adjunct, as explained, being a necessity in most cases, the following other points must be kept in mind:

1st. The various insulated elements that are produced in gelatin or mixed in gelatin may not be of the same type or struck, so to speak, on the same kind of resin: the resins may be different for each type, so as to constitute themselves another differentiating adjunct: for instance they may be of different resistance to alkaline or acid treatments and in other properties as may be taken advantage of in processing.

2nd. The main purpose of a mixed grain emulsion in color photography is to provide means for recording and reproducing images of at least two different colors in the established laws of the art, which are thus to be followed. For instance, of the insulated elements present in a mixed grain layer, at least two should be reciprocably sensitive to rays of complementary colors. Materials bearing in a single layer or in two or three layers at least two grains of differentiated properties, may be made to reproduce in direct or reversal treatments images in the same colors as that of the rays affecting them or colors complementary to them or in any other given color desired. The mixed grains should also be in certain quantity relatively to each other. For instance, in a material intended for use by daylight there should be more grains sensitive to red rays than grains sensitive to blue-violet rays, and the reverse for materials intended for use in artificial light of the incandescent filament kind. The grains sensitive to green-yellow rays may be in both cases the same relative quantity, an intermediate number between that of the other two.

3rd. It is not necessary for a good material for color photography to contain in a single layer grains for three colors. Three separated layers, all on one side or distributed between both sides of a support may be employed. Two layers may be provided instead, one with grains for one color and the other with grains for two other colors. Grains for two or three colors may be in a layer that may be placed over another layer of plain ordinary emulsion intended to produce, for instance, a thin black image to be left black, or another color. Finally, grains for one or two colors may be mixed with plain emulsion of the usual kind intended for black image or for an image in a second or third color: in such cases

the processing should be such as to produce a color or colors in the grains and another in the interstices between them, that is in the plain emulsion between them, which, of course, may be appropriately sensitised and contain also a color former and the like or be associated with a salt of a metal other than silver.

A two-layer material carrying in each layer a grain in a plain emulsion, so as to produce three colors and a black record, may constitute a successful embodiment of this invention.

4th. Consideration must be given to the fact that if a multitude of highly colored grains of different colors, more or less complementary of each other, which would absorb among them rays of all colors were admixed in a layer, the latter would result of practically no depth of resolution, as the action of incident rays would be practically arrested at the plane of incidence. It is, therefore, almost a necessity that a layer comprising three and even only two insulated elements of different color sensitivity should not owe their exclusive color sensitivity to light filter, that is to color that be embodied in the elements, or at least not mainly or solely to the color of all and each element, although a certain amount of color in all or in some only of the elements might help.

In any case, a compensating light filter, such as may be eliminated afterwards in treatments, may be either incorporated in the gelatin or plain emulsion in which the insulated elements of this invention are suspended, or may be coated in suitable layer over them.

5th. Basis for color. The insulated color elements preferably embody an adjunct for independent color formation, that is a means by which each element of a type may be made to produce a color independently from that which may be produced by other elements of another type or in surrounding plain emulsion in which they may be embedded. Such means may be one or more of the following:

(*a*) The resin itself on which the insulated elements are struck, as I have already mentioned: resins of different resistance to alkali or acids, or of different water repellent properties, or of different hardness, or of different solubility will lend the different types of elements of which they are part to differential treatment that acts, penetrates, softens, dissolves one type of elements and not another.

(*b*) Color formers, in the widest and most comprehensive meaning of this expression, which is used to include any chemical agent, substance or compound adapted to yield a colored reaction or compound by oxidation, reduction, diazotation, or in any other way. Color formers may be chosen for different types of insulated elements with either of three criteria: different color formers, to react all with a common developer; different color formers, each requiring a developer which does not act with the others; a common color former which reacts differently with different developers; a color former in only one type of elements while another type of elements or an adjoining plain emulsion are provided with no color formers, the whole being intended for use with a developer that is capable of producing a color with the one color former and another by itself. The first of these criteria of choice may appear the simplest and most indicated for amateurs; the second will surely afford the safest and most precise means for best results; the third and fourth require the concomitance of other adjuncts and may appear indicated for particular aims. Two or more of these criteria may guide the choice for one and the same embodiment of this invention.

(*c*) Metal salts, other than silver, incorporated in the insulated elements either by their presence in precipitation or by successive addition. These may be utilised to mordant dyes that may be present in the elements or emulsion, or to produce metal salt colored images by toning methods, or metal-organic compounds.

(*d*) One and the same material may be provided, in a single layer or in two or more layers, with insulated elements not necessarily all carrying the same basis for color, so that this very difference may afford means for differentiating treatments.

6th. Treatments. Means for differential treatment are known, such as slow penetration, controlled penetration, and the like, in conjunction with metal toning, dye toning, color development, "ozobrome." These may be applied, if desired and convenient, and materials incorporating my insulated elements may be produced so as to serve these and other known processing methods. However, it is one of the characteristics of the present invention that the embodiment in the insulated elements of diversificating adjuncts, as described, not only imparts distinctive properties to the elements, but also facilitates treatments. The latter will be dictated by the nature of the diversification adjuncts present in the insulated elements and will consequently consist in the use of agents which will act contemporarily or successively on one, some or all of the resins, color formers, metal salts, dyes, and the like present in the elements.

It is a relevant point that after all suitable treatments have been imparted, the resins in the elements or layers of a material may be subjected to controlled action of heat to harden, fuse, or generally render more durable the image-bearing layers: to this purpose suitable plasticisers should be embodied in the elements or applied previously to heating.

The present invention affords a variety of applications for the production of materials for color photography.

The following examples illustrate my invention:

Example 1

A single layer for three color is composed by mixing three lots of emulsion as follows:

Lot 1

A.	Alcohol	cc	20
	Isamine blue q. s. to saturation, say	gr	0.05
	2: 4 dichlor-alpha naphthol	gr	0.20
	Acetone	cc	5
	Mastic gum	gr	2
B.	Silver nitrate	gr	5
	Alcohol	cc	75
	Isamine blue q. s. to saturation, say	gr	0.25
C.	Water, distilled	cc	100
	Gelatin	gr	4 to 7
	Potassium bromide	gr	4
	Potassium iodide	gr	0.05

A is to be filtered. Mix first A and B, warm the whole; bring C to about 60° C., and add AB to C in fine stream during a time of 3 to 10 minutes. All usual requirements of emulsion making are to be followed, including addition at proper moment of extra gelatin. Filter, wash and set.

Lot 2

A.	Alcohol	cc	25
	Dragon's blood	gr	150
B.	Alcohol	cc	25
	Nickel chloride	gr	0.60
	Ammonia q. s. or	cc	1
	Pinacyanol (1 in 1000) sol	cc	1½
C.	Alcohol	cc	50
	Silver nitrate	gr	5

D. As (*c*) of previous lot.

Warm A, B and C. Mix A and C. Bring D to 60° C. and add to it first A—C and then of B. Follow usual practice of emulsion making.

Lot 3

100 cc. of plain emulsion, strongly orthochromatised, preferably by addition of:

Alcohol	cc	10–15
Cobalt chloride	cc	0.50
Ammonium bromide	cc	0.20
Pinaverdol or orthochrome T (1 in 1000) sol	cc	2
Ammonia q. s. or	cc	1

Add also: tartrazine gr. 0.25 and naphthol green gr. 0.10. Mix the three lots and coat. The material so produced is, after exposure, treated in a developer containing diethyl-p-phenylene diamine and a coupler for yellow, for instance benzoyl acetone, with the usual quantity of sodium carbonate and very little sodium sulphite, if any. Such developer will produce blue in the blue-sensitive elements of Lot 1 and yellow in the remainder of the surface. Fix in plain hypo, wash well, then bleach in a bath composed of:

Water	cc	1000
Ammonium oxalate	cc	25
Ammonium citrate	cc	50

Take 100 cc. of this and add to it 10 cc. of a 10% solution of potassium ferricyanide. Ammonium bromide, for contrast, may be also added. Wash. Treat in a bath composed of:

Water	cc	1000
Sodium carbonate		30
Dimethylglyoxime, gr. 1 in alcohol and acetone	cc	100

Rinse, fix again in very weak hypo bath; final wash. Thus in only 4 main operations: developing, fixing, bleaching, red bath, a picture is obtained in three colors in the direct system, that is in the same colors of the rays photographed but with inverted luminosities: black for white and vice versa, light blue for dark blue and vice versa, and the same for the other colors. On printing from such negative color picture on like material, a color positive is obtained in correct colors and luminosities. The originally exposed material may instead be developed in black, then reversed (the resins helping the material to withstand the acid treatment) and the color processing then applied, resulting in an image in complementary colors: printing on like material and treating with same procedure will again give picture in correct colors.

EXAMPLE 2

Two layers are provided.

First layer is an emulsion produced in usual manner, strongly orthochromatic, to 100 cc. of which is added a solution of 2-amino-5-hydroxy-toluene gr. 0.30 in alcohol q. s. Add also tartrazine gr. 0.25 and naphthol green gr. 0.10.

Second layer is composed of:

Lot 1

As Lot 1 of previous example, with plain alpha naphthol substituted for the 2:4 dichloralpha-naphthol, same quantity as indicated for the latter.

Lot 2

Plain emulsion, again 100 cc. sensitised for red by addition of:

Water	cc	10
Nickel chloride	gr	0.50
Ammonia	s. or cc	1
Pot. bromide	gr	0.25
Pinacyanol (1 in 1000 sol.)	cc	1½

Mix the two lots and coat very thinly over the first layer. Treatment after exposure is very simple indeed: development is carried out only in a 3 to 7% sodium carbonate (anhydrous) solution, with very little sodium sulphite, for instance 1%, and a little potassium bromide if required for contrast. The alkali will easily penetrate through the interstices between the elements of the upper layer, to the layer underneath and will act on the toluene compound, which, in the practical absence of sulphite, will at one and the same time reduce itself into a yellow coloring matter and react with the alpha naphthol of the upper layer to give in that element red. The silver in the other emulsion of the upper layer is reduced to black.

Wash. Fix in plain hypo.

Then bleach in:

Ammonium citrate, 20% sol	cc	22½
Nickel chloride, 10% sol	cc	15
Potassium ferricyanide, 10% sol	cc	10

Wash again, then treat in

Water	cc	100
Diethyl-p-phenylene diaminehydrochloride	gr	1
8-hydroxy-quinoline sulphate	gr	1.50
Sodium carbonate (anhydrous)	gr	1

This will produce blue-green in the black parts of the upper layer.

Again in this case, with only four simple operations there is obtained a three color negative picture, with the middle band color rays (yellow and green) directly and abundantly reproduced in yellow for the whole of a layer, while the other two extreme band rays are reproduced in complementaries, blue for red and red for blue: all in negative luminosities, and with intermediate bands thus: orange for green, and green for orange.

Printing such a picture on like material results in correct picture.

EXAMPLE 3

Two layer material adapted to be processed at will so as to give either a negative color picture in direct colors (and inverted luminosities) as in Example 1 or a negative color picture with direct color in middle band rays (yellow and green) and with complementaries in the extreme band colors (blue for red and red for blue), as in Example 2.

First layer is composed of an emulsion of the usual kind in 100 cc. of which about gr. 2 of acetoacetanilide in alcohol q. s. are dispersed. The color former may be in insulated silver halide grains, if desired. The emulsion is made

strongly orthochromatic for instance with a solution of cobalt salt and green sensitiser as that prescribed for Lot 3 of Example 1, and is to contain tartrazine gr. 0.25 and naphthol green 0.15.

Second layer is composed of

Lot 1

As Lot 1 of Example 1, with alpha naphthol substituted for the 2:4 dichlor alpha naphthol, same quantity.

Lot 2

As Lot 2 of Example 1.

Mix the two lots and coat thinly over first layer.

Treatment for direct colors: precisely the same as that prescribed for Example 1.

Treatment for direct middle band and complementary extreme bands: develop in the usual sodium carbonate solution and little, if any, sulphite, with about 2 gr. of 5-amino-2-hydroxy-toluene hydrochloride (or sulphate) per 1000 cc. of solution. Wash, fix in plain hypo. Bleach and proceed with nickel chloride bleach and then 8-hydroxy-quinoline sulphate bath as in formulae given for treatment of Example 2. It will be noticed that advantage is taken of the fact that alpha naphthol, present in the blue sensitive element, can be made to produce blue with a developer and magenta red with another, the two developers used in the alternative treatments just outlined.

EXAMPLE 4

A two-layer material, intended for simple and rapid processing, and of the simplest manufacture, as the upper layer may be considered similar to an anti-stress coating:

First coat is composed of two lots mixed together:

Lot 1

Emulsion of the usual type, orthochromatised with the green sensitive-cobalt salt mixture previously mentioned, and containing, for 100 cc. of emulsion, gr. 2 of acetoacetanilide in alcohol q. s.

Lot 2

A. Alcohol	cc	25
Dragon's blood	gr	2
1-phenyl-3 methyl-5 pyrazolone	gr	0.20
B. Alcohol	cc	25
Nickel nitrate	gr	0.65
Ammonia q. s. or	cc	1
Pinacyanol (1 in 1000 sol.)	cc	1½
C. Alcohol	cc	50
Silver nitrate	gr	5

D. As C of Lot 1 of Example 1.

Mix first A and B, add C. This mixed solution is then warmed, poured in fine stream on D that is brought at 60° C., and the emulsion is finished in usual manner, with ripening to such a point that the speed to red of this lot is equal to the speed to green of the other lot. The two lots are mixed preferably in proportion of 3 parts, by volume, of Lot 1 to 2 parts of Lot 2.

Top layer:

A. Alcohol	cc	25
Isamine blue q. s. to color solution		
Benzoin or mastic	gr	2
B. Acetone	cc	25
8-Hydroxy-quinoline	gr	0.80 to 1.20
C. Silver nitrate	gr	45
Alcohol	cc	50
Isamine blue q. s. to color solution		
D. Water, distilled	cc	100
Gelatin	gr	7
Potassium bromide	gr	4
Potassium iodide	gr	0.06

Mix A and B: add C. Warm the whole and add in fine stream to D kept at 60° C. Finish emulsion in recognized manner, and finally dilute, before coating, with equal parts, or thereabout, of this emulsion and a gelatin solution: to every 100 cc. of the latter from gr. 0.20 to gr. 0.40 of tartrazine should be added. The degree of such dilution, strength of gelatin, and quantity of tartrazine depend on the thickness of the layer that the coating appliance employed allows. A thin coat is desired, equal to no more than half the thickness of the first layer.

Processing is effected with a biethyl-p-phenylene diamine developer, followed by fixing and subsequent removal of black silver. Some of the latter may, if desired, be left in, when soft color effects are desired. A picture is obtained in negative luminosities but direct colors. For a picture in complementaries, reversal may be applied after black development, but in such case the second color development should contain also a yellow color former, as the acetoacetanilide present free in first layer would not resist the acid reversal bath.

EXAMPLE 5

Material mainly intended to give by reversal direct color positives for copying multi-color originals. Three lots are required.

Lot 1

This can be an emulsion non-color-sensitised so that it should be only sensitive to blue, and may contain a yellow color former of little solubility, or nothing. Isamine blue could be dispersed in this emulsion. This emulsion is either coated in separate layer under a gelatin suspension of the other two lots, or is mixed with the latter in a single layer.

Lot 2

This consists of insulated light sensitive elements produced similarly to previous instances with:

Dragon's blood or mastic;
A blue color former, say alpha naphthol;
Nickel salt;
Red sensitiser, say pinacyanol;
Silver nitrate, halides, gelatin.

Lot 3

This also consists of insulated elements produced similarly to previous instances with:

Mastic or benzoin;
A red color former, say p-nitro-benzyl-cyanide;
Cobalt salt;
Green sensitiser, say orthochrome T;
Silver nitrate, halides, gelatin.

After development in black (in more or less neutral developers, if required), reversal is applied, followed by required color developer or developers and usual procedure. If no yellow color former was included in Lot 1 a yellow color former is mixed with the color developer; or else, diethyl or dimethyl-p-phenylene diamine hydrochloride may be used in strongly alkaline bath, with the result that yellow is produced out of the de-

veloper alone in the plain emulsion of the layer or layers, while the same developer produces blue and red with the color formers instanced in the elements of Lot 2 and Lot 3.

In a variation of this last example, the Lot 1 is made to contain insulated blue sensitive elements comprising also a yellow color former. The black produced in the plain emulsion may finally be re-formed so as to blend the colors in soft harmony.

In the accompanying drawing there is shown a sectional view of a film made according to my invention. As shown therein, a support 10 of glass, cellulose ester, paper, or other suitable material, has thereon a gelatin layer 11 containing dispersed particles of resin 12 containing silver halide represented at 13 and color-former represented at 14. It will be understood that the drawing of the particles is for purposes of illustration only, and that the resin particles usually contain more than a single silver halide grain, and that the color former is uniformly dissolved in the resin particle.

When color formers or other adjuncts are such as would be dissolved or destroyed by known acid reversal baths, a bleaching treatment requiring no acid such as will convert black silver into another salt, specially a chloride or an organic salt, of silver, may be applied instead, together with, or followed by, a solvent of the silver salt which will not dissolve unexposed bromide.

Emulsions carrying insulated color elements require much less hardening agent than generally used, if at all—depending, naturally, on the brand of gelatin that is employed.

I claim:

1. The method of forming a sensitive photographic layer capable of producing a colored image which comprises precipitating a silver halide in a solution of a water-insoluble resin containing a color former, suspending particles of the solution of resin containing silver halide and color former in gelatin and coating the suspension on a support.

2. The method of forming a sensitive photographic layer capable of producing a colored image which comprises precipitating a silver halide in a solution of a water-insoluble resin containing a color former and a plasticizer for the resin, suspending particles of the solution of resin containing silver halide, color former and plasticizer in gelatin and coating the suspension on a support.

3. The method of forming a sensitive photographic layer capable of producing a colored image which comprises mixing a solution of resin color former and a soluble halide with a solution of gelatin and a soluble silver salt to precipitate a silver halide in the solution of resin and color former, suspending particles of the solution of resin containing silver halide and color former in gelatin, and coating the suspension on a support.

4. The method of forming a sensitive photographic layer capable of producing a colored image which comprises mixing a solution of resin, color former and a soluble halide with a solution of gelatin and a soluble silver salt to precipitate a silver halide in the solution of the resin and color former, adding a plasticizer for the resin to the solution, suspending particles of the solution of resin containing silver halide and color former in gelatin, and coating the suspension on the support.

5. The method of forming a sensitive photographic layer capable of producing a colored image which comprises mixing a solution of resin, color former and potassium bromide with a solution of gelatin and silver nitrate to precipitate silver bromide in the solution of resin and color former, suspending particles of the solution of resin containing silver bromide and color former in gelatin and coating the suspension on a support.

6. The method of claim 3 in which the resin is a natural resin.

7. The method of claim 3 in which the resin is a synthetic resin.

8. The method of claim 5 in which the silver bromide grains are sensitized with an optical sensitizing dye.

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