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PROCESS FOR THE PRODUCTION OF PHOTOGRAPHIC COLOR IMAGES

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This invention relates to the manufacture of photographic color images.

It is known to convert dyestuff intermediate products into dyestuffs for the production of photographic color images on the exposed or unexposed parts of the picture directly or indirectly by means of a metal salt image, especially silver salt image. These dyestuff intermediate products which in photography are mostly called color formers may be employed in various ways. They may be incorporated into the finished photographic layers or may be brought in contact with them or may be added to the photographic emulsion before casting.

One object of the present invention is to produce photographic color images.

Still another object is to obtain these color images directly or indirectly by means of a silver- or silver halide image and by means of organic color formers.

A further object is the application of new and useful color formers for the production of photographic color images.

These and other objects will become apparent from the following specification.

In the first group of processes the color formers may be brought in contact with a suitable metal- or metal salt image which converts by its oxidizing or reducing capacity the color former into an insoluble dyestuff, the latter being precipitated in the emulsion layer, or the color formers may be brought in contact with a silver salt containing a diazo-component, the diazo-component thus forming an azo-dyestuff with the color former. The color formation may furthermore be accomplished by a so called "coupled reaction". A very important reaction is the colar forming development in which the color former simultaneously with a developing substance is brought in contact with a silver salt capable of being developed. The oxidation products formed during the development react at once with the color former yielding a dyestuff which is immediately precipitated. In the other group of processes the color formers are added to the photographic emulsion before casting. When using color formers within the photographic layers, they should not diffuse from one layer into the other. Preferably there are used in this case color formers fast to diffusion or leucodyestuffs or color formers which contain substantive groups or long chain radicals, and which on account of their affinity for the gelatin or on account of a suitable steric arrangement of the atoms in the color former molecule are not able to diffuse, though they are added to the emulsion in dissolved form. Also color formers were proposed which on account of their high molecular weight are scarcely soluble or are insoluble in water or alkalies and which therefore possess low diffusibility.

For the production of blue dyestuffs, especially in the color forming development process there come into question especially phenols and their analogs and homologs, whereas the red and yellow dyestuffs are preferably obtained with the aid of such compounds which contain reactive methylene groups, such as pyrazolones or acylacetic acid anilides. In the case of the color forming development the pyrazolones as is known yield red dyestuffs of various color shades and the acylacetic acid anilides yield yellow dyestuffs. When worked up into azo-dyestuffs similarly yellow and red color tinges are obtained.

Pyrazolones, i. e. red coupling substances in the color forming development method which may be substituted in various ways are available in great number, so that red dyestuffs may be obtained in any desired color tinge from brick-red to bluish purple, whereas contrary to that the selection among acylacetic ester derivatives is relatively limited. Here there are known only the anilides and amongst these a great number of possibilities is eliminated, because the corresponding amines are not reactive with the acylacetic esters. Especially known are the condensation products of acylacetic esters, especially benzoyl acetic esters with aniline and its homologs and analogs, such as toluidine, xylidine, naphthylamine, reaction products of two mols of acylacetic ester with benzidine, tolidine, anisidine, condensation products from terephthaloyl-bis-acetic ester with aniline and its homologs. Furthermore there are known reaction products of higher acylacetic esters, such as lauric acetic ester with p-amino benzoic acid and with aniline. Furthermore there have been proposed the condensation products of amino benzoyl-acetyl-aniline with stearic acid, abietic acid and similar substituents preventing diffusion. The short description of known acylacetic ester derivatives adapted for photographic purposes shows that in this group relatively little possibility of variation exists. The products are always aromatic amides which, moreover, are neutral or substituted with at most one carboxyl group. Correspondingly also the color tinges obtained in photographic layers with the aid of these acylacetic ester derivatives is very limited.

The solubility of the higher molecular derivatives is not always sufficient, to give enough transparency to a gelatin layer containing these compounds. It is therefore desirable to have at one's disposal new components adapted for the manufacture of red and especially yellow dyestuffs. In this way it is possible to produce a great number of color tinges with higher molecular compounds of improved solubility.

It has been found that the reaction products of diketenes with compounds containing amino groups or hydroxy groups are very suitable as color formers for red and yellow dyestuffs. Such reaction products, for example, may be obtained according to the U. S. Patents 1,982,675, 2,152,786, 2,017,815, 2,152,132, 2,152,787. Since nearly every substance containing hydroxy- or amino groups may be caused to react with diketenes, an extraordinary great number of various color formers is obtained with which a correspondingly great number of color tinges may be attained. Furthermore these new color formers may contain one or several acid groups or other groups effecting water-solubility, so that in higher molecular representatives of this group any desired solubility may be attained.

The great number of these possible diketene derivatives naturally allows one to adjust the color formers to the desired conditions with regard to fastness to diffusion, molecular magnitude and the like.

Of special significance are such derivatives of diketenes which besides the reactive methylene groups contain groups effecting solubility in water, such as carboxyl-, sulfo-, hydroxy-groups or which possess one or more nitro group adapted for further reactions, or which carry simultaneously the two last mentioned groups, furthermore the reaction products of diketenes with polymers containing amino- or oxy groups, the reaction products of diketenes with aliphatic mono- or polyvalent amines or such aliphatic amines which carry groups effecting solubility in water, the reaction products of diketenes with aromatic-aliphatic amines, in which the aromatic nucleus and one or several of its aliphatic side chains may be substituted with one or several amino- or nitro groups, the reaction product of diketenes with aromatic-aliphatic mono- or polyvalent amines which carry one or several groups effecting solubility in water, the reaction products of diketenes with heterocyclic compounds which carry one or several amino- or hydroxy groups and which, if necessary, may be substituted by acid groups, the reaction products of diketenes with urea and its derivatives, the reaction products of diketenes with ammonia and with such compounds which are themselves fast to diffusion in gelatin and other colloids or which render reaction products with other compounds, such as heptadecylamine, abietylamine, cholesterylamine, polyvinylalcohol, fast to diffusion and which besides that may contain groups effecting solubility in water.

Suitable ketene derivatives are those obtained by the reaction of diketenes with the following compounds:

Aromatic mono- and polyvalent amino carboxylic acids, such as anthranilic acid, 4-chloro-2-amino benzoic acid, 2-(m-aminobenzene)-sulfaminobenzoic acid, 4-nitro-2-amino-benzoic acid, 6-chloro-2-amino-benzoic acid, 5-chloro-2-amino-benzoic acid, 4-nitro-2-amino-benzoic acid, 5-nitro-2-amino-benzoic acid, 3-amino-benzoic acid, 6-chloro-3-amino-benzoic acid, 5-nitro-3-amino-benzoic acid, 6-nitro-3-amino-benzoic acid, 2-amino-5-acetylamino-benzoic acid, 4-amino-benzoic acid, 2-nitro-4-amino-benzoic acid, 3-nitro-4-amino-benzoic acid, 3'-nitro-4-benzoyl-amino-benzoic acid, 4-amino-benzoic acid, 3,4-diamino-benzoic acid, 3-amino-2-hydroxybenzoic acid, m-amino-benzoyl-3-amino-2-hydroxybenzoic acid, 5-amino-2-hydroxybenzoic acid, 3'-amino-4'-methylbenzoyl-5-amino-hydroxybenzoic acid, 3-nitro-5-amino-2-hydroxybenzoic acid, 3-amino-benzoyl-p-amino-salicylic acid, 4-aminobenzoyl-p-aminosalicylic acid, 3-amino-4-hydroxybenzoic acid, 3-amino-4-methoxy-benzoic acid, 3-amino-4-ethoxy-benzoic acid, 5-nitro-3-amino-2-hydroxybenzoic acid, m-aminophenolcarboxylic acid, 5-methyl-3-amino-2-hydroxybenzoic acid, p-amino-m-cresotic acid, α-aminophthalic acid, β-aminophthalic acid, 5-amino-1,3-benzenedicarboxylic acid, aminophenyl-glyoxylic acid, benzidine-dicarboxylic acid, 2,3-amino-naphthoic acid, amino-chrysene-carboxylic acid, aminohydroquinone-diacetic acid, amino-benzene-diacetic acid, 3-amino-benzoic-nitril, α-aminophenylacetic acid, 4-amino-propionic acid, phenylalanine, 2-amino-cinnamic acid, 3-amino-cinnamic acid, 4-amino-cinnamic acid, phenylacetic acid amide, 4-amino-3-acetyltoluene, 3-aminobenzoic acid-dimethylamide, 4-amino-benzoic acid-dodecylamide, 3-amino-benzoic acid-abietylamide, 4-amino-benzoic acid-oleylamide, 3-amino-1-benzoylamino-benzene, 3-amino-1-benzoylamino-naphthol, β-amino-crotonic acid anilide, 4-amino-1-(N-methyl-benzoylamino)-benzene, 3-aminophenyl-glycin, 4-aminophenyl-glycin, 2,4-diamino-benzoic acid, 2,5-diamino-benzoic acid, 3,5-diamino-benzoic acid, 2-amino-4-acetamino-benzoic acid, 3-amino-1-(3'-chloro-benzoyl-amino)-benzene, 4-chloro-2-amino-acetanilide, 6-chloro-3-amino-1-benzoylamino-benzene, 2-chloro-1-(3'-amino-benzoylamino)-benzene, 4,4'-diamino-diphenylurea-3,3'-dicarboxylic acid.

Reaction products of diketenes with aromatic sulfo-carboxylic acids, such as:

4-amino-acetanilide-2-sulfoacid, 3-chloro-2-amino-toluene-5-sulfoacid, 6-chloro-3-amino-toluene-4-sulfoacid, 4-sulfo-2-methyl-aminobenzoic acid, 4-sulfo-2-amino-benzoic acid, 5-sulfo-2-amino-benzoic acid, 5-sulfo-3-amino-2-hydroxybenzoic acid, 3-sulfo-5-amino-2-hydroxybenzoic acid.

Reaction products of ketenes or diketenes with aromatic aminosulfoacids, such as:

2-amino-toluene-4-sulfoacid, 3-amino-toluene-5-sulfo-acid, 4-amino-toluene-2-sulfo acid, 2-amino-toluene-ω-sulfo acid, 2-methyl-amino-toluene-ω-sulfo acid, 2-amino-toluene-3,5-disulfo acid, 4-amino-toluene-2,5-disulfo acid, 5-chloro-2-amino-toluene-4-sulfo acid, 2,5-dichloroaniline-3-sulfo acid, 2,5-dichloro-aniline-4-sulfo acid, 3,4-dichloro-aniline-5-sulfo acid, 3-bromo-2-amino-toluene-5-sulfo acid, 4-bromo-aniline-2-sulfo acid, 2-nitro-4-amino-toluene-6-sulfo acid, 6-nitro-4-amino-1-3-xylol-5-sulfo acid, 3-nitro-aniline-6-sulfo acid, 4-nitro-aniline-2-sulfo acid, 4-amino-diethylaniline-3-thiosulfo acid, 4-amino-2'-4'-dimethyl-diphenylamine-2-sulfo acid, 4-amino-diphenylamine-3-sulfo acid, 4-amino-1-(N-methyl-4'-toluenesulfamino)-benzene, 3-amino-1-(4'-toluene-sulfamino)-benzene, 2-amino-4-(4'-toluenesulfamino)-toluene, 3-diamino-benzene-5-sulfoacid, 4,4'-diamino-diphenylamine-2-sulfo acid, 2,4-diamino-toluene-6-sulfo acid, 2,5-diamino-toluene-4-sulfo acid, 2,6-diamino-toluene-4-sulfo

acid, 3,4-diamino-toluene-5-sulfo acid, 2,4,3'-triamino-diphenylamine-4'-sulfo acid, 4,2'-4'-triamino-diphenylamine-3-sulfo acid, 4,4'-diamino-diphenylamine- 2,3'-disulfo acid, 4-chloro-1,3-diaminobenzene - 5 - sulfo acid, 2,4 - dinitro-4'-amino-diphenylamine-3'-sulfo acid, 2,4-dinitro-4'-amino-diphenylamine-3'-sulfo acid, 6-nitro-1,3-diamino-benzene-4-sulfo acid, 2'-methoxy-4-amino-diphenylamine-2-sulfo acid, 4'-chloro-4-amino-diphenylamine - 2 - sulfo acid, 4'-methoxy-4-amino-diphenylamine-sulfo acid, 4-nitro-4'-amino-diphenylamine-2-sulfo acid, 4'-nitro-4-methyl-3-amino-diphenylamine-2'-sulfo acid, 3 - methyl - 4,4' - diamino -phenylamine-2'-sulfo acid, diamino - diphenyl - p - phenylene-diamine-disulfo acid, 4,4'-diamino-diphenyl-urea-3,3'-disulfo acid, di-p-amino-benzoyl-4,4'-diamino-diphenylurea-3,3'-disulfo acid, 2,2'-dimethoxy-4.4'-diamino-diphenylurea-3,3'-disulfo acid, benzidinemono-sulfo acid (4,4'-diamino-diphenyl-3-sulfo acid), benzidine-o-disulfo acid (4,4'-diamino-diphenyl-3,3'-disulfo acid), di-p-amino-benzoyl-benzidine-o-disulfo acid, benzidine-m-disulfo-acid (4,4'-diamino-diphenyl-2,2'-disulfo acid), mono-2,4-dinitro-phenylbenzidine-3-sulfo acid, benzidineoxamino acid, 2,2'-diamino-diphenyl-4,4'-disulfo acid, tolidine-o-monosulfo acid, tolidine-o-disulfo acid, tolidine-m-disulfo acid (3,3'-dimethyl-4,4'-diamino -diphenyl - 6,6'-disulfo acid), dianisidine-oxamino acid, 4,4'-diamino-3,3'-dimethoxy-diphenyl-6,6'-disulfo acid, diaminostilbene-disulfo acid, 3,3'-diamino-benzoyl-diamino-stilbene-disulfo acid, 1-naphthylamine-2-sulfo acid, 1-naphthylamine-3-sulfo acid, 1-naphthylamine-4-sulfo acid, 1-naphthylamine-5-sulfo acid, 4'-toluidine-2'-sulfonyl-1-naphthyl-amine-5-sulfo acid, 4-nitro-1-naphthylamine-5-sulfo acid, 1-naphthylamine-6-sulfo acid, 4-nitro-1-naphthylamine-6-sulfo acid, 1-naphthylamine-7-sulfo acid, 1-naphthylamine-8-sulfo acid, 1-naphthylamine-2,4-disulfo acid, 1-naphthylamine-2,5-disulfo acid, 1-naphthylamine-3,6-disulfo acid, 1-naphthylamine-3,7-disulfo acid, 1-naphthylamine-3,8-disulfo acid, 1-naphthylamine-4,6-disulfo acid, 1-naphthylamine-4,7-disulfo acid, 1-naphthylamine-4,8-disulfo acid, 1-naphthylamine-5,7-disulfo acid, 1-naphthylamine-6,8-disulfo acid, 1-naphthylamine-2,4,6-trisulfo acid, 1-naphthylamine-2,4,7-trisulfo acid, 1-naphthylamine-2,5,7-trisulfo acid, 1-naphthylamine-3,5,7-trisulfo acid, 1-naphthylamine-3,6,8-trisulfo acid, 1-naphthylamine-4,6,8-trisulfo acid.

Reaction products from diketenes with aminophenols and their homologs, also the corresponding carboxylic- and sulfo acids, such as:

Aminophenol, 4-chloro-2-aminophenol, 3,4,6,-trichloro-2-aminophenol, 4-nitro-2-aminophenol, 5-nitro-2-aminophenol, 4,6-dinitro-2-aminophenol, 5-nitro-4-chloro-2-aminophenol, 6-nitro-4-chloro - 2 - aminophenol, 4 - nitro-6-chloro-2-aminophenol, 2,4-diaminophenol, 2-amino-1,4-diethoxybenzene, 4-amino-1,3-dimethoxybenzene, 6-chloro-4-amino-1,3-dimethoxybenzene, 4-chloro-2-anisidine, 5-chloro-2-aminoanisol, 4-nitro-2-anisidine, 5-amino-2-acetylamino-anisol, 5-amino-4-chloro-2-oxalylamino-anisol, 5-amino-4-chloro-2-benzoylamino-anisol, 5 - amino - 4 - chloro-2-formyl-aminoanisol, 5-benzoylamino-2-amino-1,4-dimethoxybenzene, 2-nitro-5-amino-1,4-dimethoxybenzene, 2-nitro-5-amino-1,4-diethoxybenzene, 2-amino-5-acetylamino-1,4-dimethoxybenzene, 5-chloro-2-aminohydroquinone-dimethylether, 2-amino-diphenylether, 5-nitro-4-sulfo-2-amino-diphenylether, 4-sulfo-2-amino-diphenylether, 4,4'-dichloro-2-amino-diphenylether, 3-aminophenol, 3-anisidine, 2-chloro-4-aminophenol, 3-chloro-4-aminophenol, 2,6-dichloro-4-aminophenol, 2-nitro-4-aminophenol, 2-chloro-4-anisidine, 2-nitro-4-anisidine, 3-nitro-4-anisidine, 2-amino-4-acetaminoanisol, 3-nitro-4-amino-1-ethoxybenzene, 5-nitro-3-amino-2-cresol, 4-amino-2-cresol, 4-amino-2-cresol-methylether, 5-amino-2-cresol, 4,6-dinitro-2-amino-3-cresol, 6-amino-3-cresol-methylether, 2-amino-4-cresol, 2-amino-4-cresol-methylether, 3-amino-4-cresol, 5-nitro-3-amino-4-cresol, 6-nitro-3-amino-4-cresol-methylether, 6-amino-3-acetamino-4-cresol-methylether, 6-chloro-3-amino-4-cresol-methylether, 2-benzoyl-amino-5-amino-4-cresol-methylether, 3-amino-4-cresol-ethylether, 5-amino-4-methoxy-1,3-dimethylbenzene, 3-amino-1-isooctyl-4-phenyl-isopropylether, 1-amino-2-naphthol-hydrochloride, 1-amino-3-naphthol, 1-amino-5-naphthol-hydrochloride, 2-aminophenol-4-sulfo acid, 2-aminophenol-4,6-disulfo acid, 4-chloro-2-aminophenol-5-sulfo acid, 4-chloro-2-aminophenol-6-sulfo acid, 6-chloro-2-aminophenol-4-sulfo acid, 5-nitro-2-amino-1-hydroxybenzene-4-sulfo acid, 6-nitro-2-aminophenol-4-sulfo acid, 4-nitro-2-aminophenol-6-sulfo acid, 2,6-diaminophenol-4-sulfo acid, 2-anisidine-ω-methane-sulfo acid, 2-anisidine-4-sulfo acid, 1-methoxy-2-aminobenzene-4-sulfo-diethylamide, 1-methoxy-2-aminobenzene-4-sulfo-methylamide, 5-nitro-2-anisidine-4-sulfo acid, 5-nitro-2-anisidine-3-sulfo acid, 2,5-diaminoanisol-4-sulfo acid, 5-amino-2-acetylaminoanisol-4-sulfo acid, 4-sulfo-2-amino-diphenylether, 4-chloro-2-amino-diphenylether, m-aminophenol-3-sulfo acid, m-aminophenol-4-sulfo acid, 4-aminophenol-2-sulfo acid, 2-nitro-4-aminophenol-6-sulfo acid, 4-aminophenol-3-sulfo acid, 4-aminophenol-2,6-disulfo acid, 4-aminodiphenylether-2-sulfo acid, 2,4-diamino-diphenylether-4'-sulfo acid, 4,4'-diamino-diphenylether-2-sulfo acid, 3-amino-2-cresol-5-sulfo acid, 3-amino-4-cresol-5-sulfo acid, 1-amino-2-naphthol-4-sulfo acid, 1-amino-2-naphthol-6-sulfo acid, 1-amino-5-naphthol-6-sulfo acid, 1-amino-5-naphthol-2,7-disulfo acid, 2-amino-3-naphthol-6-sulfo acid, 2-amino-3-naphthol-6,8-disulfo acid, p-aminobenzoyl-2-amino-5-naphthol-7-sulfo acid, 3'-aminophenyl-5-hydroxynaphthothiazole-7-sulfo acid, 4'-aminophenyl-5-hydroxynaphthothiazole - 7-sulfo acid, 3'-aminophenyl-8-hydroxynaphthothiazole-6-sulfo acid, 1-naphthylamine-8-sulfo-3-carboxylic acid, 4-aminonaphthol-sulfo acid. These compounds may carry still other substituents, for example nitro groups, by the aid of which there may be introduced after the complete reduction further substituents into the color former. These substituents may impart new properties to the color formers. Such substituents are for instance the molecule groups preventing diffusion which were proposed in our former applications mentioned below, or are groups effecting solubility in water, such as chloroethane sulfo acid, chloro acetic acid. The reduced nitro groups may be used also for the introduction of further molecules adapted to form dyestuffs for new color tinges, such as phenols, pyrazolones, so that the dyestuff obtained in the photographic layer may be vastly influenced in its color shade.

Reaction products of diketene with sulphones, for example ditoluidine sulfon, further with azones, for example ditoluidine azone.

Reaction products of diketene with aminotriphenylmethane, m-amino-tetramethyl-diamino-

triphenylmethane, m-amino-tetra-ethyldiamino-triphenylmethane, diamino-di-o-methoxy-phenyl-phenyl-methane, diamino-di-p-xylylphenyl-methane, diamino-di-p-xylyl-o-chlorophenyl-methane, 1-amino-5-sulfonaphthyl-tetramethyl-diamino-diphenylmethane, 1-amino-2-sulfo-4-naphthyl - 4,4'-bis - (dimethylamino)-diphenyl-methane.

Reaction products of diketene with mono- and poly-valent aliphatic amines, for example methylamine, oleylamine, dodecylamine, octylamine, stearylamine, ethylenediamine, hexylenediamine, octylenediamine, putrescine, cadaverine, triethylene-tetramine, isobutylamine, diethylenetriamine, palm-kernel fatty acid amine mixture.

Reaction products of diketene with aliphatic amines containing acid groups, for example:

Sulfonated oleylamine, taurine, sarcosine, amino acetic acid, amino caproic acid, amino butyric acid, amino stearic acid, diamino succinic acid, diamino sebacic acid,

Reaction products of diketenes with aliphatic amines containing hydroxyl groups, for instance aminoethanol, oxyoleylamine, amino-oxybutyric acid, amino carbohydrates, for instance glucosamine or with amidated glycolchlorhydrin and with the amidated glycolchlorhydrin treated with ethyleneoxide,

Reaction products of diketenes with aromatic-aliphatic amines, for example benzylamine, nitrobenzylamine, nitrobenzylaminesulfo acid,

Reaction products of diketenes with aldehydes containing amino groups or ketones, for instance aminobenzaldehyde, aminoacetophenone, 3-amino-4-hydroxy-acetophenone,

Reaction products of diketenes with hydroaromatic or aromatic-hydroaromatic amines, such as are obtainable frequently as reaction products of natural substances, for example cyclohexylamine, perhydroamino-diphenyl, tetrahydro-α-naphthylamine, 1,2,3,4 - tetrahydro - 2 - naphthylamine, 5,6,7,8-tetrahydro-2-naphthylamine, amino-decalin, cholesterylamine, abietylamine,

Reaction products of diketenes with heterocyclic or aromatic-heterocyclic amines, for instance amino-quinoline-carboxylic acid, amino-quinoline-sulfo acid, aminopyridine, aminopyridine-3-sulfo acid, aminopyrazolones, aminopyrazoles, N-amino-1,2,4-triazole, 5-amino-tetrazole, 5-amino-benzimidazole, 2-aminobenzthiazole, N-(4'-aminophenyl)-piperidine, 5-aminohydrindene, 5-amino-acenaphthene,

Reaction products of diketenes with uric acid derivatives, for example 4,5-diamine-uracil, 6-amino-purine,

Reaction products of diketenes with amino compounds, such as cyanuric chloride amidated wholly or in part, whereby for instance one or two chlorine atoms are amidated and brought into reaction with ketene, whereas the third chlorine atom may be exchanged for another radical, which causes solubility in water as in the case of the taurine radical, fastness to diffusion as in the case of the abietylamine radical, or molecular enlargement as in the case of one or several amino-benzoyl groups. The amidation may be accomplished also instead of ammonia with any nitroamino compound. The nitro group is then reduced and the amino group thus obtained is employed for the reaction with ketene.

Reaction products of diketene with aminoguanidine and ammonia,

Reaction products of diketenes with amino sulfides, for example β,β-diamino-diethylsulfide, 4,4'-diamino-diphenylsulfide, 4-amino-thiophenol-2-sulfo acid, 4-amino-diethylaniline-3-thiosulfo acid, 6,6'-diamino-3,3'-dimethyl-diphenylsulfide, 4-(S-methylthio)-2-aminobenzoic acid, 4-(S-ethylthio)-2-sulfo benzoic acid,

Reaction products of diketenes with azo-compounds and their compounds obtainable by partial reduction, such as the hydrazo-compound of 4,4'-diamino-azobenzene, with 3,3'-diamino-4,4'-dimethyl-azoxybenzene, 4,6'-diamino-3-methyl-azobenzene, 2,4'-diamino-azobenzene-4'-sulfo acid.

Especially important as color-coupling substances are the reaction products of diketenes with polymers containing amino- or hydroxy groups. As examples of such polymers containing amino groups there may be mentioned the polyethyleneimine, the amidation products of polymers containing halogen- or keto-groups, for instance of polymerisates from vinylchloride, vinylbromide, of mixed-polymerisates from maleic acid anhydride and vinylchloride, from crotonic acid and vinylchloride, of the chloroacetals of polymers containing hydroxy groups, chlorinated rubber.

Important are also the reaction products of diketene with polymers containing hydroxy groups, for example polyvinyl alcohol, mixed-polymerisates from polyvinyl alcohol and maleic acid or crotonic acid or itaconic acid. Not only the reaction products of diketene with the polymers belongs here, but also the polymerisate from monomeric ethyleneimine and ketene.

Generally speaking by means of the aforementioned reaction products it is possible to combine the ketenes with molecule radicals effecting fastness to diffusion as described in our former patents and patent applications: 2,179,238, 2,178,612, 2,186,849, 2,179,244, 2,186,732, 2,186,733, 2,186,851, 2,186,734, 2,186,719, 2,186,852, Ser. No. 284,257, filed July 13, 1939; Ser. No. 284,258, filed July 13, 1939; Ser. No. 333,813, filed May 7, 1940; Ser. No. 335,144, filed May 14, 1940; Ser. No. 284,250, filed July 13, 1939; Ser. No. 327,628, filed April 3, 1940.

The reaction products of the diketenes, such as diketene with amines as mentioned before, may be employed in various ways for the production of photographic color images directly or indirectly by means of a silver image. They are either brought in contact in dissolved form with the exposed silver halide or with a metal- or metal salt image or they are added in such a form to the silver halide emulsion, that they cannot be removed by the usual photographic treating baths. For that special purpose they may be further treated. The reaction product from diketene with ammonia is for example an easily soluble compound which when added to a color forming developer yields a green-yellow color image after development. If this compound be treated with an aldehyde, a resin is obtained which cannot be removed from a gelatin layer in the usual photographic baths.

It is furthermore possible to exchange one or several halogen atoms of the cyanuric chloride by the radical of acetoacetic acid amide and to exchange the remaining chlorine atoms or the remaining chlorine atom for a substituent which either imparts fastness to diffusion, special solubility in water or both or solubility at a certain hydrogen-ion-concentration.

The color formers may be employed in various ways for the production of photographic color

images. As examples may be mentioned the following:

A silver halide emulsion layer after exposure is developed in a p-diethylaminoaniline-developer containing a ketene derivative. A yellow dyestuff image is obtained.

An exposed silver halide emulsion layer may be developed in the first instance to a black-and-white picture, then fixed and the silver thus formed may be reconverted to silver halide. This silver halide image is then developed into a color image by a color forming developer.

A silver halide emulsion layer is first developed in a black-white developer, the silver image is bleached out and is converted into a silver antidiazotate image according to U. S. Patent 2,179,228. This is transformed in feebly acid solution into a yellow dyestuff image, the solution containing as a coupling component, a ketene derivative.

To a silver halide emulsion there is added as the color former a ketene derivative fast to diffusion. By direct or indirect development or by reversal development according to U. S. Patent 2,179,234 and U. S. Patent application Ser. No. 148,731, filed June 17, 1937, a yellow dyestuff image is obtained.

When using as color formers ketene derivatives which are fast to diffusion, they may be added to the silver halide emulsion at any point in the manufacturing process. The silver halide emulsion containing these color formers fast to diffusion is cast in a known manner into photographic layers, if necessary after a short washing process. The photographic layers may be arranged on one or both sides of the support or may be superimposed on one another or be sensitized for various spectral regions.

The silver halide emulsions may be worked up according to U. S. Patent 2,186,730 by arranging on a support differently sensitized silver halide emulsions containing different color formers in the form of small particles.

What we claim is:

1. A color-forming developer which contains an aromatic amino developing agent and a reaction product of a diketene with a compound belonging to the group consisting of aliphatic, aromatic-aliphatic and hydroaromatic-aliphatic amines.

2. A color-forming developer which contains an aromatic amino developing agent and a reaction product of a diketene with a compound, said compound containing groups which effect solubility in water, said compound belonging to the group consisting of aliphatic, aromatic-aliphatic and hydroaromatic-aliphatic amines.

3. A color-forming developer which contains an aromatic amino developing agent and a reaction product of a diketene with a polymer of aliphatic compounds, said polymer containing amino groups.

4. A color-forming developer which contains an aromatic amino developing agent and a reaction product of a diketene with an amino polymer of aliphatic compounds, said polymer containing hydroxy groups.

5. A color forming developer as defined in claim 1 in which, said ketene derivative contains groups causing solubility in water.

6. A color forming developer as defined in claim 1 in which said ketene derivative contains groups causing solubility in alkali.

7. A photographic material comprising a silver halide emulsion which contains as a color former a reaction product of a diketene with a compound belonging to the group consisting of aliphatic, aromatic-aliphatic and hydroaromatic-aliphatic amines.

8. A photographic material comprising a silver halide emulsion which contains as a color former a reaction product of a diketene with a compound, said compound containing groups which effect solubility in water, said compound belonging to the group consisting of aliphatic, aromatic-aliphatic and hydroaromatic-aliphatic amines.

9. A photographic material comprising a silver halide emulsion which contains as a color former a reaction product of a diketene with a polymer of aliphatic compounds, said polymer containing amino groups.

10. A photographic material as defined in claim 7 in which said color former contains at least one group which causes solubility in water.

11. A photographic material as defined in claim 7 in which said color former contains at least one group which causes solubility in alkali.

12. A photographic material comprising a silver halide emulsion which contains as a color former a reaction product of a diketene with an amino polymer of aliphatic compounds, said polymer containing hydroxy groups.

13. A photographic material as defined in claim 7 in which said color former contains groups fast to diffusion.

14. A process for producing a dye image in a photographic silver halide emulsion which comprises converting the reaction product of a diketene with a compound selected from the class consisting of aliphatic, aromatic-aliphatic and hydroaromatic-aliphatic amines into a dyestuff in the presence of an image selected from the class consisting of metal and metal salt images.

15. The process as defined in claim 14 wherein said reaction product contains a group which causes solubility in water.

16. The process as defined in claim 14 wherein said reaction product is of a diketene with a polymer of aliphatic compounds, said polymer containing amino groups.

17. The process as defined in claim 14 wherein said reaction product is the reaction product of a diketene with an amino polymer of aliphatic compounds said polymer containing hydroxy groups.

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