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COLOR PRINT BY MULTIPLE COLOR DEVELOPMENT

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3 Claims. (Cl. 95—6)

This invention relates to couplers for the color development process of color photography and particularly to aryl hydrazide couplers.

It has been mentioned in our patent application Serial No. 151,811, filed July 3, 1937, that not only the insoluble salts of sulfonic or carboxylic acids or of acid methylene compounds can be added to the emulsions, but also those of naphthols, phenols and their higher analogues and homologues which may be decomposed by the alkali or the sodium carbonate of the developer, if the alkali salts formed do not diffuse. Of course, the developer may also be prepared with other inorganic or organic bases of the desired strength according to whether decomposition or stability of the component salt is desired.

It is not easy to add such completely insoluble salts, because, just as in the introduction of insoluble free phenols, naphthols and acid methylene compounds of corresponding molecular size, the danger of crystallizing out exists, especially when alcoholic or acetonic solutions are used, regardless of the fact that according to experiments of Charriou and Valette, the color sensitivity and general sensitivity is reduced (Phot. Ind. 1934, 1306; 1932, 1150; Zeits. f. wiss. Phot. 34, 268). It is, therefore, well to add the non-diffusing or slightly diffusing alkali salts of higher molecular coupling components (for example, palmitylaceto-β-naphthalide or palmityl-pyrazolone, or of the condensation product of acrylic acid, or polyacrylic acid chloride and any amino-α-naphthol), since these salts are not inclined to crystallize out and do not change the sensitivity. If necessary, solutions of pure alcoholic or aqueous lye are used according to Claisen. Alkalies here include not only the salts of potassium and sodium but also those of lithium, ammonium, ethylene diamine, diethylene diamine, piperazine, piperidine, tri-methylene diamine and other aliphatic or mixed higher amines, among which are especially those which are able to increase the general or color sensitivity of the silver halide gelatin emulsion. Also, the higher molecular bases are suited for this purpose, as described in the Swiss Patent 176,023,24,25; 179,945 and German Patent 622,809. One must, however, calculate that after longer storage under the effect of the carbon in the atmosphere in some cases these soluble, but not diffusing or hardly diffusing salts are decomposed with liberation of phenol which harms the sensitivity. This is hardly the case with phenols and naphthols which are substituted in the o- or p-position or in both by halide or by acid methylene compounds which are chlorinated in the methylene group. In order to oppose this gradual decomposition, an excess of the bases mentioned is added to the emulsions, of course, only weaker bases or those which have no harmful effect on the gelatin. Also lithium carbonate, guanidine carbonate, piperidine, piperazine, ethylene diamine and higher aliphatic diamines are considered for this purpose, especially those which have a favorable effect on the sensitivity. Less suitable are the di-, or tri-sodium phosphate, borax, etc. These additions are also recommended with higher molecular naphthols, phenols, hydroxy quinolines, acid methylene compounds, etc., which in the free state are almost or entirely insoluble, and, therefore, hardly reduce the sensitivity when they are added to the emulsion; they also resist the developers containing sodium carbonate, as the dibenzoyl methane mentioned by Fischer (Phot. Korr. 1914, 21) or the higher aceto-acetic arylides.

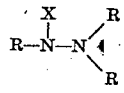
Of course, insoluble salts of the naphthols, etc., with such organic bases may be added to the emulsions, which are decomposed by stronger organic or inorganic bases in the developer under liberation of the not entirely insoluble, but in itself or in the form of the salts of non-diffusing or slightly diffusing naphthol or phenol derivatives, of higher molecular methylene compounds, etc. (German Patents 229,814; 485,523; 514,421; 519,051; U. S. Pat. 1,953,309).

The hydrazides of the aceto-acetic homologues and analogues, of the α-naphthol-carboxylic acids, hydroxy-quinoline-carboxylic acids, arylalkyl-pyrazolone carboxylic acids and sulfonic acids obtained with asymmetrical diphenyl hydrazine are especially difficultly soluble. They may be easily obtained by heating with the ketonic acid ester to above 100° C. or conversion with the other acyl chlorides at ordinary or moderately high temperature in the presence of tertiary bases. Their salts with the bases mentioned are usually insoluble, non-diffusing or slightly diffusing through the gelatin emulsions. The residual hydrogen atom of the amino group may also be substituted by methyl or still higher alkyls as stearyl, palmityl, ceryl, etc., or the alkylated asymmetrical diphenylhydrazine may be used at once for the hydrazide formation. On the other hand, one may also use asymmetrical naphthylphenyl hydrazine, asymmetrical dinaphthyl hydrazine, asymmetrical phenyl-palmityl hydrazine as well as other arylalphyl hydrazines. Less used are the symmetrical substi-

tuted aliphatic, aromatic and mixed hydrazines on account of their difficult preparation. Still better are the bis-hydrazides which are easily obtained from the dihydrazines of benzidine, diphenylene, naphthidine, etc., alkylated or arylated in the amino group. The urea chloride or isocyanate (B. 36,3155) formed from asymmetrical diphenyl hydrazine with phosgene may be converted with amino-α-naphthalene and other coupling components containing an amino group.

We claim:

1. The method of forming a colored image in a photographic layer which comprises developing a silver halide layer in an aromatic amino developer and coupling the oxidation product of the developer with an aryl hydrazide coupler having the structure



in which X is an acyl group, at least one R is an aryl radical, and the remaining R's are selected from the class consisting of hydrogen, alkyl radicals, and aryl radicals.

2. The method of forming a colored image in a photographic layer which comprises developing a silver halide layer in an aromatic amino developer and coupling the oxidization product of the developer with an aryl hydrazide of acetoacetic acid.

3. The method of forming a colored image in a photographic layer which comprises developing a silver halide layer in an aromatic amino developer and coupling the oxidization product of the developer with an aryl hydrazide of α-naphthol carboxylic acid.

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