

UNITED STATES PATENT OFFICE

2,484,477

PROCESS FOR MAKING COLOR COUPLERS

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6 Claims. (Cl. 260—309)

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This invention relates to photography and particularly to a novel method of preparing couplers for color photography.

Color forming compounds which react with the development product of aromatic amino developing agents to form colored images on photographic development have been the subject of numerous prior patents. The dyes formed in this way are insoluble in water and in the ordinary photographic developing and fixing baths, although the silver images formed simultaneously with them during the photographic development may be removed from the photographic layer to leave pure dye images in the layer. Such a compound which is employed in conjunction with the developing agent for the silver and which couples with the development product of the developer during photographic development is referred to herein as a coupling component or coupler. When these coupling components are incorporated in the photographic layer prior to exposure, they do not affect the exposure and development of the layer in the usual way but when the development is carried out with a suitable developing agent they combine with the oxidation product of the developer to form a colored image in situ with the silver image.

The coupling portion of the coupler molecule usually consists of a radical with a phenolic hydroxyl group or a reactive methylene group, and to this portion may be attached substituents which render the coupler suitable for use in various processes, such as those described in Mannes and Godowsky U. S. Patent 2,304,940, granted December 15, 1942, Jelley and Vittum U. S. Patent 2,322,027, granted June 15, 1943, and Peterson U. S. Patent 2,296,306, granted September 22, 1942. In the process of the Peterson patent, for example, couplers are used containing imino or mercapto groups which permit the formation of an insoluble metallic salt. It is frequently difficult to prepare couplers having the desired properties with respect to coupling and color formation, and also having the necessary groups which control diffusion and other properties.

It is, therefore, an object of the present invention to provide a novel method for the preparation of color couplers. A further object is to provide a method for the preparation of couplers suitable for use in the process of Peterson U. S. Patent 2,296,306. Other objects will appear from the following description of our invention.

These objects are accomplished, according to the broader aspects of our invention, by joining two different primary or secondary amines, one or both of which may be couplers, or one of which may be a heterocyclic compound containing a reactive mercapto or imino group, or one of which may be a non-coupling aliphatic or aromatic amine, by means of a two-step conden-

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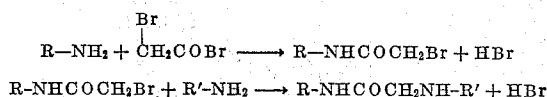
sation involving the use of an acyl halide having replaceable halogen atoms of different reactivity to said amines.

More specifically, our invention provides for the joining of a coupler containing an amino group, to another amine, such as a heterocyclic compound containing an amino group, by the use of bromoacetyl bromide or sulfobenzoyl dichloride as the condensing agent.

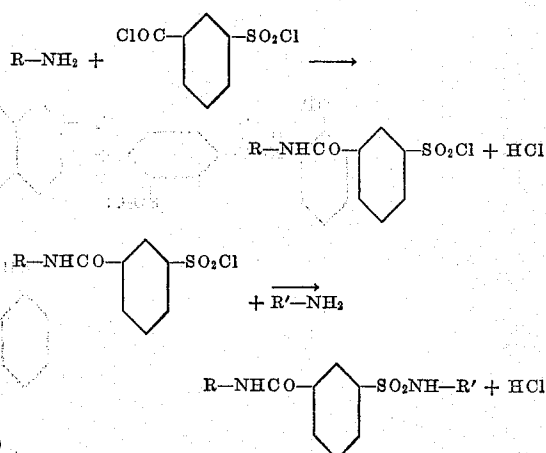
Couplers containing amino groups are well known. Porter and Weissberger U. S. Patent 2,376,380, granted May 22, 1945, describes amino pyrazolones; French Patent 836,144 discloses aminophenols.

If these or similar couplers containing amino groups are treated with sulfobenzoyl dichloride (Annalen, 102, 1857, page 249) or bromoacetyl bromide (Berichte, 24, 1891, page 2219) in the presence of a base to take up the hydrogen halide which is split off, a condensation takes place, and an intermediate compound is formed which has coupling properties and contains a replaceable halogen atom. If this intermediate, which may or may not be isolated, is reacted with another amino compound, again in the presence of a base to take up the hydrogen halide, a second condensation takes place, and a compound is formed which retains its coupling properties and which possesses characteristics introduced by the second amino compound.

In the case of bromoacetyl bromide, the reaction proceeds as follows:



where R represents a coupler molecule and R' represents a second coupler molecule or a heterocyclic system containing an NH- or SH-group. A similar reaction takes place in the case of sulfobenzoyl dichloride as follows:



where R and R' represent the same groups as before.

The order of the condensations may be reversed, and the heterocyclic compound reacted first with the acyl halide. Four general types of compound containing heterocyclic groups may, therefore, be formed, having the following general structure:

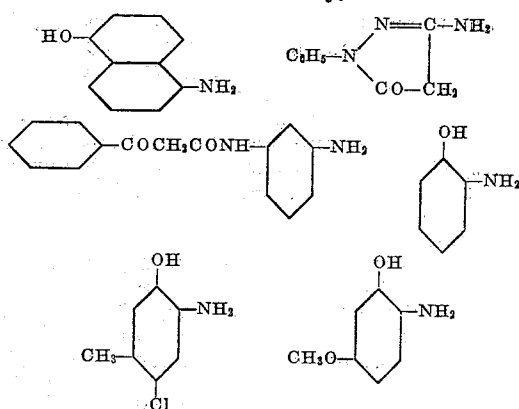
Type I. Coupler—NH—CH₂—CO—NH—heterocyclic.

Type II. Coupler—NH—CO—C₆H₄—SO₂—NH—heterocyclic.

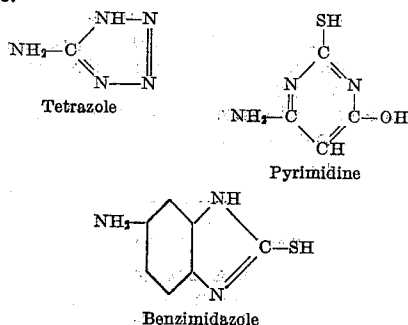
Type III. Heterocyclic—NH—CH₂—CO—NH—coupler.

Type IV. Heterocyclic—NH—CO—C₆H₄—SO₂—NH—coupler.

Couplers containing amino groups which may be condensed with the acyl halide are as follows, this list being illustrative only.



Heterocyclic amines containing —NH or —SH groups which may be condensed with the acyl halide are as follows, the list being merely illustrative.

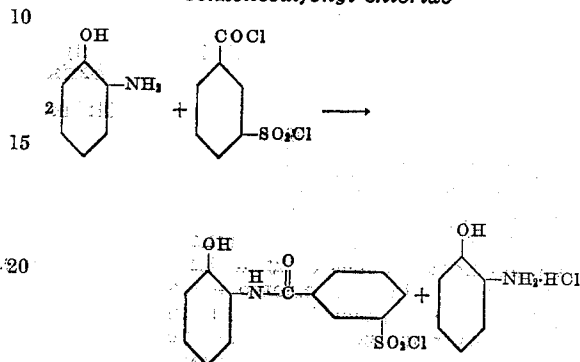


Any of the heterocyclic compounds disclosed in

Peterson U. S. Patent 2,296,306, when substituted with an amino group, may be employed.

The following examples illustrate the method of forming the compounds according to our invention:

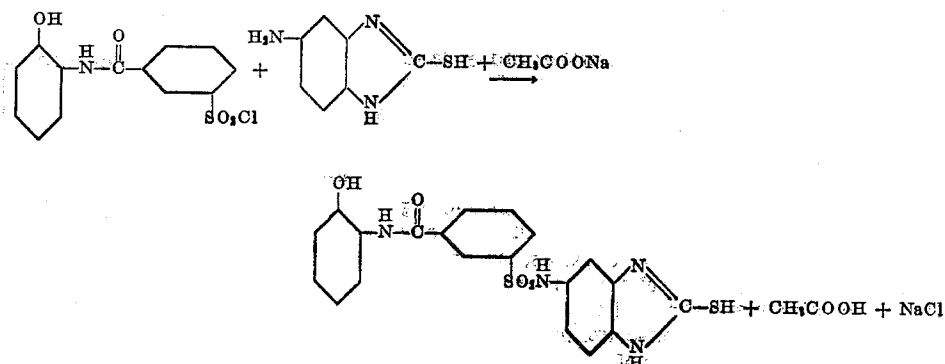
Example 1.—*m*(2'-hydroxyphenyl) carbamylbenzenesulfonyl chloride



In a 2-liter, 3-necked flask, equipped with a thermometer and stirrer, is placed 700 cc. of dioxane dried over anhydrous calcium chloride. In this solvent is dissolved 43.6 grams (0.4 mole) of recrystallized (from 10 parts of alcohol) o-aminophenol by heating to 70° C. The clear pink solution is cooled to 25° C. and to it is added 48 grams (0.2 mole) of *m*-sulfonylbenzoyl dichloride with continuous stirring. The temperature rises to about 40° C. and, after a few minutes, the viscous pink material, which has separated, crystallizes. After the mixture has been stirred for 15 minutes, it is filtered by suction and the residue of o-aminophenol hydrochloride washed on the filter with 100 cc. of fresh dioxane.

The filtrate is diluted with 800 cc. of ligroin and stirred for 5 minutes. The sulfonyl chloride which separates is filtered and washed on the filter with 1 liter of petroleum ether. The solid is dried at 100°. Crude yield is 50.3 grams. The product is crystallized as a tan solid from 600 cc. of tetrachloroethane which has been dried by the distillation of about 25 cc. of forerun. The mixture is filtered and the product washed on the filter with 2×50 cc. of fresh tetrachloroethane followed by 300 cc. of hexane to remove tetrachloroethane. The product is dried at 100°. Yield: 43 g. (69%) M.P. 186°.

5-[*m* - (2'-hydroxyphenyl) carbamylbenzenesulfonylamido]2-mercaptobenzimidazole



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Type III

Type II

Type II

Type II

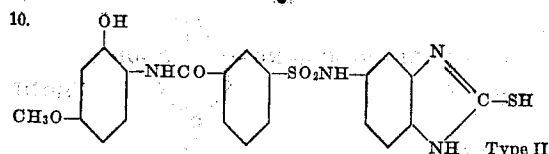
Type IV

Type II

Type II

Type I

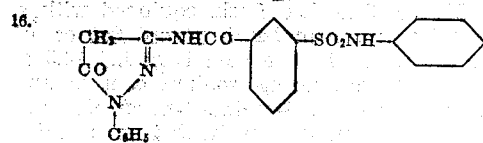
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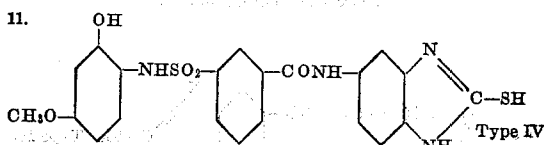
5-[3'-(2'-hydroxy-4'-methoxyphenyl carbamyl)-benzene sulfamido]-2-mercapto benzimidazole

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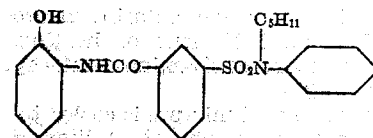


1-phenyl-3-(3'-phenyl sulfamyl)-benzamido-5-pyrazolone

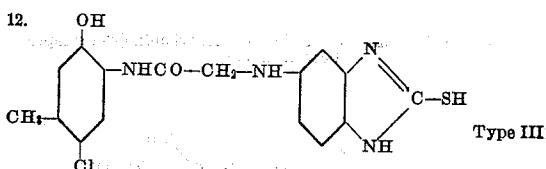


5-[m-(2'-hydroxy-4'-methoxyphenyl-sulfamyl)-benzamido]-2-mercapto benzimidazole

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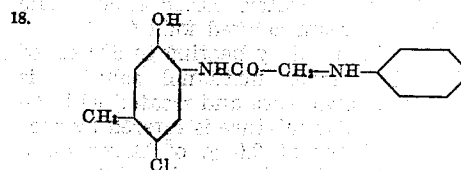


m-(2'-hydroxyphenyl carbamyl)-benzene-N-amylsulfanilide

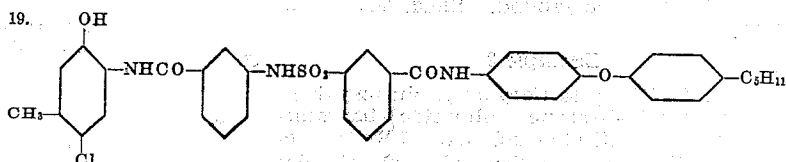


5-[(2'-hydroxy-4'-methyl-5'-chlorophenyl carbamyl)-methylamino]-2-mercapto benzimidazole

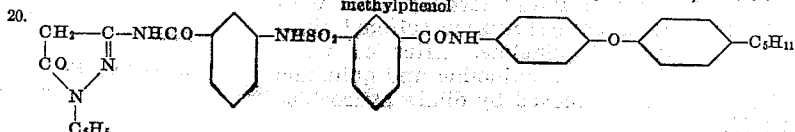
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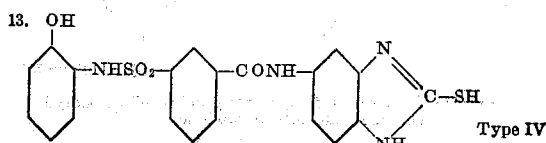
2-anilinoacetyl-amino-4-chloro-5-methylphenol



2-[3'-(3''-(4'''-(p-tert. amylphenoxy)benzene carbamyl)benzenesulfamido)-benzamido]-4-chloro-5-methylphenol

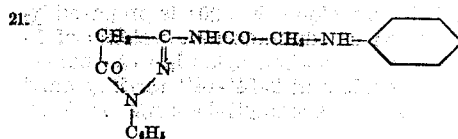


1-phenyl-3-[3'-(3''-(4'''-(p-tert. amylphenoxy)benzene carbamyl)-benzenesulfamido)benzamido]-5-pyrazolone



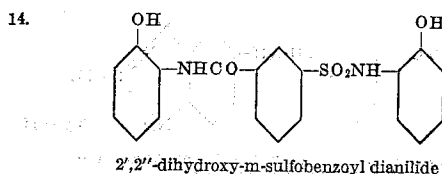
5-[m-(2'-hydroxyphenyl sulfamyl)-benzamido]-2-mercapto benzimidazole

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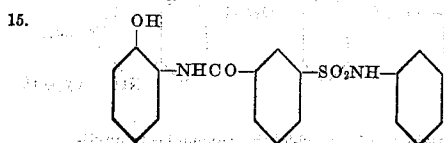
1-phenyl-3-anilinoacetyl-amino-5-pyrazolone

The following compound illustrates the union of two coupler molecules containing amino groups by our method:



2,2'-dihydroxy-m-sulfobenzoyl dianilide

The following compounds illustrate the combination of a coupler with a non-coupling aromatic amine by our method:



m-(2'-hydroxyphenyl)-carbamyl benzene sulfanilide

The aromatic amino developing agents used with the coupler compounds of our invention include the mono-, di- and tri-aminoaryl compounds and their derivatives formed by substitution in the amino group as well as in the ring, such as alkylphenylenediamines and alkyltoluylenediamines. These compounds are usually used in the salt form, such as the hydrochloride or the sulphate, which are more stable than the amines themselves. Suitable compounds are diethyl-p-phenylenediamine hydrochloride, mono-methyl-p-phenylenediamine hydrochloride, dimethyl-p-phenylenediamine hydrochloride and dimethyl-p-phenylenediamine sulphate. The p-aminophenols and their substitution products may also be used where the amino group is unsubstituted. All of these compounds have an unsubstituted amino group which enables the oxidation products of the developer to couple with the color-forming compounds to form a dye image.

The following examples are illustrative of developing solutions which may be used to develop

emulsion layers containing the couplers made according to our invention.

Example 1

p-Aminodiethylaniline sulphate	grams	2.5
Sodium sulphite anhydrous	do	2
Sodium carbonate anhydrous	do	20
Potassium bromide	do	1
Water to	liters	1

Example 2

p-Aminodiethylaniline hydrochloride	grams	2
Sodium sulphite anhydrous	do	5
Sodium carbonate anhydrous	do	20
Water to	liters	1

The couplers used according to my invention may be incorporated in silver halide emulsion layers in various ways but we prefer to form a solution of the sodium salt of the coupler in alcohol and add this to the emulsion. For example, 3 grams of coupler may be dissolved or suspended in 50 cc. of ethyl alcohol and sodium hydroxide added in the amount of 1½ equivalent weights of the coupler. The sodium hydroxide may be added as solid or as a concentrate solution. The sodium salt of the coupler is thereby generated in a solution of 50 cc. of alcohol and this solution is added to 1 liter of a gelatin silver halide emulsion. The pH of the emulsion may then be adjusted if desired by adding a suitable acid such as acetic or sulphuric acid to neutralize all or part of the sodium hydroxide used to form the sodium salt of the coupler.

The coupling components may be incorporated either in gelatin or in other colloidal materials such as collodion, organic esters of cellulose or synthetic resins. The emulsion may be carried by a transparent medium such as glass, cellulose esters, or synthetic resin or a non-transparent reflecting medium such as paper or an opaque cellulose ester. The emulsion may be coated as a single layer on the support or superposed layers containing the couplers may be coated on one or both sides of the support. The superposed layers may be differentially sensitized for the formation of a natural color image in the well known manner.

The examples and compounds set forth in the present specification are illustrative only and it is to be understood that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. The method of reacting sulfobenzoyldichloride with two different primary amines in successive stages, at least one of which amines contains a group reactive with the oxidation products of primary aromatic amino photographic developing agents, which comprises selectively reacting a cool solution of one of said amines with the carboxylic acid chloride group of said sulfobenzoyldichloride to produce a carboxylic acid amide reaction product containing an unreacted sulfonyl chloride group, and then heating said reaction product with the other of said amines to produce a sulfonic acid amide.

2. The method of reacting sulfobenzoyldichloride with two different primary amines in successive stages, one of which amines contains a reactive methylene group and the other of which amines contains a 5-membered heterocyclic group containing a mercapto group, which comprises selectively reacting a cool solution of one

of said amines with the carboxylic acid chloride group of said sulfobenzoyldichloride to produce a carboxylic acid amide reaction product containing an unreacted sulfonyl chloride group, and then heating said reaction product with the other of said amines to produce a sulfonic acid amide.

3. The method of reacting sulfobenzoyldichloride in successive stages, with a 1-phenyl pyrazolone having a reactive methylene group in the 4-position and having a primary amino substituent, and with 5-amino-2-mercaptobenzimidazole, which comprises selectively reacting a cool solution of one of said amines with the carboxylic acid chloride group of said sulfobenzoyldichloride to produce a carboxylic acid amide reaction product containing an unreacted sulfonyl chloride group, and then heating said reaction product with the other of said amines to produce a sulfonic acid amide.

4. The method of reacting sulfobenzoyldichloride in successive stages, with a 1-phenyl pyrazolone having a reactive methylene group in the 4-position and having a primary amino substituent, and with 5-amino-2-mercaptobenzimidazole, which comprises selectively reacting a cool solution of said pyrazolone with the carboxylic acid chloride group of said sulfobenzoyldichloride to produce a carboxylic acid amide reaction product containing an unreacted sulfonyl chloride group, and then heating said reaction product with said 5-amino-2-mercaptobenzimidazole to produce a sulfonic acid amide.

5. The method of reacting sulfobenzoyldichloride in successive stages, with a phenol having a primary amino group in the 2-position, and with 5-amino-2-mercaptobenzimidazole, which comprises selectively reacting a cool solution of one of said amines with the carboxylic acid chloride group of said sulfobenzoyldichloride to produce a carboxylic acid amide reaction product containing an unreacted sulfonyl chloride group, and then heating said reaction product with the other of said amines to produce a sulfonic acid amide.

6. The method of reacting sulfobenzoyldichloride in successive stages, with a phenol having a primary amino group in the 2-position, and with 5-amino-2-mercaptobenzimidazole, which comprises selectively reacting a cool solution of said phenol with the carboxylic acid chloride group of said sulfobenzoyldichloride to produce a carboxylic acid amide reaction product containing an unreacted sulfonyl chloride group, and then heating said reaction product with said 5-amino-2-mercaptobenzimidazole to produce a sulfonic acid amide.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
1,663,474	Ackerman	Mar. 20, 1928

FOREIGN PATENTS

Number	Country	Date
503,752	Great Britain	1939