Patented Dec. 29, 1942

2,306,410

UNITED STATES PATENT OFFICE

2,306,410

COLOR DEVELOPMENT

Karl Schinzel, Rochester, N. Y., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application July 3, 1937, Serial No. 151,811. In Austria July 7, 1936

3 Claims. (Cl. 95—2)

This invention relates to color photography, and particularly to processes in which insoluble or non-diffusing coupler or developing compounds are present in the photographic layers.

The processes described herein involve simultaneous production of color-separation images by direct color development or by reversal, or by redevelopment of the bleached negative image. This includes the use of insoluble or non-diffusing compounds in the photographic layers, either developing agents or compounds which function merely as couplers, forming a colored image by coupling with another compound.

A. Primary Development with Insoluble Color Developers

Color developers may be added to the three emulsions which have no effect on silver bromide when they are neutral, but develop each of the three latent images to the proper color on bathing a solution of sodium carbonate or even weaker alkalies. This is possible on the basis of my observation that the exposed silver bromide, or that which has been made developable in any other manner, can be developed by completely insoluble or at least not noticeably diffusing color developers. Often coupling takes place also between added components and developers of this composition, but more readily, of course, between these components and a developer in solution. In the first case, different coupling components and developers can be added to each emulsion, while in the latter case the components must be selected so that they yield the desired color in each layer or kind of grain with the same dissolved developer.

It is an unnecessary complication to add mixtures of insoluble components and insoluble developers to each emulsion, and it harms the transparency of the layers, because a large excess of component must be present in order to yield brilliant color images. This is of value only if it is desired to obtain different colors with the same insoluble component, as for example, higher molecular, insoluble α-naphthol derivatives with free 2- and 4-positions and linked amino groups in the second nucleus, with the aid of two different developers: α-naphthol yields blue with p-amino-dimethylaniline, red with p-aminophenol (β-hydroxynaphthoquinone-β-hydroxyanil). The water-soluble p-aminophenol is, of course, not added but may be used in the form of its insoluble salts with phosphotungstic acid, etc., its 3-aminophenyl derivative (developer "Diphenal") or rather, and in a round-about way, the products obtained by linking two or three molecules of the latter with the external amino group by means of sebacinic acid dichloride, cyanuric chloride, triazine tricarboxylic acid-trichloride, etc., according to the methods for components described later, or polyvalent aminophenols similarly prepared from the developer "Edinol." p-nitrophenols containing an amino group or an easily exchangeable halide in ortho- or meta-position, are especially suited for those condensations with acid chlorides or poly-amines. One must, of course, reduce the nitro-group to the amino-group and p-nitro-salicylic acid chloride. Worth mentioning are oo'-dibenzhydryl-p-aminophenol obtained by catalytic reduction, p-aminophenols prepared from other cryptophenols by diazotization, nitration or nitrosation, p-aminonaphthol-2-tetramethyldiamino-diphenylmethane, benzocarbazol-p-aminophenol, the bis-derivative of o-diphenol, of diaminodinitro-diphenyl-hexane and -octane (diamino groups are substituted by dihydroxy groups, nitro groups reduced, acylated, then introduced into the pp' positions of the hydroxyl amino groups), of di-α-naphthol, of 1,8-dihydroxy-phenanthrene quinone, or the bis-β-aminophenol of the German Patent 488,611. Paraphenylene diamines with one amino group arylsulfonylated can be compared to p-aminophenols. They are difficultly obtained from higher molecular p-diamines by direct arylsulfonylation, but easily from suitable intermediary products, as mm'-dinitro-oo'-diaminodiphenyl, by p-toluolsulfonic chloride and subsequent reduction. Still higher developers of this kind can be prepared even from p-nitraniline and its higher substituted analogues, from nitrated naphthylamines and anthramines, with the aid of di- and trisulfonic chlorides mentioned in the synthetic part of this description under IV B. These polyvalent sulfonic chlorides permit also linking of several molecules of o-hydroxyphenyl-hydroxylamine with ester formation and subsequent conversion to the substituted p-aminophenol derivative. If nitrobenzol sulfonic chloride is used for esterification and is reduced after conversion, a further linking may be obtained by the polyvalent carboxylic acid chlorides or cyanuric chlorides mentioned, because the external amino group reacts more easily than that in the nucleus.

Higher derivatives of p-amino-dimethylaniline are obtained in a similar manner, because the simpler substitution products are not sufficiently insoluble or stable, as for example, 2-anilino-, 3-dimethylamino- derivative, also the piperidine

derivative prepared with dibrompentane. It is more advantageous to allow two or one molecule of ethylene oxide to act on p-nitraniline or its mono-methyl derivative, and to esterify the hydroxy-alkyl ethers obtained with cetylic or stearylic acid- or cerotinic acid chloride, etc., or to allow cetyl- or ceryl-bromide to act directly on the initial products and to reduce later. These products can also be linked by the polyvalent acid chlorides mentioned under IV B. Meta-phenylene diamine and analogues are also suited for this, if one amino group is dialkylated in the manner just mentioned, directly by simpler or higher molecular residues or through hydroxalkyl ether. It is finally nitrosated or coupled with a diazo compound, and the linked, highly-substituted p-amino-dialkylaniline obtained by reduction. The corresponding derivatives of m-aminophenol can also be used for chaining, and often the p-nitro- or -nitroso compounds, so that the subsequent azo-coupling can be dispensed with. Bis-derivatives are also obtained from the corresponding oo'-diamino- or oo'-dinitro-compounds of diphenyl, diphenyl-amine, diphenylene oxide, etc. by dialkylation in the manner described and by introduction of a -amino group. Both p-situated amino groups in the oo'-dimethyl-amino-benzidine could be removed by diazotization, then nitrosated to the dimethylamino groups in the p-position or diazo compounds allowed to react and reduced. Especially high molecular products are obtained, if the chlorides of carboxylic acids or sulfonic acids of the described developers or of their intermediary products or other derivatives of the same with easily exchanged halides, as for example, 6-hydroxy-3-nitro-benzylchloride, are combined with high-polymers cited under V at the end of the description.

It is better to add simple developing leuco-compounds of dyes to the emulsions, preferably those which possess approximately the same developing power. They must develop the exposed silver halide in sodium carbonate solution or weaker alkalies, and they must be insoluble in it or, in special cases, in alkali. It is, as a rule, advisable to conduct the development without oxygen, and in the same manner the following washing out of the unused leuco-form with alkali, or in those with sulfonic or carboxylic acid groups, with sodium carbonate, because also these insoluble or at least not diffusing and negligibly water- and soda-soluble leuco-bodies are easily oxidized. Rather simply constructed leuco-developers should be combined with the emulsions so that they may be easily washed out by sodium carbonate or alkali and yet yield completely insoluble dyes. If the leuco-compounds are not entirely insoluble in water, they can be precipitated within the emulsions as insoluble salts by phosphotungstate and similar inorganic complex compounds in a 10% gelatine solution. In this absolutely insoluble state, they have no harmful effect on the silver halide, particularly if reduced inorganic complex compounds are used as precipitants. Leuco-developers of acid character are precipitated by inorganic bases or higher molecular organic bases, as benzidine, naphthidine, diamino benzidine, tetraminoditolylmethane, leuco-bases of triphenylmethane dyes, di- and triphenylguanidine, quaternary bases of the naphthoquinoline and naphthothiazol series or of the tetramethyl diamino-benzidine, alkaloids, also easily washed out basic dyes: auramine, acridine yellow, thioflavine T etc.; or by polyethylene polyamines linked by cyanuric chloride and their quaternary ammonia compounds. Stabilizing compounds may also be added to the emulsions, not only those mentioned in my patent application S. N. 139,759, now U. S. Patent No. 2,226,639, but also sodium sulfite, salts of benzolsulfinic acid, also the sulfonic acids of triphenylmethane dyes or their bi-sulfite addition products. Salts or also alcohol may be added to the solution of sodium carbonate or they can be more concentrated in order to prevent diffusion as much as possible in the event of decomposition of the insoluble salts.

Suitable leuco-developers are principally the more stable leuco-compounds of my patent application S. N. 139,759, now U. S. Patent No. 2,226,639 of December 31, 1940, as substituted hydroquinones, reduced lignone dyes and higher molecular generators of the same, as also some vat dyes or stable leuco-forms of the latter and their carbomethoxy- and benzylcarbonic acid ester easily decomposed by sodium carbonate, ammonia or fixed alkali, or triphenylmethyl ester which can be split more easily with acid, as well as other easily decomposed acyl derivatives of the leuco-bodies.

Leuco-forms of indophenols, indamines and azo-methines where the dyes themselves are not entirely insoluble in water, such as thymol blue or the azomethine of aceto-acetic ester and NO-dimethylaniline, are not suitable. Also the simpler leuco-bodies can probably be used only in form of insoluble salts, but rather the arylated leuco bodies or those of carbazol indophenols or halogenated leuco-bodies. Of special insolubility are the bis-compounds and still higher molecular leuco-bodies as they can be prepared with the following higher or linked components and the previous polyvalent developers by oxidation and reduction, which also holds true for the azomethines and the azomethides insensitive to acids, similarly to the carbazol indophenols.

B. Reversal Development with Insoluble Color Developers

Complementary color negatives are obtained by the preceding method, and these result in correctly colored positives by printing under the same conditions. There are two ways to obtain these directly:

(1) The latent images are first developed with a neutral non-coupling developer, such as ferrous oxalate, as in the three-color reversal development of my Patent No. 2,226,639. Then the residual silver halide of all three layers or kinds of grain are made developable by pretreatment with thiourea, stannous salt, masking dyes etc. Conversion of the metallic silver into its ferrocyanide or its removal in order to make exposure possible is less advisable on account of the danger of oxidation of the developing leuco-compound. The final image dyes are then formed by color development in sodium carbonate solution.

This has the advantage that insoluble color developers of different rapidity can be used, because the primary development which determines the character of the part images was carried out in layers with the same developer. It is unnecessary to counteract fog formation by large amounts of potassium bromide or several percent of potassium iodide, as long as absolute exclusion of oxygen is guaranteed. If insoluble salts of high-molecular sulfonic or carboxylic acids of developers with quinine, etc., or phosphotungstate, etc. of basic developers are added

to the emulsions, it is of little importance, whether these salts are decomposed by sodium carbonate or slight diffusion takes place, because primary development and pre-treatment, together with several thorough washings have been survived by the color developers in the form of their insoluble salts. The unused color substance is washed out by alkali, sodium carbonate or ammonia without oxygen. If the leuco-bodies are present in form of insoluble calcium-, barium-, magnesium salts, hydroquinone with acetone sulfite can also be used for primary development, and calcium- or barium hydroxide for coupling.

Reduced azomethine from p-amino-dialkylaniline and palmityl acetic ester, or better -anilide or diacylanilide serves for the yellow, the pyrazolone obtained from this ester and nitrophenylhydrazine, or better the reduced lignone from two molecules of 2-phenyl-α-naphthol or the reduced hydroxynaphthoquinonimide from p-naphthoquinone-4-sulfonic acid and p-aminophenol, aniline etc. for the red, and the leuco-indophenol from α-naphthol-2-carboxylic acid naphthalene etc., for blue-green.

It is less advisable to develop with sodium carbonate immediately after exposure, and to destroy the primarily formed indophenol with acid, if necessary, in the presence of phosphotungstate or other precipitants, in order to prevent solution of the unchanged leuco-body, and to make the residual AgBr developable with thiourea etc., and then to develop the final image dye with sodium carbonate and to remove the silver. The primarily formed indophenol or indamine could also be converted into easily washed out addition products by combining sulfite, bisulfite, thiosulfate, arylsulfinic acid with hydroxy- or carboxylic groups, which is particularly easy with the carbazol indophenols, which are stable to acids and yield the most diverse colors. The residual AgBr is then made developable and developed with sodium carbonate, the silver removed and the addition products washed out with sodium carbonate or lye.

The middle emulsion can contain a leuco-derivative which is developed even with very weak alkali, so that a possible diffusion does no harm, if sodium carbonate or lye are used for the two other leuco-bodies, or vice versa, the two easily developed leuco-derivatives can be in the upper and lower emulsions, provided they are not dissolved by weak alkali. The middle emulsion needs no developer at all and is developed after completion of the two other images with a dissolved color developer.

C. Primary Development with Insoluble Components

Insoluble or non-diffusing coupling components can also be added to the emulsion; these yield the corresponding colors with the same developer.

Fischer and Siegrist have tried this method of primary three-color coupling, but they failed in the application of this invention (Phot. Korr. 1914/18–22; 208–211) because technically it cannot be carried out in the form indicated by Fischer and Siegrist for the production of color photographs with a triple layer or even a triple grain layer. The inventors made the mistake of believing it necessary that the components mixed in the layers had to be dissolved first by the alkali of the developing solution so that coupling could be accomplished (Ph. Korr. 1914/22, 211), which necessarily causes diffusion of the components from one layer to the other, even if gelatin layers are interposed, so that only washed-out three-color images can be obtained.

The inventor claims it as his merit to have recognized the fact that coupling is also possible in many cases with insoluble or non- or hardly diffusing components, even in the presence of sodium carbonate or still weaker alkalies. Most of the insoluble phenols, naphthols, arylsulfonylamines, etc., indicated later, are suitable, also in the form of insoluble lacquers, phenolates, complex salts, etc. Further, those sulfonic acids and carboxylic acids of these coupling components which as alkali salts possess sufficient affinity to gelatine, so that during decomposition of completely insoluble salts and of those not harming the sensitivity which are added to the emulsions may be used, and no diffusion of any importance is to be feared by the alkali developer.

It was further recognized that coupling with components having properties as mentioned before can also be brought about by the use of undeveloped silver halide which was made developable by pre-treatment with proper substances, as 0.02% solutions of thiourea, thiosinamine and analogous sulfur derivatives, or with a 0.001% solution of zinc chloride by means of arsenite, hypophosphite, thallo salt, masking dyes or other suitable agents which could be added to the developer; this is, however, not so favorable.

This primary three-color coupling can be used to advantage, if on one side of a thin film, the red-sensitive silver bromide emulsion is coated, on the other side a yellow-green-sensitive silver bromide, and above this a highly sensitized silver chloride gelatine emulsion. The silver chloride emulsion can be developed first with a simple yellow developer under conditions which do not affect the exposed silver bromide of the two other emulsions.

Primary three-color coupling can also be accomplished in such manner that the silver reduced by an ordinary non-coupling developer, as ferrous oxalate, is converted after fixing into silver ferrocyanide, silver bromide, or better, into the more strongly oxidizing silver chloride, by means of mercuric chloride.

D. Reversal Development with Insoluble Components

The Fischer process had the great disadvantage, not counting all other defects, that only complementary negatives were possible, which only by printing could be converted into the correctly-colored positive. A primary ordinary non-coupling development was not considered, because the components proposed in the patent, as aceto-acetic ester for the yellow image, p-nitrobenzyl cyanide for the red, and α-naphthol for the blue part image, are noticeably soluble in water, and therefore, do not survive, even without alkali, a general development with subsequent thorough washing, further removal or conversion of the reduced silver and repeated washing, without diffusing into the adjacent layers or grains.

The residual silver bromide can be reduced after removal or conversion of the primarily separated metallic silver, with an ordinary developer or a reducing agent and can then be converted into silver chloride, because this acts much more vigorously as an oxidizing agent after exposure or pre-treatment, or is more easily reduced, especially if mercuric chloride is used for the conversion. Coupling is then also successful with slowly acting components. If salts decom-

posed by sodium carbonate are added to the emulsions, ferrous oxalate, hydroquinone with acetone sulfite or other neutral developers serve for reduction of the residual silver bromide.

The reduced, highly dispersed silver possesses a rather strong absorption ability for dyes, and naturally, also the indophenols, indamines, azomethines, etc., which are combined, so-to-speak, in statu nascendi. If the dyes or their sulfonic or carboxylic acids are not entirely water-proof, it is sometimes advisable to convert them into insoluble salts even before removal of the silver previously reduced. This is especially true for indamines which are more strongly basic than indophenols, especially if a color developer with several dimethylamino groups or other basic residues is used, which results in especially insoluble phosphotungstates, etc.

The pre-treatment of the residual silver bromide with thiourea and similar agents mentioned on the preceding page for coupling with p-amino-dialkylanilines, p-amino-phenols, 1,2-dihydroxynaphthalene-4-sulfonic acid, -carboxylic acid, -thiosulfonic acid, etc., represents essential progress in comparison with the exposure method because this presupposes removal of the primarily reduced silver.

If the three latent images are first registered then the residual silver bromide made developable by prolonged exposure to ultraviolet rays or X-rays through the reduced silver, or by pretreatment with thiourea, etc., or exposure to white light after removal, or conversion of the metallic silver, the following methods are open for immediate production of correctly colored positives:

(1) Second development with an approximately 1% solution of p-aminodimethylaniline or analogues in a solution which is as little alkaline with sodium carbonate as practical; then the silver is removed with hyposulfite and potassium ferricyanide and the components washed out with ammonia, alkali or sodium carbonate.

(2) One could develop at once primarily with p-aminodimethylaniline or any other coupling developer, perhaps also p-aminophenols or oo'-dichlor-p-aminophenol, to an insoluble indophenol or indamine and destroy this, as under B2, by the action of acids, or convert it by means of sulfite etc. into addition products which are thoroughly washed out only later. Even if no splitting takes place, the acids are washed out with the same facility as in the basic dyes of the Uvachromy in those cases where stronger basic indamines are formed by coupling with p-aminodialkylanilines which are substituted by dimethylaminoguanido-, biguanido-, or also quaternary ammonia groups. The indophenol which is temporarily formed could also be reduced by thiosulfate, bisulfite or hydrosulfite which are partially without effect on the residual silver bromide. The leuco-forms produced are soluble in alkali and can be washed from the residual components after formation of the final image dye; then the procedure is as follows:

(*a*) The residual component is condensed in each layer to the corresponding image dye after exposure or pretreatment of the residual silver halide with p-aminodimethylaniline or another suitable coupling developer in the manner described at the beginning. The temporary dye or its split products are then thoroughly washed out with sodium carbonate or alkali in which the final indamine is insoluble. If this does not couple with diazo bodies, but the reduced original indamine or indophenol couples on account of its free hydroxyl group, diazonium compounds with many hydroxyl groups, also with carboxylic or sulfonic acid groups could be allowed to react on it in order to obtain better solubility in sodium carbonate.

(*b*) Diazonium salts can be allowed to react on the residual component, taking care in the choice of the components that azo dyes are formed which are correctly complementary colored as required by the theory, lemon-yellow, purple and green-blue. Indophenols, indamines or azomethines forming during primary coupling may show entirely different colors. Unfortunately, it is very difficult to find three colorless components of this type which yield the required dye with the same azo body. Pyrazolones usually couple with p-nitraniline to yellow and o-naphthol derivatives to red dyes; similarly also α-naphthols with 4-position occupied; but a blue azo dye can hardly be obtained with it. It is simpler with films coated on both sides, because one can allow another diazo compound to react on one side. The emulsions can also be coated in reverse order, so that the red-sensitive layer is on top, and the green-blue part image is produced in this layer by any surface process. Another method is available by adding a colored component to one or two emulsions, in the simplest case, azo- or triphenylmethane-, or anthraquinones dyes themselves which are capable of further coupling on account of hydroxyl and amino groups present. A yellow component can be added to the upper and also middle emulsion, a red component to the lower emulsion; the latter two should produce the final purple or green-blue image dye. In order to prevent coupling of the final lemon-yellow dye present in the upper emulsion, during the action of the diazonium solution, but allow coupling of the two other components, the o- and p-positions to the hydroxyl groups of phenol or naphthol can be substituted by halide or partially also by alkyls, so that only the formation of indophenol is possible with substitution of the halide, but not coupling to the diazo dye. If the emulsions contain amino compounds, these can be converted into derivatives of β-hydroxy-naphthoquinoneimides of mostly red to blue color by development with 1,2-dihydroxynaphthalene-4-sulfonic acid, 4-carboxylic acid or 4-thiosulfonic acid. The above-mentioned derivatives can be washed out by alkali. The amino dye remaining at the places of the residual silver halide can be diazotized and coupled after coupling the residual phenol or naphthol, present in one or both other layers, with p-nitraniline. In addition to the coupling components, one can add a stable and insoluble diazo body to the layers, or also the insoluble salt of an antidiazotate or of a stable diazonium compound, or an anhydride or its sulfonic acid, or carboxylic acid in form of insoluble salts. The two latter, however, are stable only to very weak alkalies and this must be taken into consideration in indophenol coupling of the component. The use of antidiazotates is safer, because they are entirely stable to alkali; they must be converted into the diazonium salt by acid before coupling of the residual component. The precautions indicated in my Patent No. 2,226,639 must be observed, since without them only poorly defined and unsuitable pictures are obtained. Components and diazotizable amines indicated in these patents can be used in the emulsion, as in the invention, but so that one does not depend upon the substantivity of the components and dyes

towards the gelatine, but mixes them in form of insoluble salts which are stable to the developer, with organic or inorganic bases. In films coated on both sides, it is sufficient to mix them with one emulsion, or in a normal triple layer with two emulsions, since after completion of the two first part images, the residual component of the third emulsion can be directly coupled with a dissolved diazonium compound. Ortho-aminobenzol sulfanilide which is insoluble in water, is also as stable as the antidiazotate. The former is split by dilute mineral acids and then couples to diazo dyes; with the aid of the arylsulfamino group it also couples with the developer to indophenols. Analogous in their behavior towards the primary developer are also those aminonaphthols and other phenols with one, also external, amino-group in which "intramolecular" coupling to a diazo dye takes place after diazotization, to which also diazo oxides and their sulfonic acids are capable on prolonged action of alkali. One could also allow nitroso-dimethylaniline, nitrosophenols, etc., to act on the residual component, but this is without special importance.

(*c*) If the residual component represents the generator of a dye formed by oxidation, it is oxidized to the final image dye and this especially holds true for the preliminary forms of lignone dyes and indigo dyes which develop much slower than they couple in sodium carbonate solution or with still weaker alkalies. The insoluble higher homologues of thio-indoxyl are less suitable. With the exception of some more stable ("thio-") indoxyls of the anthraquinone and benzanthrone series, sulfurlindoxyl and (thio-) pyrindoxyl are the principal generators of lignone dyes for this purpose, to which in certain respects belong also the arylmethyl-pyrazolones which change to pyrazolone blue during oxidation. Compounds which can be added to the lower emulsions are tetramethoxy-phenyl-α-naphthol, insoluble in water, or a higher pyrazolone, as phenylpalmitylpyrazolone, or higher analogues of 4-methoxy-naphthol which are easily prepared, or also 4-ethoxy-α-anthrol, etc. Compounds added to the middle layer are 2-phenyl-α-naphthol, also insoluble in water, or higher analogues of 2-methoxy-α-naphthol or α-anthrol which all yield, with p-aminodimethyl aniline, indophenol dyes that are washed out or destroyed in the primary development at the places of the latent image. The residual component is oxidized to the lignone dye by iron chloride, bichromate, persulfate, etc., in acid solution. The formation of the upper yellow part image in this manner presents difficulties. Yellow dyes with coupling hydroxyl groups or coupling groups attached could be added to the upper emulsion, as salicoyl-α-aminoanthraquinone, the salicoyl derivatives of yellow dyes, etc., as far as they are stable to the oxidizing agents used. If the upper emulsion contains silver chloride, the residual silver chloride can be converted to yellow mercaptide with thioanilide which acts only on this compound.

(3) For primary development of the latent image, a developer is used which, on account of the hydroxyl-, carboxylic acid- or sulfonic acid groups contained in its molecule is able to convert the added components, also with p-amino-arylsulfonylamines, as for example, p-amino-resoroin, p-aminophenol, or p-amino salicylic acid by coupling into indophenol or indamine dyes which are soluble in water or sodium carbonate, whereby the color of the products obtained is immaterial. These dyes are washed out of the residual component either directly or after formation of the final image dye, by bicarbonate, borax, sodium carbonate, ammonium carbonate, ammonia, alkali, etc. depending on the circumstances. This can be assisted by splitting of the indophenol by means of acid, or by formation of more easily soluble addition products, as described under (2). 1,2-dihydroxynaphthalene-4-sulfonic acid, -4-carbonic acid and -thiosulfonic acid deserve special mentioning, because they permit coupling to a soluble compound of insoluble components with amino groups, especially of amino dyes, by formation 2-oxy-α-naphthoquinoneimides soluble in alkali or sometimes even in sodium carbonate, especially, if also the other nucleus is substituted.

(*a*) Before or after removal of these (hydroxy)-indophenols, the residual components are converted, according to (2*a*), (*b*) and (*c*), into the final image dyes by repeated development with p-aminoalkylaniline, etc., coupling with diazo bodies or by oxidation.

(*b*) One could, of course, also proceed reversely with formation of complementary colored negatives by developing first generally with ferrous oxalate, etc., then coupling the components to soluble compounds at the places of the residual silver bromide and converting its residue, as mentioned, into the final image dye.

E. Reversal Development with Coupling (Leuco-) Dyes

Although indophenols, indamines and azomethines, which are obtained in the manner described before, are sufficiently light-proof, their instability to acid, with the exception of certain carbazolindophenols, is a great disadvantage.

It appears reasonable to add the final dyes or their leuco-derivatives to the emulsions, in as far as they contain a developer-coupling hydroxyl-, amino- or arylsulfonyl group in the nucleus or in one side chain, and to remove them in the first development of the latent images by methods of primary "coupling to a soluble compound." The residue of the dye derivative is converted into the final image dye by oxidation, reduction or hydrolysis, the coupling products or their parts are washed out then or earlier with sodium carbonate, lye, ammonia or weaker alkalies or also acids in the case of basic dyes, and the silver is finally removed with Farmer's solution.

Only in the upper layer is it possible to add the final coupling dye in the amount required for the formation of saturated images. They can be added to all three layers, only for printing purposes, because here one layer can be sensitized for infrared which easily penetrates the dyes of the other two layers. According to earlier statements of the applicant the coloring can be kept so light that the originals obtained appear sufficiently rich on white paper background, even if too weak for projection.

A great defect of Fischer's primary three-color coupler method was that the components showed very different coupling speeds (Ph. Korr. 1914/22), so that aceto-acetic ester, for example, yields very weak images in solution containing sodium carbonate. Of course, the reversal development automatically takes care of equalization, since the development of the residual silver halide can be extended to any desired length, especially, if the residual silver bromide has been converted into highly dispersed silver chloride in the manner mentioned before.

In order to obtain equal coupling speed in all

three emulsions, it was desirable to combine the (leuco-) dyes with the same coupling group. In view of the fact that simple acylated aminoanthraquinones represent excellent dyes, coupling algol dyes were preferred, since they are easily prepared. Instead of acylating with benzoylchloride, salicylic chloride, m-hydroxybenzoyl chloride, α-naphthol-2-carboxylic acid chloride, etc., are taken in order to obtain all colors of the spectrum with very simple amino- or amino-hydroxyanthraquinones. The salicoyl derivative of 1-aminoanthraquinone is greenish-yellow, its 4-methylamino- and 4-methoxy derivative are blue, its 5-methylamino- and 5-amino derivative purple or red; by condensation with 44'-dibromdiphenyl, one obtains green-blue to blue-green dyes. By linking of several molecules with the aid of acid chlorides mentioned later under IV B a still greater variety of color tones is possible; in cyanuric chloride the first two chlorine atoms can be converted with aminoanthraquinone or its alkyl derivatives and other substitution products, then the last chlorine atom with m-aminophenol or an amino-α-naphthol. The algols can be converted into the very stable anthrone form or its condensation product with formaldehyde, the so-called methylene anthrone, by suitable reducing agents in the known manner. The dye is finally regenerated from them by hydrogen peroxide containing sodium carbonate, persulfate, potassium ferricyanide, preferably, however, by acid oxidizing agents.

Generally colored substances, even if they cannot be used in textile dyeing, can be combined with coupling acid chlorides mentioned under syntheses IV, A and C and other coupling phenols, naphthols etc. with reacting halides, by means of their own amino- or hydroxy groups, for example, (leuco-) amino-malachite-green with salicoyl chloride etc. On the other hand, also chlorides of the carboxylic or sulfonic acids of the different (leuco-) dyes, also those of the anthraquinone group, can be combined with m-amino phenol, amino-α-naphthol etc., also dyes with a chloracetyl group etc. In order to obtain coupling products, the sulfonic chlorides are simply combined with aniline or α-naphthylamine, o- or p-aminophenol. The indamine formed during development, easily decomposes by hydrolysis in the presence of acids or alkalies to the sulfonic acid amide of the dye which is insoluble in water and acids, but mostly in sodium carbonate.

The final yellow image dye can be added to the upper layer, a yellow or colorless leuco-derivative to the middle layer, and even a red reduction product to the lower layer, if it is red-sensitive. Leuco-bodies can also be added to one or two layers, a reduced red azomethine to the middle layer and a leuco-indamine to the lower layer which develop the residual silver halide even on immersion into a solution of sodium carbonate and produce the dyes.

The dyes must not be too highly molecular, since the indophenols formed during coupling to a soluble compound with amino-resorcin, amino-salicyclic acid etc. are too difficult to dissolve in sodium carbonate, and strong alkali is not permitted.

These (leuco-) dye derivatives could also be coupled directly in the primary development with p-amino-dialkylaniline to insoluble indamine derivatives and the residual components removed by alkali, as under C, but this cannot be recommended, because only complementary color negatives are possible. It is still less advisable to reduce the indophenols and azomethines resulting from them and to add them to the layers, analogous to A and B. Generally speaking, only the working methods mentioned under (D1), (2) and (3) are of practical importance, while those described under (2*a*), (*b*), (*c*) and (*d*) must be changed accordingly in order to create the final complementary-colored image dyes in each layer.

Contrary to this is the method of "fixed coupling," analogous to the procedure of (D1). The latent image is first developed with ferrous oxalate or another neutral developer in the usual manner, then the residual silver bromide is reduced with a coupling developer. The indamine formed at these places is insoluble in lye, so that the (leuco-) dye derivative which is still unchanged can be easily washed from the other parts, whereafter the silver is removed with Farmer's solution.

If, in the two preceding cases, the (leuco-) dye-indophenol formed or its oxidation product shall not be left as such in the image, the indophenol group is split by acid, if necessary, in the presence of phosphotungstate or other precipitants for the basic indamine. The final image dye appears then to be combined only with a quinone- or hydroquinone group and the latter has practically no effect on the color, the former only moderately so. The quinone residue can also be reduced to the hydroquinone- or pyrocatechine group which are sufficiently stable, as can be seen from many natural dyes.

Coupling to a soluble compound could also serve for the purpose of removing the residue of the perhaps colored components after primary coupling development.

F. Combinations of the Procedures A–E Among Themselves and with Three-Color Development

Simple color developers can be used for one or two layers, that is, insoluble components are added to only two or one layers. Many variations are possible by combination with the numerous methods of execution described in my prior application, but only few seem to be of any importance. It is not easy to produce a brilliant lemon-yellow part image in the upper layer with acet- acetic derivatives, as is required by the theory of the three-color photography, since these derivatives couple quickly enough only in the presence of large amounts of alkali, they must also be present in large excess in order to yield pure pictures; it is, therefore, preferable to develop in a simple yellow developer. One can add insoluble or non-diffusing leuco-forms of yellow dyes to the upper layer, as they are formed from the high-molecular acid methylene compounds and p-nitroso-dimethylaniline or β-naphthoquinone-4-sulfonic acid described later, azothines and azomethides, and add components insoluble in sodium carbonate or coupling (leuco)-dyes for the purple and green-blue part image to the two other layers. After general development with ferrous oxalate, etc. and perhaps repeated exposure after removal or conversion of the primarily reduced silver, or pre-treatment of the residual silver bromide with thiourea, etc., color development is effected in the upper layer alone by immersion into a solution of sodium carbonate; then the components of the two other layers are coupled to the corresponding final or temporary dyes at the places of the residual silver bromide by development with p-aminodimethylaniline, etc., and the final image dye produced,

if necessary, with the quinone- or hydroquinone group attached. The residual silver halide of the upper layer can also be exposed alone, provided the yellow filter dye or yellow coloring of the upper layer is still intact, and it is developed with a dissolved yellow developer, as those given in the main patent, for example, o-amino-symmetrical m-xylenol. All previously reduced silver is then removed or converted into ferrocyanide and the residual silver bromide of the two other layers exposed or made directly developable with thiourea, and the part color images developed with a coupling developer, finally all metallic silver removed at once with Farmer's solution.

Coupling components can very easily be added to two emulsions, preferably to the upper and lower emulsions, which even in the presence of borax or bicarbonate yield dyes with p-aminodimethylaniline, while the last color image is formed in the third silver bromide emulsion with a dissolved direct-developer. Such a component can be present only in one, for example, the middle layer which can consist of silver chloride. This is developed first, then the two others are developed with sodium carbonate by self-development. One of the layers is preferably on the other side of the film or consists of silver chloride in order to permit individual development.

An insoluble α-naphthol derivative can be in the lower layer, and a yellow component which is not entirely water-proof, in the upper layer, while the middle layer contains no component. After general ordinary development, the residual silver halide of the upper layer alone is developed with p-aminodimethylaniline causing coupling to the yellow image dye, then the green-blue part image formed in the lower layer and finally the middle layer treated with a dissolved purple developer. The silver is then removed with thiosulfate and potassium ferricyanide.

If components are in the upper and lower layers only, but not in the middle layer, and this middle layer which can also consist of silver chloride, is developed directly after general development with a simple self-developer, a slight diffusion of the not entirely water-proof or soda-stable components is of little harm, since they are separated by the middle layer, together with the adjacent intermediate layers. A compound developer can also be used last, if the unused components are previously thoroughly washed out.

It is important to omit exposure of the residual silver halide of the middle layer, since this presupposes removal or conversion of all previously-reduced silver, if the use of thiourea is not desirable. In a triple layer with a component only in the middle emulsion, this is attained very simply in reversal development by coupling to a soluble compound this perhaps yellow-colored middle component or a coupling purple or green-blue (leuco-) dye during the first general development by means of amino-resorcin, amino-salicylic acid, etc. If insoluble developing leuco-compounds have been mixed to the two other layers, one cannot, usually, use sodium carbonate, but has to use weaker alkalies as bicarbonate, borax, disodium phosphate, etc., since otherwise primary color development takes place. This indophenol image could, of course, be destroyed by acid or converted in the manner described into washable addition products. The formation of the final image dye in the upper and lower layer is done only at this stage by immersion in a solution of sodium carbonate, followed by coupling of the residual component of the middle layer to a red azo dye through the action of a diazonium salt solution.

When using dissolved simple color developers for the upper and lower layers, the procedure is analogous. The middle component is coupled to a soluble compound in the first general development by amino-resorcin or amino salicylic acid, etc., or coupled with aminodimethylaniline and the indamine formed is destroyed by acid or converted into washable addition products. The upper and lower emulsions are then exposed one after the other and developed to the corresponding part color image, best with simple yellow and green-blue or purple developers. The residual component of the middle layer is then converted into the final dye of the last part image by coupling with a diazonium compound, perhaps also before the colored development of the two other layers. If the middle layer contains silver chloride, one could, after coupling to a soluble compound in first development, reduce the residual unexposed silver chloride alone by prolonged treatment with quinone sulfonic acid and sulfite, or with dilute hydroquinone or the developers indicated in my prior patent application. By this a black separating wall is formed in the middle layer, so that independent exposure of the upper and lower layers appears to be guaranteed, when the filter dyes have been destroyed or discolored, and also the sensitizing power is lost. The same effect is possible, if an insoluble vigorous ordinary developer is included in the middle layer which is able to reduce the residual silver bromide of the middle layer also without exposure.

With reverse order of the layers, one can add an insoluble α-naphthol derivative to the middle red-sensitized layer, and after coupling to a soluble compound and general development and drying superficially develop the residual silver bromide of the upper yellow-green-sensitive layer with seleno-indoxyl, then convert the residual component of the middle layer into the green-blue indophenol by means of nitrosodimethylaniline, and finally, after exposure through the back to blue light which cannot penetrate the yellow filter between middle and blue-sensitive layer, the residual silver bromide of the lower layer is reduced by a simple yellow developer, the silver removed and washed out.

The formation of the middle part image by coupling to a soluble compound is of importance in combination with the methods of controlled diffusion, as the preceding example shows forming only the upper part image through superficial diffusion, then directly or after removal of all silver which has been previously reduced, the lower part image. The triple normal distance between the upper and lower emulsions can, so to speak, be created, if the residual silver bromide of the middle layer is developed with an included insoluble developer or an ordinary dissolved developer, after or without exposure or pre-treatment of all three layers. Thorough washing out of the two residual components is presumed.

An insoluble leuco-indophenol or -azomethine for the green-blue or purple part image can be added to the middle layer. After general neutral development, the upper layer alone is exposed to blue light and developed with a yellow developer without sodium carbonate, which is especially easily possible with residual silver chloride, then the two other layers developed to the middle part image by sodium carbonate solution after pre-

treatment with thiourea etc. or the lower layer is developed with a simple or compound color developer containing sodium carbonate. The upper part image could be produced also by controlled diffusion or in any other manner, before or after completion of the other images.

The middle emulsion can contain an insoluble color developer, the other two components. The middle image is first produced in the presence of sodium carbonate, then a solution of p-aminodimethylaniline containing sodium carbonate is allowed to act on the two other layers, whereby a slight diffusion of the components which perhaps are liberated only at this stage from their insoluble salts, is insignificant. On the other hand, an insoluble component can be contained in the middle layer and the two other layers contain insoluble color developers which develop on addition of sodium carbonate, after which p-aminodimethylaniline is allowed to react on the middle layer. The middle layer may also contain no additions at all and, at the end, is developed in color with a simple or compound direct color developer. All this is principally intended for the reversal process, less for primary coupling. Coupling dye derivatives described under E of the easily prepared leuco-indophenols and leuco-azomethines could, of course, also be used as added insoluble color developers.

The final (leuco) dyes capable of coupling can be added to the middle and upper layer, and the residual silver bromide only of the lower layer reduced to blue-green or purple with a simple color developer, either after exposure through the back to red light, if it is still sufficiently sensitive for this, or to blue light, if red or yellow filters are between this and the middle layer.

In re-development, the middle layer can contain an insoluble α-naphthol derivative or other phenol which produces an insoluble green-blue image even in the first development with p-amino-dimethylaniline, etc. This is then fixed and rehalogenated and the two other layers developed in color and finally the silver removed and washed out. One can also develop in the usual manner and convert the primarily reduced silver into silver ferrocyanide, then expose the residual silver halide and develop with p-aminodimethylaniline, whereby an indamine is formed only in the middle layer which is destroyed by acid. One can also develop with amino-resorcin, p-amino-phenol or p-aminosalicylic acid and wash the indophenol out at the proper time. The silver ferrocyanide is then converted into silver chloride, the upper and lower layers exposed in succession and developed individually in color, preferably with simple color developers. The residual α-naphthol derivative of the middle layer is coupled before or after this to the corresponding dye with a diazonium compound and the silver removed. The same procedure is used in controlled diffusion. The regenerated AgCl or AgBr is made developable by exposure or pre-treatment with thiourea, etc., and the upper layer first developed by superficial action of a preferably simple yellower developer, then the lower layer, and finally, the residual α-naphthol derivative of the middle layer converted into the purple azo dye. The silver ferrocyanide itself could also be developed in color.

In primary development with insoluble leuco-developers in the middle or lower layer, an upper AgCl layer is first developed with a simple color developer alone, then the layer containing the leuco-developer is developed with sodium carbonate solution, and finally, the latent image of the last layer with an ordinary color developer.

If the upper or middle layer or kind of grain consists of silver chloride without coupling component, an individual color development can take place. The development of the yellow image can be accomplished with o-amino-symmetrical-m-xylenol and borax, or about 0.1% sodium carbonate for a long time; then follows color coupling of the components contained in the two other layers with a solution of p-aminodimethylaniline containing sodium carbonate, by primary, reversal or redevelopment, perhaps after preliminary conversion of the residual silver chloride into silver bromide or silver ferrocyanide, or KBr or potassium ferrocyanide is added to the new developer. If the upper AgCl layer contains a coupling yellow dye, the residual silver chloride can be converted into silver ferrocyanide after coupling the yellow dye to a soluble compound in the first development. All silver and silver chloride can also be simultaneously converted by a mixture of potassium ferri- and ferro-cyanide, after which the components in the two other layers are coupled to the corresponding image dyes by development with p-aminodimethylaniline in a weak solution of sodium carbonate. If the upper silver chloride layer contains the leuco-form of a yellow azomethine, etc., the yellow positive image is produced after first development with ferrous oxalate by bathing in the solution of an alkali which is preferably weaker than sodium carbonate, then the residual silver bromide of the two other layers is developed in color with direct color developers or by coupling with components added to these two layers.

Silver chloride in the middle layer with nitrophenylmethylpyrazolone added is developed to the red part image with p-aminodimethylaniline even in the presence of bicarbonate; with phenyl-J-acid and a small amount of sodium carbonate the blue-green part image is formed. These weak alkalies are also sufficient for the formation of red to blue hydroxynaphthoquinoneimides when using 1,2-dihydroxynaphthalene-4-sulfonic acid.

A blue-sensitive AgCl layer can be situated at the bottom, above it a green-sensitive AgBr layer with an insoluble α-naphthol derivative which is superficially sensitized also for red by pinacyanol. After general development the AgCl alone is first developed in color, then by superficial diffusion of indoxyl, the AgBr.

G. Combinations with Conversion-, Mordanting- and Subface Processes

The original silver chloride of the upper or also middle layer produced from individually reduced silver perhaps with lead ferrocyanide, can be converted into colored ferrocyanides, complex compounds, mercaptides, mordanting bodies, precipitants oxidizing agents and tanning substances, etc., and the corresponding part color image be developed in the manner described there. Some of these processes are useful also for a triple layer or a two-zone or two-grain double-layer, if they are changed accordingly. If the upper part image is to be produce by pinatype, reverse order of the layers is advised, the blue-sensitive emulsion at the bottom. To a certain extent highly dispersed AgBr like silver chloride can be converted with thiophenols and anti diazotates can be used for the upper layer after ultra- or high sensitization by suitable dyes, if very high aperture lenses are available. In this case it is best to allow the converting solution to penetrate only

superficially, so that the coarser grained AgBr of the middle layer is not also affected. Similarly, the highly dispersed metallic silver of the upper layer can be converted individually into AgBr or AgCl by short time superficial penetration of a solution of potassium ferricyanide and KBr or NaCl. This can then be developed in color or the silver chloride or ferrocyanide be converted as just mentioned into the yellow upper image.

If the silver chloride or ferrocyanide is converted with antidiazotates, the solution of a component can be used for azo coupling, or it is in the emulsion in an insoluble state. Since sulfonic acids and carboxylic acids do not attach themselves so firmly to gelatine, their insoluble salts with organic or inorganic bases, as cinchonine, diphenyl-, and triphenylguanidine, etc., are added to the emulsion. The silver antidiazotate is then converted into the diazonium salt by acid, observing precautions in order to prevent diffusion of the diazonium salt. The coupling is then dissolved out by sodium corbonate, perhaps with decomposition of the insoluble salt of the component sulfonic acid. The silver chloride or silver ferrocyanide could, of course, be converted into mordanting substances for diazonium salts and this allowed to react with the added component observing the same precautions. Be it observed that obviously according to the invention, isomerization to the diazonium compound and coupling to the azo dye can be carried out in all three layers, in order to obtain sharp images. According to the invention, also insoluble, nonsulfonated phenols and naphthols, amines and acid methylene compounds, especially, higher molecular ones are suitable.

Reduced silver or silver ferrocyanide containing AgCl which is present at the image, yields colored ferrocyanides by the action of HCl with insoluble carbonates, phosphates, etc., of certain metals contained in the layers. Since vanadyl- and uranyl-ferrocyanide are unsuited on account of their strong tanning action, titanium ferrocyanide is used, according to the invention, for yellow or also lead- and zinc yellow obtained with chrome yellow from lead- and ferrocyanide, nickel-dimethylglyoxime formed from nickel ferrocyanide is used for red. The residuel silver chloride of the upper layer can be converted to the yellow mercaptide with thionalide. The middle layer can contain a coupling component for blue-green, the lower layer an insoluble nickel salt, the upper layer titanium carbonate or vanadyl phosphate, which yield the corresponding dyes in the manner described, while blue-green results with p-aminodimethylaniline.

All the processes described here, serve, according to the invention, primarily for the production of reversal images of the residual silver bromide.

Insoluble and Non-Diffusing Coupling Components

In order to make the methods of three-color photography described in the preceding pages technically practical, so that really approximately true-colored images are obtained, it is necessary that the dyes formed are, first of all, entirely water-insoluble, and that they do not diffuse into each other during the washing out of the developer. It is, for example, entirely wrong to choose aceto-acetic ester as yellow component, as proposed in many patents, because the yellow azomethine dye formed bleeds even in several hours immersion in water on account of its small molecule. More suitable are esters with higher aliphatic alcohols or phenols, as well as the aceto-acetic anilide and especially its higher arylides, also heterocyclic ones with dihydrothiotoluidine, or arylides with one hydroxyl- or amino group which can be alkylated with ceryl bromide or esterified with cerotinic acid chloride; also mono-acetic acid benzidide. Especially considered are also the higher aliphatic homologues, as undecyl- and palmityl acetic ester and their arylides. The repeated introduction of the coupling function also yields better results, as is proven by the di-aceto-acetic anilide and terephthaloyldiacetic acid anilide, even if the color obtained with the latter is unsuitable.

The blue image expected from phenol and p-amino-dimethylaniline does not appear, because the dye is too soluble, and also the thymolblue is washed out of the layer overnight by pure water. Ortho-hydroxydiphenyl is better, and 1:5-dihydroxynaphthaline which yields on development with p-amino-dimethylaniline blue or dark-blue bis-indamines which are almost entirely insoluble in water. The same holds true for palmityl-phenyl-pyrazolone.

It is seen from these examples that by enlarging of the molecule of the component or repeated introduction of the coupling group the insolubility of the dye resulting from coupling is considerably increased. One is not dependent on double or triple combinations of the same kind, but can also have entirely heterogeneous functions in the molecule: the α-naphthol or phenol group yielding blue indamines, the pyrazolone group yielding red azomethines, or the 1:3-ketonic acid group and the 1:3-diketones shifting towards yellow. A mere enlarging of the molecule with indifferent residues decreases the yield of the dye. It is therefore more advisable in the synthesis to use more than one of the same or different coupling groups several times in the new molecule.

A further requirement is that no diffusion of the components take place, either during superimposed coating of the three emulsions, or through action of the coupling developer. The most favored three components proposed in the patents mentioned: α-naphthol for the blue-image, aceto-acetic ester for the yellow image and p-nitrobenzyloylanide for the red image, can in no respect be considered as insoluble in water. The latter, as well as most acid methylene compounds and the dibrom- or trichlor-α-naphthol often mentioned are soluble even in sodium carbonate and still weaker alkalies. Since no coupling takes place at all in the developer without alkaline reacting substances, or only very slowly, the inventors of those patents could not attain their goal.

These inconveniences are especially disturbing in reversal development which forms the most important part of the invention, because it allows the making directly of correctly-colored positives. Even if the slower working ferrous oxalate, hydroquinone-acetone sulfite or any other neutral developer can be used for the first development of the latent image, and the residual silver halide be made developable with thiosimanine, etc., without preliminary removal of the reduced silver, and neither repeated thorough washing nor the use of alkaline reacting substances in the coupling developer can be omitted.

There was even the general opinion until now

that coupling takes place only with the dissolved components, as undoubtedly can be seen from the fundamental work of Fischer and Siegrist (Ph. Korr. 1914/22, 211). I have now found that coupling also takes place with components which are entirely, or at least practically, so insoluble in water that they do not diffuse into the adjacent layers to any appreciable extent (for example; tri-α-naphthol-triazine, α-naphthol-2-carboxylic acid-naphthalide, α-naphthol-4-benzoyl ketone, or its hydrazine compound, but especially the high-molecular coupling components or their insoluble salts which are easily obtained by linking methods which will be discussed in detail later), even if the developer is prepared with sodium carbonate or still weaker alkalies (borax, bicarbonate, ammonium carbonate, sodium glycocoll, etc.), also with fixed alkalies, if the coupling component is insoluble in it, as the so-called cryptophenols.

Some of the azo-components in the insoluble state, are able to couple under vigorous conditions to azo dyes, yet this was uncertain in regard to the formation of indamines or azomethine dyes, and even less certain, whether the exposed silver bromide or that made developable by thiourea, etc., would be able to perform such condensations by oxidation.

A certain improvement in the methods of coupling development is attained even if a practically insoluble component is introduced into the middle layer, while the two other layers contain difficultly diffusing components. During the development, the unused yellow component will diffuse, while the lower component only begins to diffuse, while the upper and middle image is developed for the greatest part. Diffusion can be made very slow, if salts (sodium chloride, sodium sulfate, sodium carbonate, etc.) are added to the developer or the triple layer is previously allowed to absorb those salts, less practical with pure water, and only then immersed into the alkali-free developing solution. This salting out is generally applicable and of special importance in the reversal coupling in the sense of this invention, where these salts can also be added to the solutions serving for the removal or conversion of the silver and for pre-treatment of the residual silver bromide, if lower molecular components are not entirely water- and soda-insoluble or form inslouble salts with it which are very difficultly soluble, but not entirely insoluble, as for example, aceto-acetic acid-diphenylamide, diphenyl-pyrazolone, etc.

In especially high-molecular coupling components or those which are combined with colloids, the developer can also be prepared with ammonia, aliphatic amines and diamines, polyethylenepolyamines or their quaternary ammonia compounds, guanidine or fixed alkali, because the salts formed by it show usually also high-colloidal character, and possess no special tendency to diffuse, especially, if salts are added to the developer.

To the insoluble, e. g. non- or only difficultly diffusing components, are to be compared their similarly obtained salts, themselves easily or not too easily soluble, e. g. diffusing components. Until now it was unknown that these salts are able to couple with p-aminodimethylaniline during development. The salt does not have to be absolutely insoluble, it is sufficient that it does not diffuse too much. This is determined not only by the molecular structure of the component, but also of the precipitant, because also simpler soluble components form salts of very little diffusing power with high-colloidal precipitants (as polyethylene polyamines just mentioned or their quaternary ammonium salts), whereas with high-molecular components even simpler ones are sufficient, as diphenylguanidine, thioflavine T, etc. To most complete precipitations are usually obtained, if both, components and precipitants are of high-molecular structure. The use of salts is sometimes of advantage here also. Precipitation of the insoluble salt can also take place outside of the silver bromide collodion emulsion, so that with later introduction into the emulsion a possible substantivity of the component to the emulsifying agent is of little importance and is rather to be considered as a disadvantage on account of the difficulty of washing the same.

Components containing a carboxylic acid group (1:5-dihydroxynaphthalene-dicarboxylic acid) or sulfonic acid group, have an individual position, since especially the latter often causes a rather strong substantivity to gelatine which was recognized, when the less suitable "naphthol-sulfonic acid" was suggested for this purpose. Although the finished dye is held more tenaciously by gelatine than the unused component, it is very difficult to wash the latter out completely; if it is stable enough to light, it may be left in the image, at least in motion picture films. Nevertheless, according to the present invention, high-molecular sulfonic- and carboxylic acids of components as completely or approximately insoluble or non-diffusing salts is recommended. Carbonyl-J-acid and p-amino-benzoyl-J-acid, for example, as α-naphthol sulfonic acids, yield dark-green images in development with p-amino-dimethylaniline (the latter, however, not very easily), which are somewhat, but not completely stable to washing and dilute solution of sodium carbonate.

Aromatic hydroxyls and the acid methylene group do not cause a sufficient affinity to gelatine on account of their extremely weak acid character, as can be seen from the relatively easily washed rosolic acid dyes, as well as from the non-sulfonated phenol- and α-naphthol azo dyes, although the latter are derived from one-sided diazotized benzidine or 4-hydroxy-4'-aminodiphenyl or analogous substitution products of diarylureas, diphenyleneoxide, diphenylether, diphenylmethane, stilbene, diphenylamine, carbazol, etc. Dihalogenation in the oo'- or opposition increases the acid character, nevertheless, erythrosine and eosine, as well as the still higher molecular brominated naphthofluoresceine and resorcin-anthraquinone belong to the easily washed out dyes. Halogenation brings about a certain affinity to gelatine only in very high-molecular coupling components. It is true for the acid methylene group in aliphatic, isocyclic and heterocyclic systems, whose affinity to gelatine is increased by introduction of bromine into the methylene group, or also of nitro-groups into the nucleus.

The determining influence of the sulfonic acid group for the affinity is very well demonstrated by thiazol bases, where basic thioflavine T is very easily washed from gelatine, its sulfonic acid, however, is tenaciously held by it. Affinity to gelatine is present even when the sulfonic acid group is in the side-chain. Ethylene oxide can be allowed to act on the amino- or hydroxyl group and this esterified with chlorsulfonic acid.

Substantivity is, however, a very extensible

concept, because even the typically highly-colloidal azo dyes diffuse in spite of their sulfonic acid groups and this disadvantage is so disturbing that measures must be taken to counteract it. It is no wonder, therefore, that the sulfonic acids of high-molecular azo components are by no means stable to the developers containing sodium carbonate; many of them can, however, be added to the emulsions in form of their insoluble salts with quinine, cinchonine, diphenylguanidine, polyethylenepolyamines and similar organic bases, in so far as they derive from α-naphthol. It could not be foreseen that they are coupled to indophenols and azomethines in development with very weakly alkaline p-aminodimethylaniline.

If the well-elaborated methods of synthetic preparation for the formation of high-molecular substantive cotton dyes with sulfonic acid- or carboxylic acid groups are used, this signifies by no means that the non-sulfonated coupling intermediate products obtained possess any practically sufficient substantivity for gelatine, but the diffusion ability is determined simply by the enlargement of the molecule and the highly-colloidal character obtained by it, and this space-filling within the pores of the gelatine is much more pronounced in the salts with higher-molecular bases.

It was found that in the α-naphthol and its 2- and 3-substitution products, also in ketones, a halide-, sulfonic acid- or carboxylic acid group in the 4-position is replaced, so that completely insoluble indophenols and indamines result. If the 4-position of the α-naphthol or the p-position of phenol is occupied by non-splitting residues, as alkyl, aryl, acoyl, carboxylic acid arylide, acylamine, etc., coupling takes place in the 2-position, whereby a 2-halide-, sulfonic acid or carboxylic acid group in that place is also split off The 4-derivatives of α-naphthol mentioned, also the tri-α-naphthol-triazine, couple with p-aminodimethylaniline during development of the latent image and in the presence of sodium carbonate to blue-green indamines, while eugenol and di-isoeugenol yield black o-indamines with it. The ortho-coupling leads exactly as in the azo-pure coupling to more insoluble dyes.

In rarer cases, o-coupling takes place also in the development with o-aminodialkylanilines.

By splitting of acid radicals in the 4-position it is possible to obtain completely insoluble indophenols from coupling components which color the gelatine substantively. These indophenols do not bleed, if the residual components are removed as much as possible by vigorous washing with solutions containing sodium carbonate or alkali. The affinity to gelatine could be entirely removed by NO-phenol or NO-resorcin with splitting of the sulfonic acid group making the residual component more easily washed out.

Since sulfonic acids are often of greater stability than naphthols, they can, under certain circumstances, be left in the image. Also halogenated phenols are more stable to oxidizing agents, so that it is advisable to add them to the layers as coupling components, if necessary, in form of insoluble phenolates. The same holds true, if the carboxylic acid-, or sulfonic chloride of a phenol is combined with (leuco)-dyes in order to make them coupling.

Similar to the phenols or rather their dihalide derivatives soluble in sodium carbonate and to acid methylene compounds are the aryl-sulfonyl-arylamines which are formed just as easy as phenols in the development with p-aminodimethylaniline, etc. If 4-sulfonic chloride of α-naphthol is combined with aromatic amines, the product obtained contains two coupling functions: the hydroxyl group and the arylsulfonylamino group, so that more insoluble bis-indamines are formed in development. Several molecules of an aromatic amine can be linked to high-molecular, non-diffusing structures by using aliphatic long-chain or aromatic di- and tri-sulfonic chlorides. One must, however, take care that the o- or p-positions are still available by being free or containing splitting halide-, sulfonic acid or carboxylic acid groups. By applying the methods given in the synthetic part of this description, under IV and V high-molecular products can be obtained, that the sodium carbonate-solubility present in the lower homologues is lost, or that they are not even soluble in lye and in this respect approach the "cryptophenols" as the still relatively simply constructed dodecamethylenediamine show. Ca, Ba, Mg, Pb and Zn salts are often insoluble in water. In order to avoid splitting of these salts by the developer, quicklime or caustic baryta is added to the developer instead of sodium carbonate or lye. Insoluble salts are also obtained with higher molecular aromatic and heterocyclic bases, alkaloids, guanidines, dyes and other precipitants, as is common with aromatic sulfonic acids. Most of them are stable to a developer containing sodium carbonate, but coupling takes place just the same. The solubility in alkalies can be removed by alkylation.

The aromatic amines couple much more difficulty in development with p-aminodimethylaniline than phenols and naphthols, more easily coupled are the polyvalent amines, as m-toluylenediamine which yields a blue, but not water-insoluble image, the higher molecular amines, as tetraminodiphenyloctane, or oo'-tetramethyldiamino-benzidine, dithio-m-toluylenediamine. The components can be added to the emulsions as insoluble phosphotungstates which are decomposed by a developer containing sodium carbonate; in the presence of salts, however, no great tendency for diffusion is present. The aromatic and heterocyclic amines, also (leuco-) dyes with a free amino group couple during development with 1:2-dihydroxy-naphthalene-4-sulfonic acid, -4-carboxylic acid, -4-thiosulfonic acid, also with 3-chlor-derivatives in very weak alkaline solution, into from red to blue hydroxynaphthoquinoneimides.

In order to protect the sensitivity of the emulsion, it is usually not sufficient to add difficultly- or non-diffusing components, but they must be added in form of completely insoluble salts which can withstand the preparatory operations of the reversal development. In the subsequent development of the residual silver halide, splitting of the salt by the sodium carbonate or other alkali in the developer can take place to facilitate coupling, without fearing appreciable diffusion into the adjacent layers with high-molecular components, especially in the presence of salts, as which are also considered alcohol, acetone, etc., which, as a rule, do not possess solvent power for alkali salts of sulfonic- or carboxylic acids. Also an addition of precipitants to the developer is sometimes advisable, and also the intermediate layers can contain them which, as for example, di- and tri-phenylguanidine, form sodium carbonate-stable salts with sulfonic or carboxylic acids of higher molecular components, while the salts with quinine, cinchonine and many other organic

bases added to the emulsions are split by sodium carbonate.

Although the indophenols and indamines formed by coupling with the sulfonic- or carboxylic acids of components show a strong substantivity to gelatine, it is advisable to convert them before the removal of the silver by suitable precipitants into completely insoluble, preferably also sodium carbonate-stable salts. In the presence of lacquer- or complex-forming groups, they are converted into insoluble lacquers or complex salts; a possible color change must be avoided by the proper choice of the components or metal salts. The formation of internal insoluble salts is desirable, and instead of p-amino-dimethylaniline, it is better to use its dimethylamino derivative as developer for this purpose. It is, of course, still more advantageous to choose substantive components with splitting sulfonic- or carboxylic acid groups in the manner described before.

Among the phenols or naphthols such high-molecular or substituted or linked representatives must be chosen which yield in the perhaps necessary alkaline development similar to cryptophenols, salts which do not or only very difficultly dissolve or diffuse. Or their insoluble salts are added to the emulsions with those organic or inorganic bases which are decomposed only by the sodium carbonate of the coupling developer, so that free phenol is present only for a short time. If insoluble Ca or Ba-phenolates or naphtholates are added to the emulsions, their decomposition during coupling development is prevented by using calcium oxide or caustic baryta instead of sodium carbonate and by conducting the second development without carbon dioxide and air. It is pointed out that naphthols yield insoluble phenolates not only with inorganic bases, but also with organic, especially higher-molecular bases. Coupling components which are not entirely insoluble with complex-forming groups, as for example, o-hydroxy-acetophenone, the oximes of α-naphtholaldehyde, salicylic aldehyde, vanilline, o-hydroxy-acetophenone, o-hydroxy-quinoline, biguanido-α-naphthol, etc., can be added to the layers in the form of their insoluble complex salts, which have been perhaps prepared from the finished dye.

Basic coupling components are added to the emulsions as phosphotungstates etc. or as insoluble salts with higher-molecular organic acids. Before removal of the silver, the indamine dye which is often absorbed to it, can be made insoluble by these precipitants.

High-molecular coupling components, especially those which are combined with high polymers, (see V) can often not be washed out, not even with dilute alcoholic lyes which are usually sufficient for cryptophenols, so that they must be left in the image, unless they are unsuited on account of their color or instability in air. The removal of unused washable components is best accomplished without air. Complete washing of the first developer is often unnecessary.

The triple layer with insoluble components can also serve for the procedure of the main patent by developing each part image not with a color developer, but with a coupling developer.

In the choice of the components, one should consider that subsequent corrections of the individual part images are possible. One can add components of very different coupling speed, even those which couple with borax, others which couple only with sodium carbonate, so that each layer can be treated individually, especially, if developers of different developing speeds are used.

The insoluble components or their salts are added to the layers in a quanity of about 3 to 20 grams per liter of AgBr gelatine emulsion. The developers are used in ½ to 2% solutions with about 5% sodium carbonate or the equivalent amount of weaker alkalies. The insoluble components are, if necessary, most finely dispersed in a 10% gelatine solution with the aid of a colloid mill and this emulsion added to the silver halide colloid emulsion.

It is advisable to deposit the insoluble or non-diffusing components on the silver bromide grain or to let them be absorbed. One should produce insoluble naphtholates or insoluble salts of acid methylene compounds or sulfonic or carboxylic acids of the components within the emulsion, preferably done after ripening, so that no decomposition of the salts occurs, and because the absorption is of special importance with fewer, dispersed silver halide grains, on account of the larger inter spaces. Precipitation can be accomplished in gelatine-poor emulsions and the necessary amount of gelatine added only later, or centrifuged silver bromide or that which has been separated from gelatine emulsion after dispersion in water, glycerine, etc., can be used for this purpose; later, this can be finely divided in gelatine solution, washed out and replaced with the corresponding amount of sensitizer. Completely insoluble higher-molecular phenols, naphthols, pyrazolones, etc. are dissolved in the necessary amount of alcoholic lye, this added to the silver halide gelatine emulsion of normal or considerably less than normal gelatine content and then precipitated by the calculated amount of acid, brought to the correct gelatine content, finely broken up and washed out.

The components do not absolutely have to be added to the lightsensitive emulsions, but may also be contained in a pure gelatine layer situated above or below the corresponding silver halide layer. The reversal process is best suited for this purpose, since the residual silver bromide is in direct contact with the gelatine layer containing the corresponding coupling component which would be below in this case. Below the blue-sensitive layer, a layer with the yellow component is arranged, below the yellow-green-sensitive emulsion, a gelatine layer with the purple component, and below the red-sensitive emulsion, a colloid layer with the green-blue component. As indicated under B, also the developing leuco-forms of the corresponding finished dyes could be added instead of the components. One can add even the correct final dyes, if they are combined, according to E, with a coupling group; below the blue-sensitive layer, a gelatine layer containing salicoyl-α-aminoanthraquinone is arranged; below the yellow-green-sensitive emulsion, a layer with its 5-methylamino derivatives; below the red-sensitive emulsion, a layer with its 4-methoxyl derivative. These finished image dyes serve at the same time as light-filters. Of course, only less sharp and weaker multiple color photographs of the character of ozotypes are obtained.

As material for the execution of the present procedure, not only the triple-layers, two-zone and two-grain double-layers of my prior application may be considered, but for printing also a three-grain layer: one grain for green, another for orange and the last for infrared sensitivity or any other variations. Printing is done with-

out blue light, not only under black images, but also through multiple color images whose colors do not correspond entirely to those of nature, but have been chosen with regard to the types of light necessary for printing. In addition to the substances of my prior application used as filter dyes for the triple layer, also the yellow dienol of acetonedioxalic ester is considered, as red filter formacyls and homophthalimide derivatives, which are all discolored at once by acid, and also the easily oxidized carmine red. The added sensitizers or the part which is not absorbed by silver halide, are converted into insoluble or at least non-diffusing salts by acid or basic precipitants, as described in my prior application; excess precipitant may remain is the layers. Properly chosen indifferent components or precipitants can also serve at the same time as precipitants for the sensitizers. The same holds true also for the filter dyes.

All variants described before can also be used with one or two layers or kinds of grains. Especially numerous are the possiblities with films coated on both sides which can be so thin that during development a paper is used as support which is permeable to the developer. Also viscose film impregnated with highly-sensitized silver halide can be used coated with silver halide gelatine or collodion emulsions and moderately tanned on both sides.

The sound record can be arranged according to methods of my prior application, preferably in the layer nearest to the supoprt, in order to protect it from damage. It is best to cover the border of the film at first, and before or after completion of the three-color image print the sound record on one, two or all three layers, also as primary or reversed silver image.

In the following, under I, II and III, the known or easily prepared monovalent- and polyvalent compounds which are more or less suitable for coupling purposes, are given. Part IV is concerned with the synthetic preparation of high-molecular components by linking of simpler ones, Part V with the combination of simpler with high-polymer components. These syntheses are similar to those of the azo dye technique and are usually easily performed. They are involved almost exclusively with the reaction between acid chlorides and amines or phenols, alcohols, etc., which usually takes place easily in the presence of tertiary bases, such as pyridine or diethylaniline. The selection of proper solvents is the only difficulty. The preparation of the sensitive acid chlorides of phenols or amines which are often used, is best accomplished by the excellent Ciba process (British Patent 401,643). Until now, there was no special need for the formation of high-colloidal components and dyes by the methods cited under V, because they have certain disadvantages in dyeing on account of their high-molecular structure, and the need arose only with the advent of color photography, so that only little data is available in the literature.

I. Monovalent Phenols

(a) *Aromatic and heterocyclic phenols*

Alpha-anthrol, also the hydrated form, o- and m-hydroxydiphenyl, p-hydroxy- and o-hydroxy-dibenzyl, o-hydroxy-stilbene, o- and p-hydroxy-diphenylpropane, o- and p-hydroxy-diphenylethane and ethylene, o-benzylphenol, o-butylphenol, p-amylphenol, cyclohexylphenol, m-cresol with one 4-heptyl, decyl, ceryl, groups, eugenol and isoeugenol, o-arylallyl phenols monoethers of higher pyrocetechines, benzyl-o-ethyl phenol, 2-hydroxy-1:3-diphenylbenzol, o-hydroxy-propylene-diphenyl ether, hydroxy-diphenylene oxide, di- and tri-isobutylene phenol, butyl-β-naphthol, 2- and 4-aryl-α-naphthol, 4- and 2-acyl-α-naphthol, 3-aceto-α-naphthol and 2-aceto-α-naphthol, 2-phenyl-1:3-dihydroxy-naphthalene, 8-sulfamide-α-naphthol and its 4-chlore-derivative, α-naphthol - 3:6 - disulfamide, 2 - anisal - aceto - α-naphthol, hydrazides of o-ketophenols, 4-brom-β-ketophenols, chalcones, phenylhydrazines of salicylic aldehyde, of vanilline, etc., salicylic aldehyde compound of aminodiphenylamine and anils of other phenolaldehydes, as well as their reduction products, especially the different hydroxy-benzyl-naphthylamines, salicylic aldehyde-semicarbazones, salicylamine aldehyde, salicylic tetrazones, salicylal - methylhexanone, salicylal - acetophenone, etc., especially also the analogous compounds of α-naphtholaldehydes, as well as their hydration products, α-triphenyl-β-(2-phenol-) ethane, hydroxy-triphenylmethane, o- and p-hydroxy-triphenyl-carbinol and analogous compounds, 2-hydroxy-hexamethoxy-triphenylmethane, hydroxy- and dihydroxy-leuco-crystal-violet, m- and o-hydroxy-leuco-malachite green, 4-hydroxy-acenaphthene, hydroxy- fluorene, hydroxy-chrysene, 3-hydroxy-benzofluorenone, hydroxy-tetraphenyl-methane, cyanuric acid-dihydroxy-phenyl ether, 1- and 4-hydroxy-xanthone and higher homologues, salicylal-hydrindone, tetrahydrolnaphthylphenol and similar products, as well as the hydrated amino-α-naphthols and their acyl derivatives, etc., dinaphthol-methane, oxidized 2:6-dihydroxy-naphthalene, as well as the formaline compound of 2:7-dihydroxy- naphthalene, 2-hydroxy-1:8-phthaloyl-naphthalene, dihydroxy-phenyl-anthranol, hydroxylated meso-phenylanthrones, tetra- and octo-hydro-anthranol, hydroxylated flavones, benzolsulfone-m-hydroxy-phenylmethane; o-hydroxy-phenyltolyl-sulfone, o-hydroxy-diphenylsulfide and other o-hydroxy-sulfides and selenides, 3-hydroxy-diphenylamine, m-hydroxy-benzidine, a-naphthol-permimidine, hydroxy-phenyl-naphthindol, hydroxyphenyliminazol, hydroxyphenyl-azimino-benzol- or -naphthalen, o-hydroxy-isoxazol, o-hydroxy-guanazylbenzol, m-hydroxy-carbazol, 7-hydroxy-1:2-naphthocarbazol and analogues also tetra-hydrated. 8-hydroxy-quinoline, β-hydroxy-naphtho-quinoline, reduced hydroxy-quinolines 2-phenol lepidine, 6-methoxy-m-hydroxy-2-phenyl-quinoline and other phenyl-quinolines. Dehydrothiotoluidine and primuline base diazotized to phenol, 3-hydroxy-1:2-naphthacridine and other hydroxy-naphthacridines, hydroxy-flavinduline and its dihydro-product as well as the compounds obtained through addition of m-aminophenol or amino-α-naphthol, euxanthine and other xanthone dyes, sudan G, m-hydroxy-azo-benzol, the products from salicylic aldehyde or vanilline with arylhydrazines, with anthraquinonylhydrazines, with azodye hydrazines, or with azo dyes themselves, as aniline, or with fuchsine and any other amino dye; further the reduction products of these dye anils, or stable coupling leuco-dyes themselves, among others also some N-acyl-hydroxy-hydrazo dyes, thianaphthenesulfone, homothioindoxyl, anthraquinone thioindoxyls, rhodamine and similar ring formations.

(b) *Aroyl derivatives*

Most of the aromatic and heterocyclic phenols

mentioned before yield o- and p-carboxylic acids by the Kolbe salicylic acid synthesis or by means of carbon tetrachloride, which through their chlorides or in the presence of PCl_3 easily form the corresponding arylides with aniline, naphthylamines, anthramines, aminofluorene, dehydrothiotoluidine, primuline base, cholestylamine, cetylamine, cerylamine, myristicylamine and other aliphatic and aromatic or heterocyclic amines, especially also with those amines which for further linking contain a nitro-group which is to be reduced later, also one-sided with diamines or with benzoylhydrazine.

These higher phenol-carboxylic acid chlorides yield esters constructed analogous to salol and its known homologues and self-condensation products, for example, with o-, p- and m-hydroxydiphenyl, with hydroxyquinoline, quinine and cinchonine, with cholesterine, laurylalcohol, myricylalcohol, cerylalcohol, etc., also with ricinoleic castor oil or its hydration product, as well as with other hydroxy- and amino-compounds.

Instead of carboxylic acid chlorides, also sulfonic chlorides, with naphthols—preferably substituted in the second nucleus, can be used for enlarging of the molecule by the action on amines or phenols, aminonaphthols, etc., especially also the easily obtained disulfochlorides and disulfonic fluorides of α-naphthol.

(c) *Increase of the molecule by higher, indifferent radicals*

A very extensive enlargement of the molecule is attained by esterification of the different α-naphthol carboxylic acid chlorides and sulfonic chlorides, of the different o-hydroxy-quinoline-carboxylic acid chlorides, of salicylic acid chloride, of the methylphenylpyrazolone-carboxylic acid chloride or sulfonic chloride with amines or phenols, naphthols, anthrols which contain further hydroxy- or amino group in the nucleus having been substituted in the manner mentioned by high-molecular alkyls, aryls or acyls, in amino groups also mixed, as ceryl-bromide, actadecyl bromide, laurylchloroacetate, also obtained from the mixture of higher alcohols of natural waxes by saponification, or by reduction of the corresponding carboxylic acids, cerotinic acid chloride or mixtures of higher fatty acid chlorides from natural waxes and fats, chlorcarbonic acid cetylic ester, chlorides of sulfonic or carboxylic acids of anthracene, fluorene, etc. Excellently suited is also tri-α-naphthol-triazine in which one or both residual hydroxyl groups are substituted by the radicals mentioned. Other esters concerned and containing a free hydroxyl group are those of mannite, of the sugars or acetone sugar with palmityl chloride, oleic acid chloride further lecithine or diglycerides as αα′- or αβ′-distearine or the corresponding higher compounds with melissinic acid, erucic acid, etc.

The coupling acid chlorides mentioned at the beginning can be allowed to act further on: cholesterine-amine, cholestyl alcohol, cerylic alcohol, myricylic alcohol, dimyristicylic carbinol, p-hydroxy- or p-amino-dibenzyl- and diphenyl propane as well as their reduced nitrobenzoyl derivatives, diphenoxy-phenylanthranol and -diphenyl-anthranol, further on products which are obtained by allowing p- or m-nitrobenzoyl chloride, after preliminary reduction to the amino group which is maintained as such, to react about four times on cetyl- or cerylamine, dehydrothiotoluidine and other aromatic or heterocyclic amines. In the same manner, one can also repeatedly use anthranilic acid chloride, or similarly-acting isato-acid anhydride. All these amines react also with aceto-acetic esters.

A great enlargement of the molecule can be obtained in a similar manner in amino-α-naphthols or diamino-α-naphthols with free 2- or 4-position and in acid methylene compounds which contain an amino- or hydroxy group in the aryl-ring or in the arylido residue. The latter is, however, less suitable, as it does not react as easily as the amino group and the danger exists that with more rigorous conditions the acid methylene group is also attacked. In the simplest case, one can allow these compounds to react, if necessary, in the presence of copper bronze, with: ceryl bromide, octadecyl bromide, etc., laurylchloroacetate, m-chloracetyl-acenaphthene and -anthracene, further with the chlorides of the palmitinic acid, cerotinic acid, melissinic acid, oleic acid, erucic acid, also with ketostearinic acid chloride or ketoerucic acid chloride and prepare from these derivatives possibly the phenylhydrazones. Instead of using this acylating or alkylating agent directly, one can allow dinitrochlorobenzol, picrylic chloride, dinitrobenbylchloride, dinitrobenzoyl-chlorides, etc., to act before on the amino- or hydroxy group of the component. One can also allow nitrobenzoyl-chloride, anthranilic acid chloride, isatoic acid anhydride, etc., to act repeatedly on the original or newly introduced amino groups, as described in the preceding chapter.

Also the arylides of α-naphthol-2, -3-, and -4-carboxylic acid can be subjected to the reaction just described, if they possess a free or monoalkylated amino group in the arylido residue.

In o-nitrophenol, etc., the hydroxyl-group can be alkoxylated by hexadecyl bromide, ceryl- or myricylic chloride, etc., after which, analogous to the Guajako synthesis, one reduces and converts by diazotization into the high-molecular phenol.

The different dialkylamino-, phenylamino- and naphthylamino phenols and -naphthols, preferably substituted in the second nucleus, are practically insoluble; also their N-acylation products, not only those of the m-series, but also those of the o- and p-derivatives and α-naphthol which is perhaps also substituted by acyl- or carboxylic acid-arylido groups in the 2- or 4-position, and this especially when using stearyl- or cerotyl chloride, etc. Also the NN′-diacetyl-disteryl derivatives of the 3:5 diarylamino phenols are suitable as components, and often show the character of cryptophenols. Also very simply constructed components, as the ac.tetrahydro-amino-naphthol, are excellent by their insolubility in alkali, and, if necessary, they can be added in form of their insoluble phosphotungstates. On account of their strongly basic character, they have a very favorable effect on the sensitivity.

Many of the phenols mentioned before yield useful o- and p-ketones by condensation with acids or their chlorides, similar to α-naphthol, which are especially insoluble or colloidal when using higher fatty acids or aromatic acids, especially those which have unsaturated conjugated double bonds, as in Japan lacquer. The preparation of their completely insoluble phenylhydrazones is sometimes of advantage. While 4-ketones of α-naphthol are very soluble in lye and sodium carbonate on account of their pronounced acid character, this is not the case with 2-ketones, its 2-benzoyl derivatives being not even

soluble in N/15 NaOH. It must, therefore, be considered as practically insoluble and it is very suitable as a coupling component, producing blue images on development with p-amino-dimethyl-aniline containing sodium carbonate. In addition to the coupling components mentioned, the "cryptophenols" which were thoroughly studied by Auwers, are of significance on account of their insolubility in alkali or at least in sodium carbonate solution, of which the o- and p-hydroxy-triphenylmethane should be especially mentioned. Similar to it is a modification of p-hydroxy-triphenylmethane carbinol, namely the easily obtained octo-hydro-anthranol and its p-brom-derivative, the phenylimine of o-hydroxy-benzophenone, homothioindoxyl, benzanthrone-thioindoxyl, anthraquinone thioindoxyl. Also 1:3-diphhenyl-5-pyrazolone, very difficultly soluble in water, is practically insoluble in dilute alkalies, since its alkali salts obtained with much caustic lye are dissociated by water, which is connected with its very weak acid character. In the development with a solution containing sodium carbonate violet-red images are produced with p-amino-dimethylaniline. Its o-methoxy derivative hardly soluble in water, is easily dissolved in alkalies.

Through the enlargement with high-molecular radicals, one can also obtain a high-colloidal, soapy character or complete insolubility of most salts of sulfonic acids of the components described herein, as is already known of the reaction products from H-acid and stearylic chloride, etc.

II. Polyvalent, Nucleus-Condensed Components

(a) Phenols

Dihydroxynaphthalene, dihydroxyanthracene, mm'-and oo'-dihydroxydiphenyl and their tetrabrom derivatives, o-bicresol, diisoeugenol, binaphthols, 44'-dihydroxydinaphtyl-11' - ketone; 22'-dihydroxy - 11' - dinaphthyl-ar. octohydride, so-called diamino-oo'-dihydroxy stilbene or its NN'-dicyl derivatives, the different dihydroxy-stibenes as well as their halide and halide-hydrogen-addition-products and their catalytically easily obtained dihydroforms, dihydroxydiphenylquinone, naphtholfluoresceine, di-(p-hydroxy-) phenyl-cyclohexanone, dihydroxytetraphenyl - ethane, dihydroxydiphenyl - dibenzyl-methane, disalicylal-resorcin and -hydroquinone, disalicylal-acetone and its hydration product diphenylene ketone-biphenol, 22' - dihydroxy - 11'-dianthralyl - methane dihydroxy - diphenyl - anthrone, bis-phenol- and resorcin anthraquinone, addition products of phenols with alizarine diquinone phenylimides of dihydroxybenzophenones, mm' - dihydroxy - diphenylamine, di - α-naphthol-66'-imine, 4:8-dihydroxy-dibenzophenazine, dihydroxy - dinaphthazine, 2-(3'-hydroxy-naphthoyl-2')4 - hydroxy - 6:7 - benzo-pseudoazimino-benzol, p-hydroxyphenyl-6-hydroxy-quinoline, etc., dihydroxy-diarylsulfones, phenol-o-disulfide, phenol - p - disulfide, dihydroxydiphenyl-disulfide and -disulfone, cyclic duple-β-xylylene-mercaptol of m-hydroxybenzaldhyde and its tetrasulfone, condensation products of o-hydroxy-diphenylacethydrazide with hydroxy aldehydes, cyanuric acid resorcin ether, di- and tri-α-naphthol-triazine, also combined with other radicals.

(b) Acid methylene compounds

Hydroxylacetic acid ester, succinyldiacetic acid ester, acetonylacetone-dioxalic acid ester, sebacyldiacetic acid ester and the analogously prepared higher aliphatic homologues, acetone dicarboxylic acid ester, acetone dioxalić acid ester (this can serve as yellow filter directly in its dienol form), terephthalolyl-, isophthaloyl-, naphthoylene- and diphenyl -44'- dicarboxyl - diacetic acid ester, as well as their arylides, especially also with higher molecular aromatic amines. Also considered are the amino derivatives, sometimes easily split by acid; less valuable, however, are the thiourea - and thiosemicarbazide - addition products, but especially the mono- and di-phenylhydrazones; all these also one-sided in the aceto-acetic acid ester simply connected by diamines and 1,3-diketones: on the other hand, this holds true also for diacetoacetic anilide and its higher analogues. It is more difficult to prepare all these derivatives, if the acid methylene group is chlorinated or brominated which, however, presupposes difficult solubility.

Di-pyrazolones: They are easily prepared from the esters just mentioned, and also with heterocyclic hydrazines, as they may also be obtained by combination of aromatic amines with dehydrothiotoluidine or primuline base by means of cyanuricchloride. On the other hand, di- and tri-pyrazolones can be produced also from dihydrazines, for example, those of benzidine, pp'-diaminodiphenylmethane, oo'-diphenyldihydrazine, etc. Also from diaminodiphenyl-hexane and -octane. Trihydrazines, as for example fuchsine, or of its leuco-base, yield tri-pyrazolones, also the different trihydrazines prepared with cyanuric chloride. Pyrazolones brominated in the methylene group often excel by complete insolubility.

(c) Metal-organic compounds

The peculiar mercury compounds which are easily obtained not only by combination of two molecules of phenol or naphthol through Hg, but also by the entrance of one or two mercuric salt residues into the molecule, are worth mentioning. They are precipitated by acids in completely insoluble form and can be added to the emulsions of silver bromide after thorough washing. If the mercury residue is in the p-position, it is replaced with indophenol formation exactly as in diazo coupling.

It is of practical importance that also the acid methylene compounds react, and the washed acetate- or chlor-Hg-compounds often couple with replacement of the inorganic residue: Hg-malonic acid ester, Hg-aceto-acetic ester, Hg-aceto-aceticanilide, Hg-pyrazolones.

In certain respects, also the salts of the enol form of the acid methylene compounds with other metals belong here, which are often very stable to developers containing sodium carbonate, ammonia, bicarbonate, etc., and can be added to the emulsions on account of their complete insolubility in water, without reducing the coupling speed too much. Similar insoluble salts are also formed by the mono-brominated methylene group. The mostly yellow-green copper salts can easily be converted into the blue basic salts. It is pointed out that the copper salts usually precipitate in ammoniacal solution, the insoluble aluminum salts which are stable to sodium carbonate and ammonia, are prepared even with potassium aluminate; also the salts of oxalic acetic ester are stable to sodium carbonate. Insoluble ferrous salts, as they are prepared from aceto-acetic ester, acetylacetone, benzoylacetone, are also taken into consideration. While aceto-acetic ester forms an insoluble salt only with

ammoniacal copper solution, with acetyl acetone and its higher homologues, as oxalyldiacetone, benzoylacetone, dibenzoylacetone, etc., a copper acetate is sufficient.

Also o- and p-nitrobenzylcyanide yield insoluble copper salts; the p-derivative which is somewhat soluble in water yields also an insoluble silver salt.

Arylsulfonic acetic ester, -acetonitril, -nitromethane, etc., show a similar behavior.

Pyrazolones which are usually very difficultly soluble after bromination are practically insoluble, and often hardly soluble in sodium carbonate, can be precipitated as a completely insoluble compound by copper-, aluminum-, zinc-, Ca- and other salts, also within the emulsion. Also the higher-molecular organic bases often produce entirely insoluble precipitates in the emulsion with coupling pyrazolones, naphthols and phenols.

III. Polyvalent, Directly-Linked Components

Coupling acid chlorides, as salicylic acid chloride, α-naphthol-2-, -3- or -4-carboxylic acid chloride, o-hydroxy-quinoline-7-carboxylic acid chloride, methyl-phenyl-pyrazolone-carboxylic acid- or sulfonic chloride can also be combined with coupling α-naphthols, also the different aceto-acetic ester-homologues, as for example, palmityl acetic ester with amino-α-naphthol or with amino-arylides of the aceto-acetic ester itself or with amino-pyrazolones.

Heterogeneous bivalent coupling components are o-acetylacetone phenols, as 2-acetyl-acetone-β-methyl-phenol; 2-acetyl - acetone - 4 - methyl-phenol, 2-acetyl-acetone-α-naphthol. They can also be added to the emulsions in the form of their insoluble copper-, aluminum-, zinc-, magnesium-, calcium- etc. salts or as ketonimines.

IV. Polyvalent Components Linked by Intermediate Members

A. Linking of acid component by polyvalent bases

(a) Linking of acid coupling derivatives by anilide formation:

It is assumed that one or two molecules react with primary amines, but that of the latter, those of phenolcarboxylic acids are usually less stable, more stable are diaceto-acetic anilide and its analogues.

Coupling derivatives are concerned:

(1) Acid chloride as: salicylic acid chloride, m-phenolsulfonic chloride, α-naphthol 2- or 3- or 4-carboxylic acid chloride or -sulfonic chloride, salicylic sulfonic chloride or α-naphthol-2-carboxylic acid-4-sulfonic chloride, naphthsultame -2- or 4-carboxylic acid- and -sulfonic chloride, chlorides of the different o-hydroxy-quinoline carboxylic acids, chlorides of the products which are obtained by the action of the acid chlorides mentioned on anthranilic acid, polyanthranilic acid or poly-p- and m-aminobenzoic acid, chlorides of the addition products of phenols and naphthols on unsaturated high-molecular fatty acids, chlorides of the reaction products of α-naphtholsulfonic- or -carboxylic acid chloride on hydroxy-stearic acid, hydroxybehenic acid, ricinolic acid, etc., or on the hypochloride addition products of oleic acid, linolic acid, erucic acid, ricinolic acid.

(2) Acid chlorides of pyrazolones, as sulfonic acid chloride and carboxylic acid chloride of technical methylphenyl-pyrazolone.

(3) Aceto-acetic ester and especially its higher aliphatic, aromatic and heterocyclic homologues, as well as palmitinic acid acetic ester and the undecylic acid acetic ester analogously obtained. Two molecules of these can be linked with formation of analogues of diaceto-acetic anilide by reaction with the same amino group of simpler amines or with different amino groups with the use of diamines which, however, can also react one-sidedly.

Suitable polyvalent conhecting members:

(1) Amines as for example: phenylenediamine, diaminophthalene, diaminofluorene, benzidine, dianisidine, diaminobenzidine, and its sulfone, xylenylamine, diaminodixenylamine, tetraminodiphenylamine, tetraminodiphenyloctane, and its reduced tetra-nitrobenzoyl derivative diaminodinaphthyls, diaminodianthranyl, phenylenediimide and other di- and tri-amines, as they are used in the production of substantive azo dye acids, also heterocyclic ones, for example, carbonyl-bis-(p-aminobenzoyl-) p-phenylene diamine or its disulfonic acid, diazo light yellow, etc., dinitrochlorobenzol, picrylic chloride, dinitrobenzoylic chloride, dinitrobenzoylic chloride can be allowed to react on these substances or on simple aromatic and heterocyclic phenols and amines and perhaps p-nitro-benzoylchloride on the reduction product in order to obtain high-molecular linking members after the reduction.

(2) Hydrazines are also considered as linking members as for example: hydrazine, fuchsine-trihydrazine, cyanuric trihydrazide, or its phenyl derivative.

(b) Linking of coupling acid derivatives by ester formation:

Derivatives mentioned under (a) can be allowed to react, in addition to the coupling components mentioned before, with one or two hydroxyl groups, also with resorcin, diphenols, dihydroxynaphthalenes, hexaoxyterphenyl and other poly-hydroxylates, condensed hydroquinones resorcyl-anthranol, dihydroxy-diphenyl-anthrone, further with glycol, glycerine, pentaerythrite, mannite, dipentaerythrite, saccharose, tetra-oxydecane, and with other natural or synthetic poly-alcohols, also diphenols with ketone groups or with the resins or Japan lacquer obtained from it, further with the hydroxyalkyl-ethers easily obtained from all these products by the action of ethylene oxide.

(c) Linking by (leuco)-dyes:

Connecting members are not only stable leuco-bases or leuco-cyanides of triphenylmethane dyes, reduced gallo-cyanides or polyhydroxy-anthraquinones, but also genuine dyes with amino- or hydroxyl groups, since in most of them the dye character is weakened or absorption shifts towards yellow or orange occur by acylation. Fuchsine produces a green dye with one molecule of salicylic acid chloride, a light yellow dye with three molecules. Triaminotriphenylmethane dyes or the corresponding leuco-derivatives where only one amino group is in the p-position, are still better suited, or even those where this is not the case, whereby the dye character is very much weakened or entirely destroyed. Especially high-molecular derivatives are obtained with the bis-tetramino-leuco-malachite green from tetramino-diphenyl-hexane or -octane, or its leuco-cyanide or leuco-derivatives of analogous soluble dyes.

Also most azo dyes are weakened or the color shifted towards yellow by acylation of their amino- or hydroxy-groups. Diphenyline or mm'-diamino-diphenyl can also be coupled after tetrazotization with two molecules of α-naphthol and

be esterified with the coupling acid chlorides, with possible preliminary or subsequent reduction to the hydrazo form. Or the stable m-hydroxy-hydrazobenzol or the bis-derivative prepared analogously from dianisidine is used directly. The stability of the hydrazo-forms can be increased by the action of phosgene or acetaldehyde or potassium cyanide or potassium rhodanate on the azo body, or by esterification of both nitrogen atoms of the hydrazo group with the coupling component.

(*d*) Linking by high-molecular intermediate members:

These are obtained by allowing salicylic acid chloride first to react, in a similar manner as for the formation of depsides, on the polyamines mentioned under (*a*1) and (*b*) or polyhydroxyl compounds, leuco-fuchsine, trinaphthylguanidine, tetrahydroxydiphenylmethane, mannite, dipentaerythrite, raffinose and other sugars, on pyrimidine sugar or anils of sugars, acetone sugar, etc., tri-α-naphthol triazine, or one allows α- or β-naphthol carboxylic acid- or sulfonic chloride, isatoacid anhydride, or still better nitrobenzoyl chloride, nitrotoluol sulfonic chloride, nitrophenyl urea chloride, dinitrochloro-benzol, etc., to react with them with subsequent reduction to amino group. Then, or after several repetitions of the process, the coupling acid chlorides or naphthols or pyrazolones are allowed to react. The products obtained from hexagalloyl-mannite, in similar manner, have an almost completely polymeric character.

Three molecules of amino-naphthol, aminoresorcin, nitraniline, nitrophenol or nitronaphthol can be linked through cyanuric chloride or triazine-tricarboxylic acid trichloride, and the former products then reduced. The amino- or hydroxy-groups are possibly again acylated by nitrobenzoyl chloride or nitrotoluolsulfonic chloride and perhaps repeatedly reduced. Only then they are esterified by α-naphtholcarboxylic acid chloride or the other coupling acid chlorides mentioned under (*a*). One chlorine atom of cyanuric chloride can also be substituted by other residues, as ceryl amine, or by ammonia or m-aminophenol, after which one allows one or two molecules of ceryl bromide, cerotinic acid chloride to react. The same procedure can be used with the residual chlorine atom of di-α-naphthol-cyanuric chloride which can also be allowed to react with all simple and higher-molecular amino- and hydroxy compounds mentioned, especially also, it can be alkylated with higher aliphatic alcohols as cerylic alcohol, myricylic alcohol, etc.

High-molecular intermediate members are also obtained by the action of chlorides of ketostearinic acid to be reduced later, hydroxystearinic acid, ricinolic acid, ricinolic ester acid, linolic acid, erucic acid, etc., on the amino- or hydroxy-compounds mentioned, followed by esterification with the coupling acid chlorides. Or, one proceeds in reverse order and allows salicylic chloride to react with hydroxystearinic acid, forming the chloride.

Both chlorine atoms of αα'-dichlorydrine can be converted with the alkali salts of melissinic acid and the middle hydroxyl esterified by α-naphthol-carboxylic acid chloride or other coupling acid chlorides.

B. Linking of basic components by polyvalent acids

Coupling derivatives with amino-, hydroxy- or sulfhydril-groups are for example:

All amino-α-naphthols, also with occupied 4-position and their 2- or 4-carboxylic acid arylides, as 7-amino-α-naphthol-2-carboxylic acid naphthalide, as well as the one-sided products of hydrolysis, especially the acyclic tetrahydro-1:5-aminonaphthol further, o-, m- and p-phenylaminophenols, also the analogous derivatives of α-naphthol and α-anthrol as well as their higher homologues (o-amino-toluolsulfonyl-) α-naphthylamine, aceto-acetic acid-hydroxyarylides, monoaceto-acetic acid benzidide, acetylo-acetatophenols and -naphthols, pyrazolones with free amino-, hydroxy- or sulfydril groups, especially also the aminated acyclic tetrahydronaphthylmethylpyrazolone from acyclic tetra-hydro-1:5-aminonaphthylhydrazine which is important on account of its stability.

An amino- or hydroxy group can be generally introduced into the arylido groups of the coupling components mentioned under (*a*) for the purpose of further linking, by allowing one molecule of salicylic acid chloride or pyrazolone carboxylic acid chloride to act on m- or p-nitraniline, or two molecules on nitrobenzidine, nitrodiphenyline or hydroxybenzidine and then reducing the nitro-group. Or 2- or 4-(m-bromacetyl) α-naphthol, also m-chloracetamino-α-naphthol is allowed to act on nitraniline, nitrobenzidine, etc., and reduced. The nitro-group to be reduced can also be in the aryl radical of α-naphthol-2- or 4-ketones, which can be obtained with nitrobenzoyl-chloride, etc. Especially high-molecular products are obtained in this manner from diacetoacetic-nitranilide, or by using 1:5-dihydroxy-naphthalene dicarboxylic acid or of 44'-dihydroxy-11'-dinaphthylketone-33'-dicarboxylic acid. All these nitro-derivatives yield dimer azoxy- or azo-compounds of usually yellow color on reduction with glucose which also are suitable as components.

In all fundamental substances mentioned before, one could, of course, also allow p- or m-nitrobenzoyl chloride or p-nitrotoluolsulfonic chloride to react with the free amino-, methylamino- or hydroxyl group, reduce, and then only link, perhaps after trying to increase the side-chain carrying the external amino group by repetition of the procedure. In this manner, for example, p-amino-benzoyl-α-naphthol and its 3-sulfonic acid, as well as the analogous derivatives of α-naphthol with amino group in 2-, 3-, 7- or 8-position, can be obtained, perhaps with a 4-sulfonic acid group, and also of the 4-amino-α-naphthol -2-sulfonic acid.

Also salicylic acid chloride can first be allowed to react with these fundamental bodies, as well as α- or β-naphthol-carboxylic acid chloride, and then only linked further.

Two molecules of these fundamental coupling substances can be allowed to react with cyanuric chloride, and several molecules of the product obtained may be converted with poly-amino- or poly-hydroxy compounds with exchange of the third chlorine atom.

Two or three molecules of α-naphthylamine or any other aromatic amine with free p- or o-position can be linked by the di- and tri-sulfonic chlorides to the phenol-like coupling arylsulfonyl compounds.

Connecting members are, for example: Phosgene, thiophosgene, carbon disulfide or ethyl-oxalate, oxalylchloride, chlorides of adipinic acid, sebacinic acid, hexadecane-mm'-dicarboxylic acid and still higher aliphatic di-acids easily accessible by electrosynthesis, imino dibutyric acid, benzol-dicarboxylic acids, m- and p-naphthalic acid, di-

benzyldicarboxylic acid, diphenyloctanedicarboxylic acid, benzophenonedicarboxylic acid, diphenyletherdicarboxylic acid, diphenylene-22'-oxide-44'-dicarboxylic acid, phenazonedicarboxylic acid, bisdiphenylene succinic acid, dithiodisalicylic acid, biphenyl- and carbazol-diphthaloylic acid, trimethylene-disulfonic chloride and other disulfonic chlorides, as those of the 2:6-naphthalenedisulfonic acid, diphenyl-33'-disulfonic acid, nitrobenzoldisulfonic acid, α-naphthol-3:6-disulfonic acid, α-naphthol-2:4:7-trisulfonic acid, di- and tetranitrodichlorobenzolsulfone 44'-dichlor-33'-dinitro-diphenylsulfone and the corresponding ketone, disulfide-disulfochloride, azinetetrasulfonic chloride as well as its reduction product and the azo-body formed from it, also obtained from hydrazine and two molecules of brom-metionic acid, as well as the chlorides from the analogous condensation products with other aromatic or aliphatic di- and polyamines, chloracetylchloride, but especially cyanuric chloride and trazine tricarboxylic acid trichloride. The simple or higer molecular poly-amino- and hydroxy compounds or their hydroxyalkyl ethers with phosgene form polyvalent urea chlorides or isocyantas and chloracarbonic acid ester; by conversion with bromacetic acid and treatment with thionyl chloride, they form also polyvalent acid chlorides.

Several molecules of polyanthronilic acid or analogues, or aliphatic mono-amino acids as they are obtained by the reaction of the half acid of sebacinic acid amide with hypobromite, are linked by phosgene or other di- and tri-chlorides, the imino group is perhaps alkylated and then converted into the polyvalent acid chloride.

All acid chlorides mentioned before and also tetra nitrodichlorsulfone can first be esterified with m-hydroxybenzoic acid or m- or p-aminobenzoic acid and then the higher dichlorides produced with thionylchloride.

When using cyanuric chloride, two halides can be substituted by higher aliphatic or aromatic residues, for example, by two molecules of p-amino-stilbazol, and the residual chlorine is then directly brought into reaction with amino-α-naphthol, or intermediate members are inserted.

Aliphatic polyacid chlorides must also be mentioned: several molecules of ketostearinic acid can be linked by di- or tri-hydrazines (for example, fuchsine, or its leuco-base or its leucocyanide); three molecules of ricinolic acid by cyanuric chloride, etc., then treated with thionyl chloride or phosgene. Two molecules of α-naphtholcarboxylic acid chloride can be allowed to act on hydroxy-, dihydroxy- or diamino-sebacinic acid, and the dichloride formed from it on two molecules of ricinolic acid or hydroxybehenic acid, as just explained.

If the polyvalent connecting member contains a hydroxyl- or reduced nitro group, further linking through cyanuric chloride, trisulfonic chloride etc. can take place. Under certain conditions, also mixed coupling components can be obtained in this manner by allowing α-naphthol-3:6-disulfonic chloride to react with two molecules of α-naphthylamine.

Dyes can also here serve as connecting members, for example prepared from diazotized, fuchsine and three molecules of salicylic acid or phenol by the action of chloracetic acid on the latter or other azo dyes with carboxylic acids containing OH- or NH-groups, fuchsine, etc., which are then converted into the chloride, or by the action of phosgene on dyes with two amino- or hydroxy groups.

C. Other linking methods

(*a*) Linking by nitrogen-carbon combination with formation of:

Guanidines, especially di- and tri-α-naphtholguanidines.—One molecule of these compounds is allowed to act on thioureas from two molecules of amino-α-naphthol in the presence of lead oxide, or two molecules of this thiourea are linked in the same manner by the action of an aliphatic or aromatic diamine. This is also successful with thiourea from two molecules of aminostilbazol and amino-α-naphthol in the third position.

Guanazyl- and formazyl compounds.—The light-yellow insoluble o-hydroxy-guanazylbenzol is suitable, the red p-monoxyformazylbenzol or the light yellow tetrazolium chloride are less suitable, and the corresponding benzidine derivatives are somewhat better.

Hydrazides.—Formed from two molecules of α-naphthol carboxylic acid.

Hydrazones.—From salicylic aldehyde and semicarbazide, forming the semicarbazone and azine, or also carbaminic acid hydrazone with aniline. Azine is also formed from two molecules of aceto-acetic ester, easily split by acids. It is important to note that not only α-naphthol-2- and 4-aldehyde, but also 2- and 4-ketones of α-naphthol form azines or bis-arylhydrazones by linking of two molecules, similarly also the 4-sulfonic acids and 4-brom-derivatives of 2-arylketones. It is better to use higher-molecular aliphatic and aromatic dihydrazines, as under II, B, also diphenylmethane-dimethyl-dihydrazine.

Bis-phenylimides.—They are obtained from two molecules of substituted benzophenones, dinaphthyl-ketone or aromatic hydroxyaldehydes capable of coupling by means of aromatic diamines which in turn can be substituted by hydroxyl- or reducing nitro-groups in order to make further linking possible.

Polyamines.—Obtained from halide compounds with exchangeable halide.

(1) In the connecting member: dodecamethylenedibromide, etc., or better chlorinated petroleum is converted, if necessary, in the presence of native copper, with amino-α-naphthol, or analogously to ethylene- or trimethylene bromide with two molecules of dihydroxybenzol, further pyrocatechinecarbonic acidhydrazide, using, however, bivalent intermediate members. Chloracetylchloride can be allowed to act on the before-mentioned amino compounds, for example, on leuco-cyanide or leuco-base of bis-tetraminomalachite green and similar bistriphenylmethane dyes or basic dihydroxy dyes.

(2) In the coupling body: Nitro-Br-α-naphthol is converted in the presence of native copper with primuline base or its higher homologues or derivatives with an external amino group, reduced and the amine further linked. Similarly used are m-chloracetyl-α-naphthol, 4- and 2-m-bromacetyl-α-naphthol, as well as m-chloracetamido-α-naphthol.

(*b*) Linking by nuclear condensation:

Diketone formation, from higher dicarboxylic acids, as sebacinic acid and dihydroxybenzols.

Tri-α-naphthol-triazine, from 3 molecules of α-naphthol and cyanuric chloride, also with o-hydroxyquinoline, α-anthrol and similar substances.

Pinacone formation, or benzoine condensation by reduction of -naphthol-4-ketones or 44'-dihydroxy-dinaphthyl-11'-ketone.

Dianthrone formation, by reduction of coupling anthraquinone derivatives which are obtained from amino-anthraquinones and salicylic acid chloride, etc., or from anthraquinone carboxylic acid- or -sulfonic chlorides or -urea-chlorides and -isocyanates with amino-α-naphthols.

V. Combination with high-polymers

A

Suitable for reaction with the original coupling bodies or those changed according to the invention with exchangeable halide, as mentioned in IV, A and IV, C, are:

(*a*) Colloidal polyhydroxy compounds:

(1) Of the aliphatic series as: polyvinyl alcohol, polyalcohols obtained by reduction from polymerized acrolein, etc., higher tertiary homologues of polyvinyl alcohols obtained according to Grignard, polyacrylic acid esters, starch and polyamyloses, alkylcellulose or its water-soluble partial alkylether or that of polyvinyl alcohol or acyl ester, also mixed with methoxyl- and ethoxyl residues; further the hydroxylalkly- ethers of all these compounds, as also of cotton, fibroine, caseine, etc., which, in turn, can be partially alkylated or acylated.

(2) Of the aromatic series as: colloids obtained by polymerization of phenols with unsaturated side-chains as vinyl phenols, vinyl-α-naphthol, p-hydroxy-styrol, m-hydroxy-styrol, hydroxylated m-chlor- and m-brom-styrols, poly-iso-eugenol, vinylnaphtholcarboxylic acid esterhydroxyphenylbutadiene, hydroxycinnamic acidallyl ester, polymerized acrylic acid arylides of amino-α-naphthols, benzal-o-hydroxy-acetophenone, the corresponding compounds with α-tetralone and bis-derivatives, as disalicylalacetone, urushiol or Japan lacquer, phenolphthaleine; further condensation products from phenol and colophonium, shellac or its easily re-agglutinated disaggregates, tannin, maclurine, caffetannic acid, catechutannic acid, digallic acid, etc., depsides which can all be penta-acylated, products from caoutchouc dibromide and phenol, phenol-formaldehyde resins or their intermediate forms, in as far as these synthetic or natural resins and colloids are not in themselves suitable as coupling components.

(*b*). High-polymer amines:

These can be prepared in the simplest manner from the colloids mentioned above by the action of nitrobenzoyl chloride or its oo'-dihalide substitution produce, nitro- and dinitrobenzolsulfonic chloride, dinitrochlorobenzol, nitrophenylurea chloride, nitrobenzyl chloride with subsequent reduction, or by means of isatoacid anhydride, anthranilacid chloride and other amino acid chlorides. Nitranilides can be prepared from polymerizing acids, as acrylic acid and cinnamic acid, and these can be polymerized and then reduced. Polyvinyl chloride and polyvinyl bromide, polyvinyl-chloroacetate or analogous mixed polymerisates, halide paraffines are converted with ammonia or amines, if necessary, in the presence of copper bronze, to polyethylene-polyamines and other polyamines. When using cyanuric chloride, one can also obtain combinations with other aliphatic or aromatic amines. This is also possible with nitranilines which are reduced later, or with nitro- or aminotoluolsulfamide or hydrazide, here and in preceding cases. Polynitrostyrol, polymerized nitrated cinnamic acid allyl ester, nitrated glyptal resin and other super-polymers formed from nitrophthalic acid and glycol, etc., are reduced to the amine. In cellulose one can, in some cases, effect an exchange of the acyl residues for ammonia or amines to "amino-cellulose" and "amino-thread," amino-sugar and polyethylenepolyamines. Aminofibroine is obtained by reduction of the coupling products with diazo bodies of cotton, silk or albumen ground very finely in the colloid mill; or diazotized silk or cotton is directly reduced, or they are coupled with aromatic amines to azo dyes with several amino groups. One can allow nitro- and dinitro-arylsulfonic chloride or diazoxide-4-sulfonic chloride or 4-carboxylic acid chloride to act on peptone, fibroine, cotton, soap, etc., and then reduce. Also the polymerized reaction products of formalin on aromatic amines are used, especially with β-naphthylamine.

Also here, one can introduce first indifferent intermediate members, as ethylene oxide or salicylic acid chloride, anthranilic acid chloride, isatoacid anhydride, etc., into the polymers with hydroxyl- or amino groups. Different coupling bodies can also be combined with the same high-polymer linking member, or the hydroxyl- or amino groups which are not used by the same coupling body, are esterified with chlorsulfonic acid, salicylic sulfonic chloride or benzoic acid sulfonic chloride, in order to obtain a better solubility, if desired.

B

In addition to polyvinyl bromide, for the linking of the coupling amino- or hydroxy derivatives of phenols, naphthols, pyrazolones, aceto-acetic homologues and their carboxylic acids mentioned under IV, B, one can also use polychloroprene, polyallyl chloride, polyvinylnaphthalene brominated in the second nucleus chloro-caoutchouc and other halide addition products of caoutchouc; further polyvinylchloroacetate, polyacrylic acid chloride, and the products obtained by means of phosgene or chloroacetylchloride or chloracetic acid and thionyl chloride from cellulose and other polyhydroxyl- or polyamino compounds, with reacting halide, also partially by means of cyanuric chloride.

The combination, according to A and B can also be accomplished before polymerization, by allowing linolic acid chloride to react with amino-α-naphthol, or -naphthol-carboxylic acid chloride with hydroxyl-styrol, salicylalacetophenone, urushiol etc., or with the esters of nitrobenzyl alcohol with cinnamic acid, acrylic acid, etc., after preliminary reduction to the amino group.

2 molecules of (amino-)α-naphthol can be linked by cyanuric chloride, and this product be allowed to react with the poly-compounds of A, or, after exchange of the residual chlorine atom for the amino group, with the intermediate members of B, or with a coupling body with an external amino group.

What I claim is:

1. A process of multi-color photography which comprises exposing to a subject a multi-layer film having incorporated in gelatino-silver halide layers, coupling derivatives of dye compounds soluble in only strong alkali, developing the film in a not strongly alkaline, non-coupling developer to produce metallic silver negative images in the layers, rendering the residual silver halide layers developable, developing the film in a weak-

ly alkaline, primary aromatic amino coupler developer to produce a coupled dye image insoluble in strong alkali, washing out the coupling dye compound in the negative portions of the layers in a strongly alkaline solution and regenerating from the coupled dye image in the positive portions the dye corresponding to the original dye compound.

2. The process of claim 1, in which the dye corresponding to the original dye compound is regenerated by the use of hydrolysis.

3. The process of claim 1, in which the dye corresponding to the original dye compound is regenerated by the use of an oxidation step.

KARL SCHINZEL.