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2,881,167

## 5-SULFAMYL INDAZOLONE-2-CARBOXYLIC ACID ESTERS

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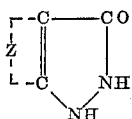
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Claims priority, application Great Britain December 10, 1952

11 Claims. (Cl. 260—239.9)

This invention relates to new color couplers for use in color photography, and to a process for producing color photographic images by the use of such color couplers.

It is known that a reducible silver salt image can be developed with a primary aromatic amino developing agent in the presence of a compound of the formula:

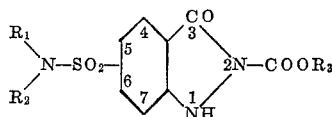


or a tautomeric form thereof, wherein Z represents the non-metallic atoms required to complete an isocyclic, heterocyclic or polycyclic nucleus. The color image obtained in this way is formed by the coupling of the oxidation product of the developer on the 2 position of the indazolone ring, that is to say on the N-atom which is in the ortho-position to the carbonyl group.

With certain 2-substituted indazolones, the color coupling takes place in an entirely different way, the indazolone ring is broken and an azo compound is formed in which the residue of the oxidation product of the developing agent is attached to the nitrogen atom which previously formed the 1-nitrogen atom of the indazolone ring.

We have found that when the substituent on the 2-position of the indazolone ring is a carbalkoxy group and there is a sulphonamide group as substituent in the 5-position, valuable magenta color formers are obtained.

According to our invention therefore, we provide new color couplers of the formula:



wherein R<sub>1</sub> and R<sub>2</sub> represent hydrogen atoms or hydrocarbon radicals and R<sub>3</sub> represents a hydrocarbon radical, provided that when R<sub>1</sub> is hydrogen and R<sub>2</sub> is 1-naphthyl the naphthyl radical must carry a substituent in the 4-position.

The color couplers of our invention are particularly valuable because owing to the pronounced bathochromic effect of the sulphonamide group they give magenta azo dyestuffs on color development with aromatic amino developing agents, for example, p-diethylaminoaniline, whereas the parent 2-carbalkoxy-indazolones without the sulphonamide group give orange azo dyestuffs under these conditions. Also when substituents other than carbalkoxy are present in the 2-position, the bathochromic effect of the sulphonamide group is generally accompanied by a marked reduction in reactivity, in which case the 2-substituted indazolones do not react sufficiently readily under the conditions of color photographic development, or by an increased ease of hydrolysis, in

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which case the 2-substituent is hydrolyzed off and coupling to form an azo dyestuff does not occur. The 2-carbalkoxy-indazolone-5-sulphonamides of our invention however have excellent all round properties, and in particular they have good stability and high coupling activity, and unlike the known indazolone color couplers containing no substituent in the 2-position, they do not give yellow oxidation products in the bleaching bath used for removal of silver.

The color couplers of our invention may be used in the developing solution or they may be included in a light-sensitive layer or in a non-light-sensitive layer adjacent to a sensitive layer or separated therefrom by a water-permeable colloid layer.

It is a preferred feature of our invention to include the color couplers in one or more light-sensitive gelatino-silver halide emulsion layers which form part of a multi-layer film or paper of the kind used for color photography. For this purpose, it is preferred to use color couplers which contain a substituent rendering them fast to diffusion, for example, a long alkyl chain containing at least 5 carbon atoms and if desired a solubilizing group. Other substituents may be present especially in the 4, 6 and 7 positions of the indazolone ring.

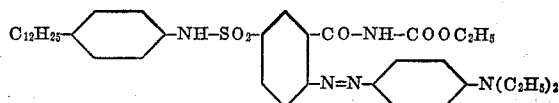
Specific examples of the color formers of our invention are 2-carbethoxy-5-(N-p-dodecyl-phenyl-sulphamyl)-indazolone, 2-carb-octadecoxy-5-N-phenylsulphamyl-indazolone, 2-carb-octadecoxy-5-N-phenyl-N'-methylsulphamyl-indazolone and the corresponding sulphononic acid and its salts, 2-carb-octadecoxy-5-(N-3':5'-dicarboxyphenyl-sulphamyl)-indazolone, 2-carb-octadecoxy-5-(N-4'-sulpho-1'-naphthyl-sulphamyl)-indazolone, 2-carb-oleyoxy-5-(N-phenyl-sulphamyl)-indazolone and 2-carb-iso-amlyoxy-5-(N-phenyl-sulphamyl)-indazolone.

The color couplers of our invention may be made by chlorosulphonating the parent indazolone and reacting the sulphonyl chloride with ammonia or with the appropriate primary or secondary amine, and then treating the indazolone-5-sulphonamide with the appropriate ester of chloroformic acid to introduce the carbalkoxy group into the 2-position of the indazolone ring.

According to a further feature of our invention, we provide a process for producing color photographic images which comprises developing an exposed gelatino-silver halide emulsion layer with a primary aromatic amino developing agent in the presence of a color coupler of the formula shown above.

The developing agents preferably used and giving the best results in connection with the present invention are the aromatic ortho- and para-diamines such as paraphenylene diamine and its substitution products.

The color coupling which occurs in the process of our invention when an exposed gelatino-silver halide emulsion is treated with a primary aromatic amino developing agent in the presence of a color coupled of the kind used in our invention proceeds by a surprising and wholly unexpected reaction, in which the indazolone ring is split and an azo dyestuff is formed in which the residue of the oxidation product of the developing agent is attached to the nitrogen atom which previously formed the 1-nitrogen atom of the indazolone ring. For example, when 2-carb-ethoxy-5-(N-p-dodecylphenyl-sulphamyl)-indazolone is used as the color coupler and p-diethylaminoaniline is used as the developing agent a dyestuff is formed which is believed to have the following formula:

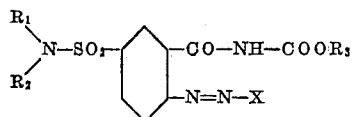


It will be noted that the substituent on the nitrogen atom

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in 2-position of the indazolone ring is not split off during color development.

According to a further feature of my invention, therefore, we provide a color photographic element which contains in at least one emulsion layer a color image comprising a dyestuff of the formula:



wherein  $R_1$ ,  $R_2$  and  $R_3$  have the significance given above and X represents the group of atoms which together with the group  $-NH_2$  forms a primary aromatic amino developer.

The dyestuff images formed by the process of our invention are superior to the known azomethine images in their chemical stability and their fastness to light and the process of our invention provides a simple method of obtaining color photographic images of good fastness properties by direct development of an exposed gelatino-silver halide emulsion with aromatic amino color developers.

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

#### Example 1

10 parts of indazolone are added to 50 parts of chlorosulphonic acid which is well stirred at 40° C. The solution is stirred at 40° C. for 6 hours and then poured into 200 parts of ice.

The mixture is well stirred and the indazolone-5-sulphonyl-chloride which is precipitated, is filtered off, washed acid free with ice cold water and dried in a vacuum desiccator.

The dry indazolone sulphonyl chloride is added to a solution of 50 parts of p-dodecyl-aniline in 150 parts of dioxane and the mixture is heated until a clear solution is obtained. The solution is poured into water and the suspension so obtained is made alkaline by the addition of caustic soda and extracted with ethyl acetate. The residual aqueous solution is acidified with acetic acid and the 5-(N-p-dodecylphenyl-sulphamyl)-indazolone so precipitated is filtered off, dried and purified by recrystallization from methanol.

10 parts of the purified compound are heated under a reflux condenser with 60 parts of dioxane and 5 parts of ethyl chloroformate until the evolution of hydrogen chloride has ceased. The reaction mixture is cooled and the 2-carb-ethoxy-5-(N-p-dodecylphenyl-sulphamyl)-indazolone (melting point 203° C.) which crystallizes out, is filtered off and washed with methanol and then with ether and dried.

The product can be added to a photographic developer solution or it can be incorporated into light sensitive gelatino-silver halide emulsions which are used for forming sensitive photographic layers and on exposure and color development, it gives a magenta dyestuff image which has much better stability to light and acid fumes than the azomethine dyestuff images formed by color development from conventional color formers.

#### Example 2

10 parts of indazolone-5-sulphonyl chloride are heated with a solution of 7 parts of aniline in 50 parts of dioxane until a clear solution is obtained. This solution is poured into 300 parts of water and the mixture so obtained is acidified with hydrochloric acid, and 5-N-phenyl-sulphamyl-indazolone which crystallizes out on standing is filtered off, washed with methanol and dried.

60 parts of a solution containing 1 gram mol of octadecyl chloroformate in 1 litre of chlorobenzene (prepared by reacting octadecanol in chlorobenzene solution with phosgene) are added to a mixture of 6 parts of 5-

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N-phenylsulphamyl-indazolone and 50 parts of dioxan and the mixture is boiled under a reflux condenser until the evolution of hydrogen chloride has ceased. The mixture is cooled and 2-carb-octadecoxy-5-(N-phenyl-sulphamyl)-indazolone (melting point 180° C.) which crystallizes out is filtered off, washed with methanol and then with ether and dried.

#### Example 3

In place of the 7 parts of aniline used in Example 2, 9.0 parts of methylaniline are used when 2-carb-octadecoxy-5-(N-phenyl-N'-methyl-sulphamyl)-indazolone (melting point 150° C.) is obtained.

10 parts of the product are added to 200 parts of dry ethylene dichloride. The mixture is stirred and 10 parts of chlorosulphonic acid are added. The mixture is stirred and heated at 60° C. for 30 minutes and then poured into 300 parts of water. The mixture is made alkaline by the addition of caustic soda and then allowed to stand for 1 hour. The lower layer of ethylene dichloride is run off, and the upper (aqueous) layer is filtered through kieselguhr. The filtrate is acidified with hydrochloric acid and 20 parts of common salt are added. The mixture is stirred and the precipitate is then filtered off, and boiled with 50 parts of methanol. The mixture is cooled and filtered and the residue washed with ether and dried. The sulphonated product so obtained melts at 256° C. and is readily soluble in dilute sodium carbonate solution.

An aqueous solution of the product can be added to a gelatin-silver halide emulsion prior to coating on a film.

The product gives a magenta image on exposure and color development.

#### Example 4

12 parts of indazolone-5-sulphonyl chloride are stirred with 15 parts of the diethyl ester of aniline-3:5-dicarboxylic acid in 70 parts of dioxane until a clear solution is obtained. The solution is poured into an equal volume of water and then acidified with hydrochloric acid and the precipitate is filtered off. The precipitate is stirred with 250 parts of water and caustic soda solution is added until the solution is alkaline to phenolphthalein. The solution is boiled for 30 minutes to hydrolyze the ester, further additions of caustic soda being made to keep the solution alkaline to phenolphthalein. The solution is then treated with decolorizing carbon and filtered. The filtrate is acidified to Congo red paper with hydrochloric acid and the 5-(N-3':5'-dicarboxy-phenyl-sulphamyl)-indazolone which is precipitated is filtered off, washed and dried.

A mixture of 10 parts of 5-(N-3':5'-dicarboxyphenyl-sulphamyl)-indazolone, 30 parts of the chlorobenzene solution of octadecyl chloroformate made as described in Example 2 and 100 parts of dry dioxane are boiled under a reflux condenser for 6 hours. 300 parts of methanol are added and the mixture so obtained is cooled. The white precipitate so formed is filtered off, washed with methanol and then with ether and dried. 2-carb-octadecoxy-5-(N-3':5'-dicarboxyphenyl-sulphamyl)-indazolone is obtained as a white powder (melting point 244° C.).

The product dissolves readily in aqueous sodium carbonate to give a clear yellow solution, which may be incorporated in a gelatino-silver halide emulsion, to form an emulsion suitable for the preparation of the magenta layer of a multi-layer color photographic material.

#### Example 5

12 parts of indazolone-5-sulphonylchloride are added to 30 parts of  $\alpha$ -naphthylamine in 80 parts of acetone and the mixture is warmed on a water bath until a clear solution is obtained. This solution is diluted with an equal volume of water, acidified with hydrochloric acid and cooled and the 5-(N- $\alpha$ -naphthyl-sulphamyl)-indazolone

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(melting point 250° C. with decomposition) which is precipitated, is filtered off, washed with dilute hydrochloric acid and dried. A mixture of 10 parts of this product, 30 parts of the chlorobenzene solution of octadecyl chloroformate prepared as described in Example 2, and 100 parts of dioxane are heated under a reflux condenser for 3 hours. 300 parts of methanol are added, the mixture so obtained is cooled and the precipitate of 2-carb-octadecoxy-5-(N- $\alpha$ -naphthyl-sulphamyl)-indazolone is filtered off and dried when it is obtained as a white powder of melting point 164–166° C. 10 parts of this product are stirred with 50 parts of dry ethylene dichloride and 8 parts of chlorosulphonic acid are added at a temperature not higher than 30° C. The mixture is stirred for 1 hour and the solid in suspension is then filtered off, washed with ethylene dichloride, and dried. The 2-carb-octadecoxy-5-(N-4'sulpho-1'-naphthyl-sulphamyl)-indazolone so obtained as a white solid melting with decomposition at 245–250° C., dissolves in aqueous sodium carbonate and the solution so obtained may be added to a gelatino-silver halide emulsion to give an emulsion suitable for forming the magenta image layer of a color photographic material.

#### Example 6

60 parts of a solution containing 1 gram mol. of oleyl chloroformate in 1 litre of chlorobenzene (prepared by reacting oleyl alcohol in chlorobenzene solution with phosgene) are added to a mixture of 6 parts of 5-N-phenylsulphamyl-indazolone and 50 parts of dioxane and the mixture is boiled under a reflux condenser until the evolution of hydrogen chloride has ceased.

The solvent is then removed by distillation under reduced pressure and 400 parts of methanol are added to the residue. The precipitate is filtered off, washed with methanol and dried. The 2-carb-oleyloxy-5-(N-phenyl-sulphamyl)-indazolone so obtained dissolves readily in oils, for example medicinal paraffin, to form solutions suitable for suspension in gelatino-silver halide emulsions to form emulsions which give magenta images on exposure and color development.

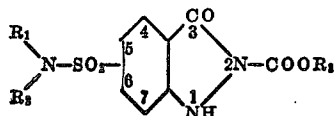
#### Example 7

In place of the 60 parts of oleyl chloroformate solution used in Example 6, 60 parts of a solution containing 1 gram mol. of iso-amyl chloroformate in 1 litre of chlorobenzene are used. The 2-carb-iso-amyl-oxy-5-(N-phenyl-sulphamyl)-indazolone so obtained is soluble in aqueous sodium carbonate, and the solution so obtained may be added to a photographic developer solution to give a developer which forms magenta images with exposed silver halide photographic material.

The present application is a division of Serial No. 396,730, filed December 7, 1953.

I claim:

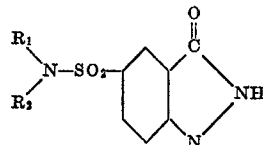
1. New color couplers of the formula:



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wherein R<sub>1</sub> is a member of the group consisting of hydrogen and lower alkyl, R<sub>2</sub> is a member of the group consisting of phenyl, alkylphenyl, naphthyl and carboxy and sulfo-substituted phenyl and naphthyl radicals, with the further proviso that, when R<sub>1</sub> is hydrogen and R<sub>2</sub> is 1-naphthyl, the naphthyl radical carries a substituent selected from the group consisting of said carboxy and sulfo substituents in the 4-position, and R<sub>3</sub> is a member of the group consisting of an alkyl and an alkenyl group.

2. Process for the manufacture of new color couplers according to claim 1 which comprises treating

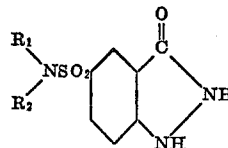


with ClCOOR<sub>3</sub> to introduce the carb-alkoxy group into the 2-position of the indazolone ring.

3. Process for the manufacture of the color couplers of claim 1, which comprises condensing indazolone-5-sulphonyl chloride with an amine having the formula



and then condensing the resulting compound



with ClCOOR<sub>3</sub> to introduce the carb-alkoxy group into the 2-position of the indazolone ring.

4. 2 - carbethoxy - 5 - (N - p dodecylphenyl - sulphamyl)-indazolone.

5. 2 - carb - octadecoxy - 5 - (N - phenyl-sulphamyl) indazolone.

6. 2 - carb - octadecoxy - 5 - (N - phenyl - N' - methyl-sulphamyl)-indazolone.

7. The sulfonated product of claim 6.

8. 2 - carb-octadecoxy - 5 - (N - 3',5' - dicarboxy-phenyl sulphamyl)-indazolone.

9. 2 - carb-octadecoxy - 5 - (N - 4' - sulpho - 1' - naphthyl-sulphamyl)-indazolone.

10. 2 - carb-oleyloxy - 5 - (N - phenyl - sulphamyl)-indazolone.

11. 2 - carb - iso - amyloxy - 5 - (N - phenyl - sulphamyl)-indazolone.

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