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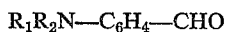
NEW PROCESS FOR COLOUR PHOTOGRAPHY

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This invention relates to a new process for colour photography.

In British specification No. 651,059 there is described and claimed a subtractively coloured multilayer photographic element which comprises a base and superimposed thereon three layers containing a cyan dyestuff image, a magenta dyestuff image and a yellow dyestuff image respectively, characterised in that the layer which contains the magenta dyestuff image also contains a yellow styryl masking image. There is also described and claimed an improved process for colour photography which comprises developing with a colour forming developer, an exposed multilayer photographic element comprising a base and superimposed thereon 3 differently sensitised silver halide emulsion layers containing respectively a cyan colour former which does not react with aldehydes to give coloured compounds, a magenta colour former which contains in its molecular structure a reactive methylene group, and a yellow colour former which does not react with aldehydes to give coloured compounds, and subsequently treating the photographic element with an aromatic aldehyde of the benzene or naphthalene series which contains at least one auxochromic group, or with a functional derivative thereof, for example an aldehyde of the formula $\text{RNH}-\text{C}_6\text{H}_4-\text{CHO}$ or



where R, R₁ and R₂ are alkyl, aryl, or aralkyl, hydroxyalkyl, halogenoalkyl, cyanoalkyl, nitroalkyl, carboxyalkyl or sulphaalkyl, or where R₁ and R₂ together with the nitrogen atom form part of a 5- or 6-membered ring, and where the benzene nucleus may carry substituents such as nitro, alkyl, halogen, sulphonic acid or carboxylic acid groups.

In this way a yellow styryl dyestuff masking image is formed in the magenta layer by reaction of the aldehyde with the residual colour coupler but the intensity of this mask must be carefully regulated by the processor of the exposed photographic material and cannot be accurately controlled by the manufacturer of the light-sensitive material.

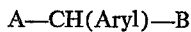
In British specification No. 673,091 there is described an improved process for making a colour corrected photographic record which comprises developing with a colour forming developer a latent image bearing photographic element obtained by exposing to light a photographic element comprising a base and at least three silver halide emulsion layers sensitive to different parts of the spectrum, one such layer containing as a magenta colour former, a homogeneously distributed water-soluble yellow styryl dyestuff, obtained by treating a reactive methylene compound with the anil of a p-substituted-amino-benzaldehyde. By this automatic masking process the necessity for after-treatment with an aromatic aldehyde is obviated but it is found that in the colour development step the reaction of the styryl dyestuff with the primary aromatic amino compounds used for development is less rapid than the reaction of the parent magenta colour coupler with the primary aromatic amino compounds.

We have now found that by using as magenta colour couplers the colourless or substantially colourless derivatives of reactive methylene compounds formed by treat-

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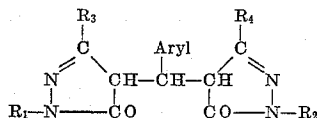
ing certain reactive methylene compounds with oximes of certain aromatic aldehydes, masking images of the correct intensity can readily be obtained by a simple treatment after the development step without any serious effect on the speed of colour development, the speed of colour development being appreciably higher than that of the corresponding styryl dyestuff.

The derivatives of reactive methylene compounds used in the process of our invention are the colourless or substantially colourless compounds of the formula



where $-\text{CH}(\text{Aryl})-$ is the residue of an aromatic aldehyde of the benzene or naphthalene series which contains at least one auxochromic group, where A and B, which may be the same or different, are the residues of reactive methylene compounds which themselves are magenta colour formers (that is to say compounds which yield magenta dyestuffs when exposed photographic elements containing them are developed with a colour forming developer, for example p-N:N-diethylaminoaniline) and where A, B or the aryl radical contains at least one sulphonic acid or carboxylic acid group. These compounds may be made by reaction of the appropriate reactive methylene compounds with oximes of aromatic aldehydes of the benzene or a naphthalene series which contain at least one auxochromic group.

For example the compounds obtained from an oxime of an aromatic aldehyde and a substituted pyrazolone may be represented by the formula



wherein Aryl is an aryl nucleus of the benzene or naphthalene series which contains at least one auxochromic group, R₁ and R₂ are hydrogen or aryl, R₃ and R₄ are alkyl, aryl, amino or substituted amino radicals and wherein R₁, R₂, R₃, R₄ or the Aryl radical contains at least one carboxylic or sulphonic acid group.

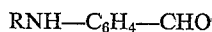
The compounds may also be made by treating 2 molecular proportions of the reactive methylene compound with 1 molecular proportion of the aldehyde or by heating 1 molecular proportion of the corresponding styryl dyestuff (itself made from equimolecular proportions of the reactive methylene compound and the aldehyde) with 1 molecular proportion of the reactive methylene compound.

According to the present invention there is provided a new process for colour photography which comprises developing with a colour forming developer, an exposed multilayer photographic material comprising three differently sensitised gelatino-silver halide emulsion layers, one such layer containing a yellow colour coupler another such layer containing a magenta colour coupler and the other such layer containing a cyan color coupler, wherein the magenta colour coupler is a derivative of a reactive methylene compound as hereinbefore defined, and subsequently treating the photographic material with formaldehyde, or nitrous acid.

As examples of suitable classes of reactive methylene compounds there may be mentioned: pyrazolones, for example 1-(4'-phenoxy-3'-sulphophenyl)-3-heptadecyl-5-pyrazolone, 1-(3'-carboxyphenyl)-3-(4'-stearylamino-phenyl)-5-pyrazolone, 1-(3'-sulphomethyl-phenyl)-3-heptadecyl-5-pyrazolone, 1-(4'-sulphophenyl)-3-octadecylamino-5-pyrazolone; oxindoles, for example oxindole itself and N-amyloxindole; rhodamines, for example N-ethyl rhodamine; diketopyrazolidines, for example 1:2-diphenyl or 1:2-di(p-chlorophenyl)-3:5-diketopyrazolidine, coumara-

ones, thioindoxyls, cyanoacetyl compounds, for example the mono-p-(omega-cyanoaceto)anilide of octadecenylsuccinic acid, cyano-acetyl urea and its N-substituted derivatives, and imidazolones.

As said, the aromatic aldehydes of the benzene or naphthalene series must contain at least one auxochromic group, for example a hydroxy or amino group or a substituted hydroxy or amino group. For example there may be used p-hydroxybenzaldehyde, 2:4-dimethoxybenzaldehyde or an aldehyde of the formula



or R'R''N—C₆H₄—CHO where R, R' and R'' are alkyl, aralkyl, hydroxyalkyl, alkoxyalkyl, halogenoalkyl, cyanoalkyl, nitroalkyl, carboalkyl or suphoalkyl, or where R' and R'' together with the nitrogen atom form part of a 5- or 6-membered ring, and where the benzene nucleus may carry substituents such as for example, nitro, alkyl, alkoxy, halogen, sulphonic acid or carboxylic acid groups. Specific examples of such aldehydes are

p-(N-methyl-N-β-hydroxyethylamino)-benzaldehyde,
 p-(N-ethyl-N-β-hydroxyethylamino)-benzaldehyde,
 p-(β:β'-dihydroxydiethylamino)-benzaldehyde,
 p-(N-methyl-N-β-methoxyethylamino)-benzaldehyde,
 p-(N-ethyl-N-β-methoxyethylamino)-benzaldehyde,
 p-(N-butyl-N-β-hydroxyethylamino)-benzaldehyde,
 p-(N-methyl-N-β-chloroethylamino)-benzaldehyde,
 p-(N-ethyl-N-β-chloroethylamino)-benzaldehyde,
 p-(β:β'-dichlorodiethylamino)-benzaldehyde,
 4-(β:β'-dichlorodiethylamino)-2-methyl-benzaldehyde,
 p-(N-methyl-N-β-cyanoethylamino)-benzaldehyde,
 p-(β:β'-dicyanodiethylamino)-benzaldehyde,
 p-di-(ethylcarboxymethyl)-amino-benzaldehyde,
 p-(N-methyl-N-β-sulphoethyl-amino)-benzaldehyde,
 p-(N:N-β:β'-disulphodiethylamino)-benzaldehyde,
 4-(N:N-β:β'-disulphodiethyl-amino) - 2 - methyl-benzaldehyde,
 p-(N-methyl-N-β-carboxyethyl-amino)-benzaldehyde,
 p-(N:N-β:β'-dicarboxydiethyl-amino)-benzaldehyde,
 p-N-di-(carboxymethyl)-amino-benzaldehyde,
 p-(N-β-sulphoethyl-amino)-benzaldehyde,
 4-(N,N-dimethyl-amino)-2-sulphobenzaldehyde,
 4-(N:N-β:β'-dichlorodiethylamino) - 2 - sulphobenzaldehyde.

By suitable choice of aromatic aldehyde-oxime for use with any particular magenta colour former, for example by suitable choice of R, R' and R'' in the above formulae a masking colour can be obtained which possesses the required absorption characteristics to compensate for the undesired blue absorption of the magenta azomethine dyestuff obtained by colour development with the aromatic amine such as p-diethylaminoaniline.

The oximes of the aldehydes may be made by heating the parent aldehyde in ethanolic solution with hydroxylamine, concentrating the solution, extracting with ether, drying and distilling off the ether.

According to a further feature of my invention I provide a process for the manufacture of a magenta colour coupler which comprises treating a magenta colour coupler containing a reactive methylene group with an oxime of an aromatic aldehyde of the benzene or naphthalene series containing at least one auxochromic group.

The reaction of the reactive methylene compound and the oxime may be conveniently carried out by heating the reagents together in aqueous alcoholic solution, for example aqueous methanolic solution and the product may be isolated by evaporating the solution to dryness. When the reactive methylene compound or aldehyde used as starting material contains a carboxylic or sulphonic acid group, this reactive methylene compound or aldehyde is preferably used in the form of a water-soluble salt for example an alkali-metal salt and the new colour coupler is obtained in the form of a salt. In general one molecular proportion of aldehyde oxime is required for each two molecular proportions of reactive methylene compound

but an excess of oxime can be used if desired, and the excess can then be recovered from the reaction mixture.

The new colour couplers may contain substituents which render them non-diffusible in gelatine for example an alkyl chain of at least 5 carbon atoms or they may be rendered non-diffusible by any other method used in practice or known from the literature for preventing the diffusion of colour formers in gelatino-silver halide emulsion layers.

The new colour couplers of my invention may be used as the magenta colour couplers in colour photographic processes in which there are employed differently sensitised silver halide emulsion layers containing different colour couplers or a layer containing a mixture of grains of differently sensitised emulsions containing different colour couplers. For example the new colour couplers may be used as the magenta colour coupler in a colour-photographic negative in which the top layer which is sensitive to blue light (that is to say is not spectrally sensitised) and contains a yellow colour coupler is separated by a yellow filter layer from a green-sensitive layer containing a magenta colour coupler and a red-sensitive layer containing a cyan colour coupler. As yellow colour couplers there may be used for example compounds of the acylacetylarylamide series and as cyan colour couplers there may be used for example compounds of the 1-naphthol series.

When the new couplers are added to silver halide emulsions it is sometimes advantageous to add hydroxylamine which appears to have a stabilising effect on the new colour couplers, especially when these are prepared from the corresponding free aldehyde or from the corresponding styryl dyestuff instead of from the oxime.

When a silver halide emulsion containing one of the new colour couplers of our invention is exposed to light and then colour developed with a p-dialkylaminoaniline a magenta image is obtained. The residual colour coupler in the emulsion is colourless and accordingly has no masking effect but by treatment with formaldehyde or nitrous acid at any stage subsequent to the colour development step, the residual colour coupler is converted to a yellow styryl dyestuff which forms the reverse masking image which corrects for the undesired blue absorption of the primary magenta image.

The formaldehyde or nitrous acid treatment may be carried out as a separate operation if desired, at any stage after colour development, but to avoid complication of the processing operations the formaldehyde or nitrous acid may be added to the stop-bath used after colour development, and the photographic material may then be bleached, and fixed.

The treatment of a colour developed photographic material with formaldehyde or nitrous acid to develop the yellow styryl dyestuff masking image from residual colour coupler can be conveniently arranged to serve also for forming the leuco derivative of a red dyestuff masking image from residual cyan colour coupler by the process of British specification No. 723,171 and this leuco compound may then be oxidised in the bleaching bath to form the red masking dyestuff.

The invention is illustrated but not limited by the following examples in which the parts are by weight:

Example 1

A multilayer light sensitive photographic material is made up as follows:

A red sensitive gelatino-silver halide emulsion layer containing 10 grams per litre of the cyan colour forming component 1 - hydroxy-2-naphthoylamino-2'-N - methyl-octadecyl-aminobenzene-5'-sulphonic acid (as the sodium salt), is coated on a transparent support. On this layer there is coated a green sensitive gelatino-silver halide emulsion layer containing 10 grams per litre of the pyrazolone-aldehyde oxime reaction product obtained as described below. A layer of colloidal silver in gelatin

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is coated on to act as yellow filter layer and finally a stop layer a blue sensitive gelatino-silver halide emulsion containing 10 grams per litre of p-stearyl-aminobenzoylacetaniline-p-carboxylic acid sodium salt (the yellow colour forming component described in Example 3 of British specification No. 486,848) is coated. The film is exposed to the light from a coloured object and then developed in a solution of the following composition:

	Parts
5-diethylamino-2-aminotoluene hydrochloride.....	2.5
Sodium sulphite anhydrous.....	2
Hydroxylamine hydrochloride.....	1
Sodium carbonate anhydrous.....	60
Potassium bromide.....	2
Water to make up to.....	1,000

The film is rinsed and transferred to a stop bath of the following composition:

	Parts
Acetic acid, glacial.....	15
37% formaldehyde solution.....	30
Sodium acetate.....	25
Water to make up to.....	1,000

The film is washed and transferred to a bleaching bath solution of the following composition:

	Parts
Potassium ferricyanide.....	100
Potassium bromide.....	25
Sodium dihydrogen phosphate.....	50
Water to make up to.....	1,000

The film is further washed, fixed in a 20% aqueous solution of sodium thiosulphate, finally washed and dried.

This processed material contains in the first layer a cyan dyestuff negative image, in the second layer a magenta dyestuff negative image and a yellow dyestuff positive image (formed by reaction of the unused colour former with the formaldehyde of the stop bath) which serves to correct the undesirable absorption of blue light by the magenta dyestuff, and in the top layer a yellow dyestuff negative image. When the negative transparency so obtained is used for making positive prints, duplicate negatives, and separation negatives, the colour rendering is greatly improved compared with reproduction from negative transparencies which have not been masked.

The multilayer material prepared as described in this example when bleached and fixed without exposure to light is found to contain substantially colourless clear gelatin layers.

If in the processing of the exposed material in the example above, the stop-bath containing no formaldehyde is used, the final magenta negative image is obtained without a compensating yellow mask. The yellow mask may then be introduced after the fixing step by treating the material with a solution of the following composition:

	Parts
37% formaldehyde solution.....	30
Anhydrous sodium carbonate.....	10
Water to make up to.....	1,000

The pyrazolone-aldehyde oxime reaction product used in the above example may be prepared as follows:

57 parts of 1-(4'-phenoxy-3'-sulpho)-phenyl-3-heptadecyl-5-pyrazolone are stirred with 175 parts of methanol, a solution of 4.4 parts of sodium hydroxide in 110 parts of water is added and the mixture is heated to 50° C. when a clear solution is obtained. 600 parts of water at 50° C. are added and the mixture is stirred while a solution of 16 parts of p-di-(ethylcarboxymethyl)aminobenzylidene oxime in 80 parts of methanol at 50° C. is added. The mixture is stirred at 50° C. for 18 hours, and evaporated to dryness in vacuo when a pale fawn-coloured solid (the sodium salt) is obtained. This sodium salt is very soluble in water.

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The p-di-(ethylcarboxymethyl)-aminobenzylidene oxime used above may be prepared as follows:

63 parts of p-di-(ethylcarboxymethyl)aminobenzaldehyde are dissolved in 500 parts of hot ethanol and a solution of 19 parts of hydroxylamine hydrochloride and 16 parts of anhydrous sodium carbonate in 130 parts of water is added. The mixture is boiled under a reflux condenser for 3 hours and then concentrated in vacuo. The concentrated solution is extracted with ether and the ethereal solution so obtained is dried over anhydrous sodium sulphate. The ether is distilled off and the residual gummy product slowly solidifies to an almost white solid oxime.

The oxime is completely soluble in dilute sodium hydroxide solution.

Example 2

A multilayer light sensitive material is made up as follows:

A transparent support material is coated with a layer of red sensitive gelatino-silver halide emulsion containing 10 grams per litre of the sodium salt of 1-hydroxy-2-naphthoylamino-2'-(N-methyl-N-octadecylamino)-benzene-5'-carboxylic acid. On this layer there is coated a green-sensitive emulsion containing 10 grams per litre of the pyrazolonealdehyde oxime reaction product used in Example 1. A layer of colloidal silver in gelatine is coated on to act as a yellow filter layer and finally as the top layer there is coated a blue sensitive gelatino-silver halide emulsion containing 10 grams per litre of 3-(p-anisoylacetamido)-4-(N-methyloctadecylamino)-benzoic acid, sodium salt. The film is exposed to the light from a coloured object and then developed in a solution of the following composition:

	Parts
p-N:N-diethylamino-aniline sulphate.....	2.5
Sodium sulphite anhydrous.....	2
Hydroxylamine hydrochloride.....	1
Sodium carbonate anhydrous.....	30
Potassium bromide.....	0.5
Water to make up to.....	1,000

The film is then transferred to a stop bath of the following composition:

	Parts
Acetic acid, glacial.....	10
Sodium acetate.....	20
37% formaldehyde solution.....	20
Water to make up to.....	1,000

At this stage the film contains the first developed silver, the azomethine dyestuff negative images in the three layers, a yellow dyestuff positive masking image produced by the formaldehyde in the middle magenta forming layer, and a colourless leuco form of a red dyestuff positive masking image in the cyan layer. The material is thoroughly washed and the silver is bleached and fixed as described in Example 1. During the bleaching stage the leuco dyestuff of the bottom layer is converted to the red dyestuff masking image.

The final material contains in the bottom layer a cyan dyestuff negative image and a red dyestuff positive image (which serves as a mask to correct for the undesired blue and green absorption of the cyan dyestuff), in the second layer, a magenta dyestuff negative image and a yellow dyestuff positive image (which serves as a mask to correct for the undesired blue absorption of the magenta dyestuff), and in the top layer a yellow dyestuff negative image.

In place of the stop bath used in the above example there may be used a bath of the following composition:

	Parts
37% formaldehyde solution.....	30
Sodium carbonate anhydrous.....	10
Water to make up to.....	1,000

Example 3

In place of the green sensitive gelatino-silver halide emulsion containing 10 grams of the pyrazolone-aldehyde oxime reaction product per litre of emulsion used in Example 1 there is used a green sensitive gelatino-silver halide emulsion containing 10 grams of the colour coupler made as described below per litre of emulsion together with 0.1 gram of hydroxylamine per litre of emulsion.

The colour coupler used in this example is prepared as follows:

57 parts of 1-(4'-phenoxy-3'-sulpho)-phenyl-3-heptadecyl-5-pyrazolone are stirred with 500 parts of methanol and 5.5 parts of sodium methylate in 60 parts of methanol are added. A clear solution is obtained. 15 parts of p-di-(ethylcarboxymethyl)aminobenzaldehyde are added and the solution is allowed to stand for 36 hours. The methanol is removed by evaporation in vacuo at 30° C. and the residue is washed with ether, filtered and dried. The pale fawn-coloured product is soluble in water.

Example 4

In place of the green-sensitive gelatino-silver halide emulsion used in Example 2 containing 10 grams of the pyrazolone-aldehyde oxime reaction product per liter of emulsion there is used a green sensitive gelatino-silver halide emulsion containing 10 grams of the colour coupler described in Example 3 per liter of emulsion together with 0.1 gram of hydroxylamine per litre of emulsion.

Example 5

In place of the green-sensitive gelatino-silver halide emulsion containing 10 grams of the pyrazolone-aldehyde oxime reaction product per litre of emulsion used in Example 1, there is used a green sensitive gelatino-silver halide emulsion containing 10 grams of the colour coupler made as described below per litre of emulsion together with 0.1 gram of hydroxylamine per litre of emulsion.

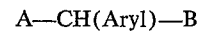
The colour coupler used in this example is prepared as follows:

57 parts of 1-(4'-phenoxy-3'-sulpho)-phenyl-3-heptadecyl-5-pyrazolone are stirred in 500 parts of methanol and 5.5 parts of sodium methylate in 60 parts of methanol are added. A clear solution is obtained. 6.1 parts of p-hydroxybenzaldehyde are added and the solution is allowed to stand for 36 hours. The methanol is removed by evaporation in vacuo at 30° C. and the residue is washed with ether, filtered and dried. The pale fawn-coloured product is soluble in water.

What I claim is:

1. A process for color photography which comprises

developing with a color forming developer, an exposed multilayer photographic material comprising three differently sensitized gelatino-silver halide emulsion layers, said layers containing color formers adapted to yield, upon exposure and development, yellow, cyan and magenta colored images in separate layers, the color former yielding the magenta colored image being an at least substantially colorless compound of the formula:



wherein (Aryl) is selected from the group consisting of phenyl and naphthyl containing at least one auxochromic group selected from the class consisting of hydroxy, alkoxy, and secondary and tertiary amino groups, A is a reactive methylene magenta color former group coupled through the carbon of the reactive methylene, B is a magenta color forming pyrazolonyl-4 group and one of A, B and (Aryl) contains at least one member of the class consisting of sulfonic acid and carboxylic acid groups, and treating the photographic material after development with a member of the group consisting of formaldehyde and nitrous acid.

2. The process of claim 1 wherein said color former yielding the magenta image is the reaction product of 2 moles of 1-(4'-phenoxy-3'-sulpho)-phenyl-3-heptadecyl-5-pyrazolone and one mole of p-di-(ethyl-carboxymethyl) amino-benzylidene oxime.

3. The process of claim 1 wherein said color former yielding the magenta image is the reaction product of 2 moles of 1-(4'-phenoxy-3'-sulpho)phenyl-3-heptadecyl-5-pyrazolone and one mole of p-di-(ethyl-carboxymethyl) aminobenzaldehyde.

4. The process of claim 1 wherein said color former yielding the magenta image is the reaction product of 2 moles of 1-(4'-phenoxy-3'-sulpho)-phenyl-3-heptadecyl-5-pyrazolone and one mole of p-hydroxybenzaldehyde.

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