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METHOD OF PREPARATION OF NATURAL COLOR PICTURES

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The greatest sharpness in the simultaneous preparation of three color separations in inseparably superimposed emulsions is obtained if the reduced silver or chemical components which are substituted in the place of the reduced silver or in the place of the residual silver halide or even better deposited right during development—are employed in the color separations. To this end these chemical compounds must be insoluble or at least not easily diffusing and they, or the silver, must have reducing, oxidizing or catalytic properties. Therefore numerous methods of color photography are possible by means of a triple or double emulsion containing the generators from the beginning on.

The most ideal method of color photography would be the direct conversion of the leuco derivatives contained in the emulsions to the corresponding dyes by means of the oxidation products of the developing solution originating from the development of the latent image. This can be easily done only in physical development by means of a 1–3% solution of hydroquinone acidified by H_2SO_4, etc., or its halide substitution products, and in the presence of silver nitrate or mercury salts. Here the quinone, etc., formed in development at once oxidizes the indigosols in the emulsions or their insoluble or at least non-diffusing salts, especially the salts of leuco sulfuric acid esters, etc., of vat dyes which are high-molecular or are combined with high-polymer radicals. Unfortunately, however, physical development of motion picture film is commercially very difficult, although it has been proposed for the development of Lippmann photographs. Solutions which in addition to silver nitrate, contain 1–5% of hydroquinone, and about 1–3% of sulfuric acid, etc., and also 1–2% of indigosol, thioindigosol, etc., may be used to advantage for physical development of monochromes. It is known and must be taken into account that physical development requires a much longer exposure. Therefore, it is usually better to proceed first with the usual development, perhaps remove the reduced silver, which is not absolutely necessary, then after long re-exposure one continues with the physical development of the residual silver halide to a vat dye image. If the silver remains in the image, it may act as nucleus for physical development, so that its removal is advisable. The danger is, however, very slight with coarse-grain metallic silver. The very fine grain silver liberated in the first development from very fine-grain silver halide emulsions may well be used for physical intensification after fixing out the residual silver halide with liberation of dye from the indigosol, etc., if the solutions mentioned above are allowed to react. The oxidation methods which will now be described are more reliable. In these methods the insoluble oxidizing agent liberated by the developer may be made to react at once by addition of acid, etc. Another possibility is to add potassium iodine, or, less desirably, potassium bromide or potassium bromate or chlorate, so that by oxidation first free iodine is formed which then acts as oxidizer on the insoluble indigosol salts contained in the emulsions. Here, however, the danger of diffusion of the oxidizing agent and, consequently, that of unsharp images exists.

DEVELOPER OXIDATION PRODUCTS

It has been found that insoluble indophenols and indamines formed in chemical development act in the presence of acid as oxidizers of indigosols and similar compounds added to the emulsions, although relatively slowly. These indophenols are obtained either by development with the corresponding leuco-indophenols, indamines, etc., or by colored coupling, as described in previous patent applications. We shall not decide the question, whether indophenols, etc., in themselves are acting as oxidizers, or the quinone liberated from it by the action of acid. In order to prevent diffusion of quinone, high-molecular phenols or naphthols are used, or those which are substituted by a large amount of chlorine or bromine, for example, 2-3-5-6-tetrachlor- or tetrabrom phenol or also tribrom phenol, so that the non-diffusing or only slightly diffusing chloranil or brominated quinone is formed. Especially well-suited oxidizers are the indophenols which are obtained by coupling of the components mentioned above in development with oo'-dichlor- or oo'-dibrom-p-amidophenol, with higher halide derivatives of p-amidophenol, or with o-amidophenol. The corresponding leuco forms may of course, also be used. It was stated above with regard to physical color development that probably quinone or its halogen substitution products (when using metol, p-amidophenol, etc., also the corresponding quinone amides) may be considered as the oxidizing agent. This reoxidizes the admixed soluble leuco sulfuric acid esters of the insoluble or soluble high-molecular non-diffusing indigosols contained in the emulsion to vat dyes. If, however, ordinary hydroquinone is used for development, the quinone deposited on the image does not yield sharp images, probably because it is too easily washed out by water. Reduced chloranil, or tetra- or tribrom quinone, or analogous derivatives of naphthoquinone or other high quinones are more suitable as developers of this type. Most high quinones, however, act very slowly. Hydroquinone substituted by diphenyl or phenyl which may be halogenated, is also suitable as a developer. So are also the sulfones of hydroquinones formed by addition of aromatic or alpihatic sulfinic acids to any quinone. They form, in development, the oxidizing insoluble quinone sulfone. If the three silver images are treated with quinone or quinone sulfonic acid or their halide derivatives in the presence of potassium bromide, according to Lumiere and Seyewetz, oxidizers, perhaps quinhydrones, are precipitated which are capable of oxidizing indigosols or their insoluble salts in the presence of acid. The concentrations used should be those chosen by the authors mentioned. Also halogen substituted lignones possess good oxidizing power for indigosols. They are precipitated on the image in development with sodium hydroxide or carbonate containing about 1–3% solutions of the corresponding halogenated diphenols, for example, tetrachlor or tetrabrom diphenol, etc. Of special importance as an oxidizer for leuco sulfuric acid esters of vat dyes and their insoluble salts is reduced indolo-anthrone, as well as the homologues, analogues, and halide substitution products of the latter, since the insoluble indolo-anthrone is precipitated on the image in development with about 1% solution which contains sodium carbonate or hydroxide. It acts as an oxidizer, when the emulsion is placed in highly diluted acids. In certain cases it is better to oxidize with addition of some potassium iodide or bromide to the acid solution, where the iodine formed indirectly acts as an oxidizer. Development should be carried out with exclusion of oxygen in alkaline solution, and the same precaution should be taken with alkaline solutions of high-halogenated diphenols, or of phenyl thioindoxyl which acts in a similar manner. The coupling components, leuco indophenol, hydroquinone, diphenol, etc., may contain one or several groups in the nucleus which act as oxidizers when acidified, but not in carbonate containing weakly alkaline neutral or developing solution. As substituents of this type may be considered: the nitroso, iodo, iodoso group, etc., but especially the chloryl and bromyl sulfamido group ($—SO_2NHBr$, or $—SO_2NHCl$), less the dihalide sulfamide (SO_2NBr_2 or $—SO_2NCl_2$), and coupling derivatives of the peroxides. One may use, for example, o-phenyl-phenol or 1-naphthol, containing a sulfamide group whose nitrogen is substituted by two or by only one molecule of halogen. Since this substitution produces a certain solubility in sodium carbonate or hydroxide, the use of high-molecular derivatives or of salts with inorganic or organic bases which form insoluble or non-diffusing salts with the SO_2NHBr group, is recommended. 1-naphthol sulfochloride, salicyclic acid chloride and similar compounds with reactive halides may be converted with more strongly concentrated hydrogen peroxide or better with sodium peroxide, or with other peroxides into organic per oxides. These are stable in weakly alkaline solution and may be coupled with the developer either during development or separately by oxidation and preparation of the leuco compound which is then used as a developer. The oxidizing action starts in the image areas, if the emulsion, perhaps with slight heating is placed in dilute acid.

Residue Methods

In the practical application of the residue methods mentioned in the previous section, ferrichydroxide, manganichydroxide, etc., is formed in those areas which have been developed. These may be used for the oxidation of leuco derivatives after acidification and under exclusion of oxygen. In this and other oxidation methods described previously it is better, and usually indispensable, to convert the silver formed first into silver ferrocyanide by means of potassium ferricyanide or other indifferent oxidizers. Otherwise on acidification the oxidizer deposited on the image would at least be partially wasted in the oxidation of silver which is also present in these areas, instead of being used for the formation or destruction of the dye.

Substitution Methods

The substitution of reduced silver or residual silver halide by chromate, bichromate, hypochlorite, etc., is impractical, because the oxygen acids diffuse too easily when liberated by acidification and unsharp separation images are the result. It is better to form from the corresponding ferrocyanides manganese or lead peroxide or similar insoluble oxidizers which is very easily accessible, and with large yield, by means of the known lead intensifier. In the conversion to peroxides the use of fixed alkalies or ammonia must be avoided, if possible, if the insoluble salts of leuco sulfuric acid esters and analogous compounds of thioindoxyl, indoxyl, hydroxy seleno naphthene, pyrogallol dimethyl ether, etc., are present in the emulsions. Otherwise these will be decomposed and diffuse, unless the precipitants chosen are strongly basic quaternary organic compounds, for example, acridinium derivatives and dyes of this and related groups. The conversion is successful also in the presence of sodium carbonate although much slower if hydrogen peroxide, ammonium persulfate etc., are used. In this case, diphenyl guanidine, triphenyl guanidine, and similar soda-stable organic bases yield salts with indigosols. If the emulsion is placed in strongly diluted 1–2% acid, oxidation begins without noticeable diffusion.

Induced Oxidation

It has been found that acidified bromate in about 1–5% solution attacks silver especially in the presence of oxidizable compounds. To these we may also add the insoluble salts of indigo sols or alkali salts of high-molecular non-diffusing indigosols added to the emulsions. Heat favors reoxidation in the image areas. The easily soluble sodium bromate in about 2% solution containing ½–2% H_2SO_4 or HCl, perhaps also some KBr, is best for this purpose.

Especially for induced oxidation, but also for catalytic oxidation it is advantageous to use solutions of free chloric or bromic acid which are obtained by precipitation of a barium or strontium salt solution with sulfuric acid and subsequent filtration and not acidified 2% solutions of sodium chlorate or bromate. In order to prevent too strong swelling of the gelatin here and in similar cases phosphoric acid, ether sulfuric acid, aromatic sulfonic acid, etc., should be used. A neutral solution of about 2% bichromate and hydrogen peroxide is not only capable of oxidizing leuco sulfuric acid esters to the vat dyes, but also of destroying the latter in certain cases. Since in this case probably perchromic acid is formed, and the latter is also formed in neutral solutions from chromic oxide and H_2O_2, lead or silver chromate images yielding very difficultly soluble perchromates, and the salts with high-molecular organic bases are also suitable for this purpose. Titanium peroxide may be considered too: it is easily obtained from titanium ferrocyanide deposited on the image. (Jahrb. f. Phot. 1900. 129, B. 31: 955: 39: 320: 60: 500.) Other oxides capable of forming peroxides (Z. anorg. Chem. 1931. 741): perhaps pernitric acid also may be taken into consideration. The residual silver halide may be converted into difficultly soluble double salts by means of thiosulfates of organic high-molecular bases, perhaps in the presence of thiourea. After washing out the excess, the picture is bathed in acidified chlorate solution whereby SO_2 is liberated yielding chloric oxides which are capable of oxidizing indigosol salts. The inducing action in all cases may be combined with an oxidizing or a catalytic effect. This happens, for example, when acidified bromate solution of chloric acid solution acts on a silver image which is only very superficially converted to vanadyl ferrocyanide or lead ferrocyanide, or where iron hydroxide was deposited in addition to silver by development with pyrocatechin ferriate. In cases previously described where in addition to silver also an indophenol, quinone, quinhydrone, etc., is insolubly deposited, the latter will not only take part in the reaction on account of its hydroquinone group, but the leuco derivative formed in the reoxidation of indigosol will also be reoxidized by the acidified bromate solution, and the bromic oxides thus formed act also on the indigosol. The oxidizing action is frequently aided by addition of safranine, methylene blue, and other acid-stable desensitizers, also by formamidine disulfide, thiourea, thiosinamine, thioglycolic acid, etc. These are, at least for a short time, stable to acid and have complex-forming properties, so that also coarse grain negative silver quickly reacts, when treated with acidified chlorate or bromate solution.

DYES FOR A TRIPLE EMULSION

The preparation of monochromes is relatively easy with aid of the reactions described, but the latter cannot be applied to the triple emulsion without modifications. We must not forget that usually only colorless of yellow generators, or at the most a yellow final dye may be added to the upper emulsion layer, and that no diffusion of the finished dyes, or their generators must take place from one layer to another, if approximately natural color pictures are to be expected. If, for example, the insoluble salt of the leuco sulfuric acid ester of a vat dye with quinine or cinchonine is added to a single emulsion layer, after which the reduced silver is converted through manganese ferrocyanide to manganese peroxide, and its oxidation action is started by bathing in a dilute solution of an acid, a perfect indigo image is obtained. It would be wrong to expect that the preparation of a natural color image in a triple emulsion was possible in an analogous manner, rather a two-color image on a double-coated film would be made that way. An alkaline reaction is indispensable in the formation of manganese peroxide, at least in the known methods proposed for photographic purposes, and the quinine or cinchonine salts of indigosols and thioindigosols are split already by dilute sodium carbonate solution, and more so by sodium hydroxide or ammonia, so that the soluble alkali salt of the leuco ester is present in the emulsion layer; the latter is, however, very easily reoxidized. It has, therefore, heretofore been doubtful whether or not the insoluble or at least not noticeably diffusing salts of leuco sulfuric acid esters are capable of being oxidized with organic bases in the insoluble state. This is now actually the case. It may be proved by converting a silver image, the emulsion of which contains the insoluble salts mentioned above, in a neutral manner to an image of silver chromate or lead chromate which yields an indigo image in the presence of acid. It may be shown still more convincingly by using the catalytic method previously described, or by precipitating by double conversion one of the insoluble indigosols mentioned above in a gelatin emulsion containing a lead or manganese peroxide image. The general diffuse or image regeneration of the vat dye from the insoluble salt of its leuco sulfuric acid ester or similar leuco derivatives is especially easy if the precipitants are organic bases which are more easily destroyed by oxidation than the vat dye is destroyed or regenerated. This is of importance in the use of catalytic oxidizers which often act so strongly that the precipitant is easily decomposed to nonbasic compounds. One must, of course, choose relatively resistant vat dyes, for examples, those of the thioindigo group.

One must differentiate whether the leuco derivatives or generators or other preliminary forms of the dyes added to the emulsions are suitable for formation, vatting, or destruction, according to the following directions:

A. Formation of dyes

Dyes suitable for the generation of images are: the stable leuco forms of vat dyes and lignone dyes, their leuco sulfuric acid esters and monosulfuric acid esters, their leuco phosphoric acid esters, and the leuco esters with phosphorous sulfochloride, as well as many other similar leuco compounds which have been mentioned in previous patent applications Serial Nos. 139,758, filed April 29, 1937, 139,759, filed April 29, 1937, 151,811, filed July 3, 1937, 177,738, filed December 2, 1937, 200,684, April 7, 1938, 214,578, June 18, 1938, and 225,836 filed August 19, 1938. It should be mentioned that especially the stable leuco forms of thioindigo dyes, etc., which correspond to indigo white are most easily obtained by reduction in the presence of a slight amount of alkali. Similarly stable leuco forms are obtained from flavanthrene, coerulignone, blue and red Russig dye. Compounds analogous to leuco sulfuric acid esters are obtained also from thioindoxyl, indoxyl, pyrogallol dimethyl ether, the 2- and 4-ether of a-naphthol and of other lignone generators. The leuco sulfuric acid esters of vat dyes and analogous compounds must be added to the emulsions in form of insoluble or not markedly diffusing salts, by precipitation with yellow dyes (auramine, thioflavine T, trypaflavine and other acridinium dyes, etc.), diphenyl guanidine, triphenylguanidine, aristochin, di- and poly-cinchonine, and synthetic high-polymer bases for example poly-ethylene diamine, especially those with a quaternary ammonium group or sulfinium group. An image of an oxidizer is therefore formed in each emulsion layer by any of the previously mentioned methods, and its oxidizing action is started by acidification or sometimes by alkalizing, after which the residual leuco derivative is washed out. The leuco esters, of course, do not necessarily have to be colorless. They may be yellow for the middle and the lower emulsions, and also for the upper emulsion so that reoxidation of the image causes only a difference in solubility without essential change in the color layers. Products which can be obtained from the anthrone form of reduced simple anthraquinone dyes (amino or hydroxy or aminohydroxy, benzoyl amino, diacyl amino, aryl amino anthraquinones) by the action of acetaldehyde disulfonic acid or monosulfonic acid, benzaldehyde sulfonic acid, etc. The meso double bond for these compounds can easily be split by oxidation with regeneration of the vat dye.

If we add stable leuco bodies to the emulsions, leuco sulfuric acid esters and similarly behaving leuco derivatives of vat dyes or of their generators, the previously mentioned stable leuco forms of highly-halogenated or otherwise suitably substituted thioindigos, etc., the anthraquinone dyes which are reduced to the anthrone form, and, perhaps, condensed in the meso-position with formalin or with other aldehydes, also aliphatic or aromatic dialdehydes, and leuco bases of triphenyl methane dyes and similar dyes, etc., then it is necessary to remove the residual leuco derivative from the emulsion on account of its light sensitivity, if natural color pictures in the sense of this application are to be obtained. In motion picture films, however, these leuco derivatives may remain in the emulsion, according to the invention. This is permissible because the projection is always very short, and harmless, especially if all chemically acting rays are filtered out from the projection light, for example, the ultraviolet, violet and blue-violet rays which can be easily done without noticeable change of the colored image. Leuco sulfuric acid esters and monosulfuric acid esters of reduced vat dyes, semi-indigoid and anthraquinone dyes, also those of the anthrone form, are especially easily washed out, because their solubility differs very much from that of finished dye.

Under certain circumstances it is better to revat and wash out the vat dye formed by oxidation of the image, and to convert the residual indigosols or other leuco derivatives or their insoluble salts which are contained in the three emulsion layers to the vat dyes by general strong oxidation. Sodium hydroxide or ammonia must be used for vatting and removal of the dye formed, because colloidal solutions can be washed out only with difficulty by boric acid or borax. The method under discussion is therefore successful only when strong quaternary organic bases or dyes have been used as precipitants, e. g. those of the acridinium group, which yield salts stable to dilute sodium hydroxide or ammonia. A further possibility exists in the addition of leucotrope S for vatting which yields an ether soluble in sodium carbonate. Unfortunately, however, heat must be applied so that the general application of this method is very limited in this process. Also vatting in the presence of acetone or alcoholic sodium hydroxide which can also be used with leucotrope S, yields satisfactory results under certain circumstances.

B. Vatting of dyes

If dyes are to be vatted in the areas of reduced silver by means of KCN or reducing agents deposited as an image, the final dye must be present only in the upper emulsion layer. The middle and lower layers may contain colorless or, at the most, yellow derivatives of these dyes, and the lower layer a red derivative. The latter however would be less practical. The compounds which one would add generally are the stable leuco forms of highly-halogenated or otherwise substituted thioindigos, etc., which have been mentioned above; stable reduced lignone dyes, reduced hexa- or octo-iodindigo, or, better, insoluble or difficultly diffusing salts of leuco sulfuric acid esters of vat dyes and similar other compounds of the latter. In order to prevent a serious attack of the metallic silver in the general reoxidation of these compounds the use of persulfate or hydrogen peroxide, perhaps in the presence of KBr, is recommended. These hardly attack silver in the presence of a small amount of acid during the short time necessary for regeneration of the vat dye, especially when non-diffusing alkali salts of high-molecular leuco sulfuric acid esters or those combined with high polymers are added.

It is, of course, still better to use those derivatives of dyes or their leuco forms or generators which regenerate the dye by hydrolysis or reduction. For example, dehydroindigo bisulfite may be considered for use. This compound with high-molecular organic bases which may be added to the emulsions just as the indigosols yields completely insoluble salts. These products are obtained not only from green-blue hexaiodindigo and different naphthalene indigos, but also from the purple red halide substitution products of indigo, the indirubine and similar dyes. Since furthermore, the final dye may be contained in the upper emulsion, all dyes necessary for the triple emulsion are available. After the first development and, perhaps, fixation, the indigos are regenerated from these derivatives by acid or alkali or reducers. This may also be accomplished by illumination of both sides. Then the areas containing silver are reduced by KCN in the presence of catalysts and sodium carbonate in order to facilitate washing out, perhaps, under exclusion of oxygen. Also suited for this purpose are the bisulfite addition products of many unsymmetrical or semi-indigoid vat dyes, and of indirubine and its analogues which also yield insoluble salts with organic bases. The dye is regenerated from these compounds by dilute sodium hyroxide or acid, preferably in the presence of very little persulfate. The N-acyl derivatives of indigo and semi-indigoid vat dyes with only one indole ring and the free imino group may be easily acylated by m-sulfobenzoic acid chloride according to German Patents 445,566 and 448,909. These acylation products are separated with dilute ammonia or ethylenediamine from their bisulfite addition products and are themselves usable as image-dyes. They have mostly a very different and more useful color, are easily spit further by aqueous or alcoholic alkalies, bisulfite derivatives or if they contain COOH or SO_3H groups they give insoluble salts with the organic bases which have been mentioned repeatedly. These can be added to the emulsions. Also the phenol ethers of certain leuco vat dyes are easily spit by alkali. The chloroformic esters of leuco vat dyes are particularly easy to spit, sometimes also phosphoric acid esters, and especially benzyl carbonic acid esters. The latter can also be split by catalytic or other reduction. In addition to the derivatives mentioned here, we also point to the many derivatives of the patent application of Karl Schinzel, Serial No. 177,738, filed December 2, 1937, which are more or less easily hydrolyzed. Since we do not deal here with coupling off, it is unnecessary to substitute the acyl groups or other closing groups mentioned in the patent to make coupling possible. It is sufficient that they are easily spit by hydrolysis, oxidation or reduction, which considerably simplifies the formation of these derivatives.

The regeneration of vat dyes by reduction from their very differently colored azo compounds German Patent 310,556; British Patent 333,506, accepted August 8, 1930; 377,024; French Patent 721,249 as mentioned in patent application Serial No. 225,836, filed August 19, 1938, is of special importance. The color of the original amino or hydroxy, or aminohydroxy vat dye is often changed to such an extent by the conversion to a combined azo dye that it may be added to the corresponding emulsion layer without undesirable absorption. For example, the yellow azo compound of a purple vat dye may be chosen for the middle layer, a yellow or red azo derivative of a greenish-blue vat dye for the lower layer, and the final image dye for the upper layer. The azo double bond is split by mild oxidizers with regeneration of the original vat dye. It is immaterial, whether the reduction progresses to the formation of the leuco form, because the latter usually is easily oxidized by air, and generally, is sufficiently insoluble to prevent diffusion, especially since the use of alkaline reducers may easily be prevented. The dye in the places containing silver is then vatted by reducers which are deposited in the image or by means of KCN. The alkali present, or acetone or alkali allows for washing it out.

HIGH-MOLECULAR DYES AND LEUCO DERIVATIVES

Instead of introducing leucosulfuric acid esters and similar leuco derivatives into the emulsions as insoluble salts, one may also use such high molecular ones that they may be added to the emulsions in form of their water-soluble alkali or ammonium salts without the danger of diffusion. Of course, if in addition these precipitants are added which have been found practical with simple indigosols, the results will be still better. It will be best to choose as precipitants quinine, cinchonine, etc., the salts of which with indigosols, are already split by sodium carbonate added in the first development. The emulsions contain then, after general development, the alkali salts of leuco esters which are so high molecular that they do not diffuse from one layer to another. They are however, almost as easily reoxidized as their aqueous solutions.

A great number of very high-molecular vat dyes are known, and further highly halogenated or otherwise substituted simpler ones which have not yet been converted to their leuco esters or analogous compounds but which are suitable for this transformation according to the known methods. Also vat dyes or related colored compounds which cannot be used for dyeing may be converted, according to the methods used, for simple indigosols, to the corresponding leuco esters, the alkali salts of which are almost completely, if not entirely, non-diffusing in a gelatin layer. With regard to these high-molecular vat dyes we refer to the scientific and patent literature of the last years, especially on the higher vat dyes which have been prepared with the aid of cyanuric chloride. The greatest difficulty is the removal of the residual high-molecular leuco ester from the emulsion. It cannot be left in the emulsion on account of its sensitivity to light except in motion picture film. In this it may be left especially when all chemically acting rays are filtered out in projection according to this invention as mentioned above.

The leuco forms of the vat dyes must, therefore, be combined with high polymers by means of their esters with phosphoric acid, phosphorus sulfochloride, cyanide chloride, or other suitable intermediate members. As we know from the patent application of Karl Schinzel, Serial No. 177,738, filed December 12, 1937, one chlorine atom of these esterifiers may be made to react with high-molecular or high-polymer organic bases. Sulfochlorides or carboxylic acid chlorides of high-molecular compounds which regenerate the corresponding resistant vat dye by hydrolysis or oxidation may also be used for esterification. Hereby the radical of the closing group may be destroyed, as in the use of polyacylic acid chloride, polyvinyl chloroacetate, etc. Esterification may, of course, also take place before polymerization if the leuco form is stable enough. This regeneration may be performed either on the image or generally, according to the method chosen for the formation of the image. One may, for example, oxidize the image by catalysis, and convert the residue of the leuco derivative by hydrolysis in the absence of air to the easily washed-out alkali salt of the simple leuco form. In the reduction of the image by KCN the original vat dyes are again regenerated in all three emulsion layers by general hydrolysis or careful alkaline or acid oxidation.

These methods can not usually be used with leuco sulfuric acid esters. An amino or hydroxy group in the molecule of the vat dye or its leuco derivative must be converted to a loose, easily split combination with high-molecular or high-polymer substances. Amino derivatives are easily transformed with polyacrylic aldehyde into the anils which are easily decomposed by acids. Hydroxyl groups may be esterified by polyvinyl chloroacetate, polyacrylic acid chloride, triphenylmethane chloride, benzyl carbonic acid chloride, etc. Here a hydroxyl group in the nucleus is esterified, whereas earlier esterification of the easily reoxidized hydroxyl groups of thioindigo white, etc., was intended.

Of particular interest is the combination through the azo group with those high-molecular and high-polymer phenols, naphthols, etc., which are suggested for coupling purposes in the patent application Serial No. 151,811, filed July 3, 1937, of Karl Schinzel. The diazotated leuco sulfuric acid esters and mono-esters of indigoid and anthraquinone dyes, etc., can be combined, according to the directions of our patent application Serial No. 225,836, filed August 19, 1938, with these high-polymer coupling components. Thus high-polymer azo indigosols of many different shades are obtained which are not capable of diffusing through gelatin even as alkali salts. In the image forming generation of the combined vat dye, the difficulty of washing out the residual leuco derivative arises. After reoxidation in the image the azo bond of the high-molecular azo indigo, etc., and of the residual azo indigosol may be split by reducers. Thus the simple indigo dye is formed in the image and the easily washed-out indigosol in the other places. If one works with general diffuse reoxidation, one can split the azo bond by reduction immediately after first development and fixation, and remove the regenerated simple vat dye from the places containing silver with KCN and KOH. If one uses in the image formation catalytic destruction with vanadium, iron, or osmium this degradation of the molecule by reduction may be accomplished either before or afterwards.

HIGH-MOLECULAR AZO DYES

In order to be able to add to the emulsions the alkali salts of high-molecular azo dye sulfonic acids of azo dyes containing hydroxyl which are for example, derived from a-naphthol, they too must have a colloidal structure. We cannot couple directly with the components mentioned in the patent application Serial No. 151,811 because the fractions formed during splitting cannot be easily washed out on account of their high-colloidal character. They are, however, easily discolored, if they are left in the emulsion. Here again we have to form easily hydrolyzed combinations and to add these to the emulsions. The conditions are here more difficult than with azo indigosols, etc., inasmuch as no insoluble vat dye is formed as the end product and the final image dye still contains the group which might be split off. Hence hydrolysis also degrades the molecule of the final image dye, and if this contains the solubility controlling sulfonic acid or OH group the desired effect is not obtained. This group therefore must be contained in the high-polymer member, so that the low-molecular, but in itself insoluble final azo dye, is liberated by hydrolysis. A chance is offered by the addition of bisulfite to only one azo bond with polyazo dyes which usually takes place on the -naphthol side; an OH or amino group in another molecule makes it possible to combine very many by polyacrylic aldehyde. The intact azo bond is split by reduction with thiourea, etc., and the bisulfite addition product is split from the large molecule, so that it can be washed out, which is not the case with the latter. The true azo dye may be regenerated in the areas not containing silver by treatment with dilute sodium hydroxide. This splits off bisulfite which is, however, still bound to the polyacrylic aldehyde. It is liberated from the latter by treatment with dilute acids under certain circumstances, or alkali perhaps with heating, preferably in the presence of phosphotungstate, etc., to prevent diffusion. Similarly one may add high-molecular triphenylmethane azo dyes or their sulfonic acids to the layers as colloidal, non-diffusing alkali salts, split the azo bond in the image and wash the degraded triphenyl methane dye (with alkali or acid, according to the position of the sulfonic acid group), reduce the residue by acid at the azo bond in the presence of phosphotungstate or organic bases, and, perhaps reoxidize the leuco base. In motion picture films, however, the high-molecular coupling components mentioned at the beginning will be used and the degradation products may be left in the image, since discoloration is hardly to be feared.

STRUCTURE OF THE TRIPLE EMULSION

The methods and (leuco) dye derivatives described above shall serve mainly for the formation of natural color images by means of a triple emulsion. This shall contain all three sensitive layers on the same side of the film, the yellow filter layer and, perhaps, a colorless red or yellow filter layer between the lower and middle sensitive emulsion. However, other arrangements are possible, especially the arrangement of one emulsion on one side of the support, and other emulsions on the other side.

Of special importance is the combination with a two-grain emulsion which contains grains that are sensitive to yellow-green and red, or in which red-sensitive or yellow-green-sensitive grains are imbedded in an emulsion sensitized for the other spectral color. On top of this is coated the blue-sensitive emulsion, perhaps separated by a yellow filter. The filter dyes, sensitizers, etc., described in application Serial Nos. 139,758, filed April 29, 1937, and 139,759, filed April 29, 1937, may also be used within reason in this invention. However in this invention we do not add components or grains to the emulsions, except for the purpose of a combined process, but the generators of the dyes or other leuco derivatives. Under certain circumstances also the finished dyes are added, at any rate to one or two emulsion layers.

It proved to be of particular importance, especially in the complex reduction at the reduced silver with KCN, thiourea, or inorganic acids, that the dyes or their generators or preliminary forms which are already contained wholly or in part in the emulsions are brought very close to the silver or the silver halide grain, because the action sphere of the metallic silver is naturally not very great. This effect is obtained by allowing the generators, etc. to be adsorbed to the silver halide grain. This means, that the insoluble leuco sulfuric acid ester salts are precipitated on the grain itself, or that the colloidal insoluble salts of leuco esters with high-molecular bases formed previously in the emulsion, but not yet precipitated, are precipitated on the silver halide grains similarly to the precipitation of the coupling components as described in the application Serial No. 151,811, filed July 3, 1937, of Karl Schinzel. This precipitation in a solution which contains as little gelatin as possible is accomplished by shaking, and more precipitant may be added later for the precipitation of an additional part of the leuco body on the silver halide grain, etc. A similar procedure is used, if we precipitate insoluble or at least non-diffusing leuco derivatives on real silver halide grains of large sizes for the double emulsion mentioned above.

It has been mentioned in previous applications that a diffusion of the sensitizers is most surely prevented if at least the excess which is not adsorbed to the silver halide grain is insoluble precipitated by a suitable precipitant, and this holds true also here. The entire emulsion may be saturated with an excess of precipitants not only for the sensitizer but also for the filter dye, unless this reduces the sensitivity too much.

It is known from the previous applications that in a certain procedure the yellow generator for the blue separation image is added to the upper emulsion layer, while the final vat dyes or azo dyes may be added to the other two layers. Although no perfect results are obtained in this manner, the effect will usually be satisfactory in the known combination with a black image. In addition to the derivatives of blue dyes mentioned previously which may already be regenerated by hydrolysis we mention especially the yellow indanthreneazine. From this the blue vat dye is easily regenerated by reduction, often already in the developing solution. This holds true also for most of its derivatives and substitution products.

I claim:

1. The method of forming a colored image in a gelatino-silver halide emulsion layer containing a leuco vat dye, which comprises forming a dye

selected from the group consisting of indophenols and indamines in the layer, and treating the layer with an acid which, in the presence of said last-mentioned dye, oxidizes the leuco vat dye to a colored compound.

2. The method of claim 1, in which an indoloanthrone is formed in the layer and is used with the acid to oxidize the leuco vat dye.

3. The method of claim 1, in which the oxidation products are formed from reducing agents precipitated in the development of the silver halide.

4. The method of claim 1, in which the metallic silver formed in the first development is converted to non-oxidizable salts by potassium ferricyanide prior to the treatment with acid.

5. The method of claim 1, in which a silver-containing image is converted to silver ferrocyanide, the ferrocyanide is treated with a peroxide selected from the group consisting of manganese and lead, under conditions which prevent decomposition of the leuco dye contained in the layer.

6. The method of forming a colored image in a gelatino-silver halide emulsion layer containing a leuco vat dye, which comprises exposing the layer to an object to be photographed and developing a silver image therein with a solution of a coupling developer and a coupling compound to form a dye selected from the group consisting of indophenols and indamines simultaneously with a silver image, and treating the layer with an acid in the presence of which the last mentioned dye oxidizes the leuco dye to a colored compound in the regions of the silver image.

KARL SCHINZEL.

CERTIFICATE OF CORRECTION.

Patent No. 2,227,981. January 7, 1941.

KARL SCHINZEL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, second column, lines 61, 67, and 69, and page 5, first column, line 6, for the word "spit" read --split--; page 5, second column, line 11, for "December 12, 1937" read --December 2, 1937--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of March, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)