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3,677,764

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3,677,764

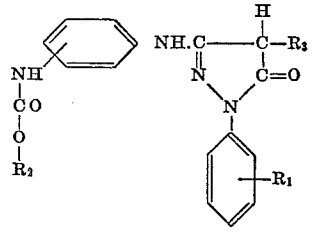
SILVER HALIDE EMULSION CONTAINING PURPLE COUPLER FOR COLOR PHOTOGRAPHY AND PROCESS OF MAKING THE SAME

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U.S. Cl. 96—100 13 Claims

ABSTRACT OF THE DISCLOSURE

A purple color coupler has the formula

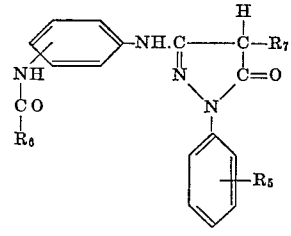


wherein R_1 is hydrogen or one of the substituents usually employed with 1-phenyl-pyrazolones; R_2 is alkyl, cycloalkyl, aryl or aryloxyalkyl or one of these groups which is substituted as customary in pyrazolone couplers; R_3 is hydrogen or a substituent as customary in pyrazolone couplers which, upon color development, is split off; and wherein at least one of R_1 and R_2 is or includes an anti-fusion straight-chain or branched hydrocarbon group having from 8 to 20 carbon atoms.

BACKGROUND OF THE INVENTION

The invention relates to a diffusion-proof color coupler which is based on the principle of chromogenic development and adapted to react with the oxidation product of developers of the p-phenylenediamine type to give purple color images. This type of purple coupler is used in practical applications in one of the three layers of a multilayer photographic color material. The other two layers include the color couplers for the yellow and the blue-green image portion.

The usual purple couplers for multilayer color materials are derivatives of pyrazolones. Particularly useful have proven in this connection the acylaminoanilinopyrazolones of the formula



wherein:

R_5 is hydrogen or one of the customary substituents in this type of pyrazolone compound

R_6 is alkyl, aryl or one of these compounds which likewise is substituted as indicated for R_5, and

R_7 is hydrogen or a phenylazo group.

This type of coupler has for instance been disclosed in U.S. Pats. 2,983,608 and 3,127,269 and in the Japanese Pat. 6,031/65.

This type of color component, however, can be produced only with difficulty in pure form. For instance, in case of acylation in acetonitrile, it is necessary to boil the amino-anilinopyrazolone with the acyl chloride for several hours. In this process darkly colored by-products are formed which cannot easily be separated.

In case of acylation in pyridine or dimethylaniline a poor yield is obtained and, besides, decomposition products also occur in this process.

In case of acylation by the so-called phosphorazo method, there are likewise rather large fractions of darkly colored by-products obtained.

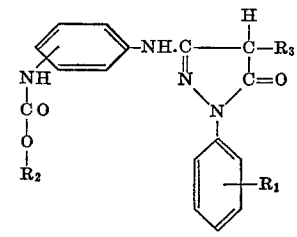
Because of these shortcomings in the manufacture, the application of acylamino-anilinopyrazolones in industrial practice is rather limited.

Therefore, it is an object of the present invention to provide for a purple coupler of the general amino-anilinopyrazolone type which can be produced without incurring any of the difficulties indicated. It is a further object of the invention to provide for a process of making this type of coupler without the shortcomings of the prior-art processes.

SUMMARY OF THE INVENTION

These objects in brief are met by forming amino-anilinopyrazolones wherein, instead of the COR group a COOR group is provided.

More specifically, the new couplers of the invention have the formula



wherein

R_1 is hydrogen, alkyl, halogen or an acid group;

R_2 is alkyl, cycloalkyl, aryl, aryloxyalkyl or a substituted alkyl, cycloalkyl, aryl or aryloxyalkyl group; and

R_3 is hydrogen, halogen, an acid group or a phenylazo group or another group adapted to be split off during the color development;

and wherein at least one of R_1 and R_2 is or includes an anti-diffusion straight-chain or branched hydrocarbon group having from 8 to 20 carbon atoms.

The invention also embraces a process for making the above compounds comprising reacting a chloroformic acid ester wherein the ester moiety includes an 8 to 20 carbon alkyl group with a 3-amino anilino-pyrazolone (5). The alkyl group is incorporated in the formic acid ester by reacting a correspondingly substituted alkanol or an aryloxyalkyl compound with phosgene.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

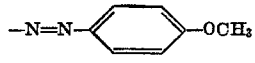
The color couplers of the invention are derivatives of carbamic acid. They are preferably made by reacting an amino anilino pyrazolone with a chloroformic acid ester. As distinguished from the reaction between amino anilino-pyrazolones with normal acid chlorides, the reaction with the chloroformic acid ester proceeds many times more rapidly. This prevents the formation of undesirable by-products and, at the same time, increases the yield in the desired final product.

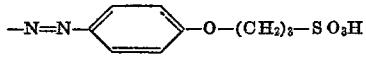
Examples of suitable esters of the chloroformic acid are for instance the following: ethylester, 2-hexylnonylester, hexadecylester, 4-bromobutylester; cyclohexylester, tetrahydrofurfurylester; phenylester, p-nitrophenylester, p-dodecylphenylester, n-pentadecylphenylester, 2,4-dichloro-6-tetradecylphenylester, o-octadecyloxy-phenylester, p-chloro-o-tetradecylphenylester; p-butylphenoxyethylester, 2-butyl-4-nonylphenylester, m-pentadecylphenoxyethylester, p-dodecyloxyphenoxypropylester, 4 - chloro - 3 - methyl-6-tetradecylphenoxypropylester.

The making of this type of ester has been described in the literature. It is also disclosed in German Pat. 1,176,479.

In the above formula of the compounds of the invention R_1 is preferably chlorine or a sulfonic acid group. Preferably, there should be three chlorine atoms attached to the phenyl radical shown in the formula. R_2 preferably is chlorophenyl or alkyl. If R_2 is alkyl, then the alkyl group may be the anti-diffusion long-chain hydrocarbon group. If R_2 is chlorophenyl, then the long-chain hydrocarbon group may be substituted in the phenyl radical. R_2 may also be alkylphenoxy wherein the phenoxy group is attached to the main molecule by instance an ethyl group which connects the oxygen of the acid group with a phenyl-attached oxygen. In that case, the long-chain hydrocarbon group may again be substituted in the phenyl radical.

R_3 may be halogen or a sulfonic acid group. In one specific type of the compounds of the invention used as masking couplers a phenylazo group is attached to the main molecule as R_3. Groups of the following formulae, e.g., may be present:





so as to form a yellow color masking coupler.

The process of making the compounds of the invention has decided advantages compared with the prior-art acylamino anilino pyrazolone couplers.

The introduction of the anti-diffusion residue in the 3-position of the pyrazolone can easily be effected by introducing a long-chain hydrocarbon group in various manners. While in synthesizing the prior-art acylamino anilino-pyrazolones it is necessary to form the long-chain acid chlorides, it is possible with the compounds of the invention simply to react a long-chain alcohol or alkylphenol with phosgene so as to form the corresponding chloroformic acid ester. This advantage is also retained in case of the introduction of the aryloxyalkyl residue as the group R_2 which is a preferred form of the invention.

The couplers of the invention can be incorporated in conventional manner in a green sensitive emulsion layer of a multilayer color material. If acid groups such as SO_3H or COOH are present in the coupler, the coupler compounds can be incorporated in the form of an alkali salt in an aqueous or aqueous-alcoholic solution. Water-insoluble compounds of the type of the invention can be dispersed in conventional manner, for instance by use of an acetic acid ester and a wetting agent and can be incorporated into the emulsion in form of the dispersion. If a critical situation arises in this process because the color component has a tendency to recrystallize in the dispersion, it is advisable to add an oil-forming compound such as dibutylphthalate. Because of the general property of excellent dispersibility, a small amount of this addition is usually sufficient, for instance one-half part of oil-forming agent for each part of the color component. The color compounds can be incorporated both for the negative/positive process as well as for the reversal process.

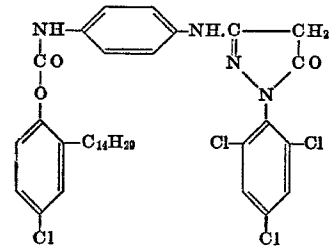
Insofar as the stability of the compounds of the invention is concerned regarding loss of sensitivity in case of storing of the emulsion layers and regarding light sensitivity of the developed color materials, the new compounds are at least equivalent to the prior-art acylamino anilino-pyrazolones if not superior. The coupling activity of the compounds is excellent with the conventional developer substances. Likewise, the absorption properties of the color materials that are formed by developing with conventional developers are excellent. This is true in particular in view of the low blue absorption.

The compounds of the invention as already indicated are of particular interest when used in the form of the 4-phenylazo derivatives as masking couplers for elimination of the blue absorption of purple color materials as has been described first in the U.S. Pat. 2,449,966. In many cases this type of azo masking compound effects only an incomplete coupling. As distinguished, the compounds of the invention permit obtaining of a complete coupling conversion. Noticeable is also the high stability of the masking dyes towards the bleaching bath. Noteworthy is also that after the coupling conversion the desirable properties of the parent couplers, that is the purple dyes, become dominant.

The following examples will further illustrate the invention:

EXAMPLE 1

This example illustrates a purple coupler of the formula



Stage 1.—4-chloro-2-tetradecylphenol

460 g. of p-chlorophenol were melted down and 7 g. of boron trifluoride was then introduced at 55° C. 196 g. 1-tetradecene were then added dropwise and while stirring during a period of 2 hours. Stirring was continued for another hour, and the mass was then poured into a mixture of 1 liter water and 0.5 liter sodium hydroxide and subjected to thorough stirring for five minutes. After the phases had become separated, the oil layer was taken up in 500 ml. benzene and several times washed neutral with dilute hydroxide and water. After evaporation of the benzene, the residue was subjected to distillation in vacuum. B.P. (0.05 mm.) 150–158° C.; yield: 220 g.

Stage 2.—4-chloro-2-tetradecylphenylchloroformate

160 g. of phosgene were introduced during a period of 40 minutes in 1.2 liter of dry toluene. A mixture of 406 g. of the phenol obtained in Stage 1, 151 g. of dimethylene aniline and 300 ml. toluene were then added dropwise during a period of 3 hours. After standing overnight, 800 ml. of ice water was added and air was long enough blown through the mixture to remove excess phosgene. The toluene solution was then separated and washed neutral with dilute HCl and water. The chloroformic acid ester was then obtained by distilling off the toluene in a 95% degree of purity. The yield was 415 g.

Stage 3.—Purple component

The starting product in this case was 1-(2',4',6'-trichlorophenyl)-3-(4''-aminoanilino)pyrazolone-(5) which has been described in U.S. Pat. 2,983,608. 7.4 g. of this material were dissolved while stirring in 35 ml. pyridine and then reacted at 20° C. with 8 g. of the chloroformic acid ester obtained in Stage 2. The temperature during this step rose to 40° C. Stirring was continued for 40 minutes without application of heat. The mass was then poured into a mixture of 50 ml. of concentrated hydrochloric acid, 80 ml. methanol and 80 ml. ethylacetate and was stirred for 5 minutes. After adding 100 ml. water, the ethylacetate

layer was separated and shaken out with dilute hydrochloric acid and water. The solvent was removed by evaporation and the oily residue was taken up in petroleum ether. The residue that precipitated after standing in the ice box was removed by suction and washed with petroleum ether.

M.P. 88–90° C.; yield 10 g.

PREPARING A DISPERSION OF THE COUPLING COMPOUND

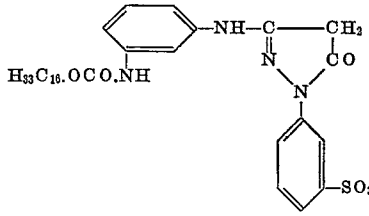
2 g. of the coupling compound dissolved in 3 ml. ethylacetate were dispersed in 16 ml. of a 5% gelatin solution which contained as wetting agent dodecylbenzene sulfonic acid sodium.

The dispersion was incorporated in conventional manner in a halogen silver emulsion, was cast on a support and was exposed photographically after drying and subjected to the reversal process. The color developer was 2-amino-5-diethylaminotoluene.

There was obtained a brilliant, clear, positive purple image. Absorption maximum of the dye: 541 mμ.

EXAMPLE 2

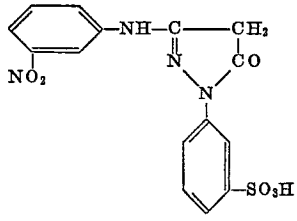
This example relates to a color coupler of the formula:



Stage 1.—β-(3-nitroanilino)-β-methyl-mercapto-acrylic acid ethylester

192 g. of β,β-dimethylmercaptoacrylic acid ethyl ester (see Laakso Suomen Kem. 17 B (1944), 2–3; (CA 1946, 4671)), 140 g. of m-nitroaniline and 0.5 g. of p-toluenesulfonic acid were heated while stirring to 130° C. Strong mercaptan separation occurred. The reaction was complete after 30 minutes. The resulting oil contained about 70% of the desired compound. Crude yield: about 230 g.

Stage 2.—1-(m-sulfophenyl)-4-(m'-nitro-aniline)-pyrazolone-(5)



53.6 g. of phenylhydrazine-m-sulfonic acid were suspended in 200 ml. water and neutralized with 70 g. of sodium carbonate. To the solution thus formed a mixture of 115 g. of the crude product from Stage 1 and 250 ml. of glacial acetic acid were added and the mixture was subjected to boiling with reflux for 60 minutes. The reaction solution was reacted with 1.5 l. of a 10% sodium salt solution. A precipitate was formed which was removed by suction and washed with methanol. The wet crude product was again formed into a slurry with 10% sodium salt solution and after removal by suction washed with methanol. The yield was 44 g.

Stage. 3.—Reduction of the nitro compound

44 g. of the nitro compound obtained in Stage 2 were added to a solution of 100 g. tin-II-chloride, 220 ml. concentrated hydrochloric acid and 330 ml. glacial acetic acid at 75° C. while stirring. After the completion of this step, the temperature was maintained at 95° C. for another 10 minutes. 600 ml. water were then added to the almost colorless solution. The precipitate that formed was removed by suction after cooling down of the solution and washed with a small amount of dilute hydrochloric acid. The yield was 25 g.

Stage 4.—Formation of the purple component

A solution was prepared upon stirring from 10 g. of the amino compound obtained in Stage 3 in 36 ml. pyridine and 18 ml. dimethylformamide at a temperature of 35° C. 10 g. of the chloroformic acid cetylester were then added. The mass was subjected to further stirring for 30 minutes at 55° C. It was then poured into 200 ml. of a 10% sodium salt solution and the precipitate that was formed was removed by suction. The wet crude product was thereupon dissolved in 50 ml. methanol and precipitated with concentrated hydrochloric acid. The precipitate was removed by suction and washed with acetone. Yield: 10 g.

FORMATION OF A SOLUTION OF THE COUPLER

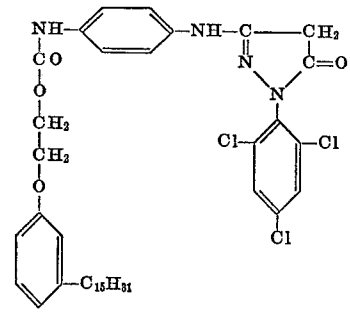
1 g. of the coupler compound thus obtained was suspended in 2 ml. methanol and reacted with dilute sodium hydroxide until neutral.

The solution was then incorporated in conventional manner in a halogen-silver emulsion and treated as described in Example 1.

Using 2-amino-5-diethylaminotoluene as the developer, a purple dye was obtained with an absorption maximum of 526 mμ.

EXAMPLE 3

This example illustrates the purpose coupler of the formula



Stage 1.—m-Pentadecylphenoxyethanol

46 g. of sodium were dissolved in 2.5 l. of abs. alcohol and added to 680 g. of m-pentadecylphenol (a product of the Aldrich Corporation of the United States of America) at 70° C. and while stirring. 161 g. of 2-chloroethanol were then added to the solution within a period of 90 minutes. After keeping at boiling point for 2 hours, the solution was then cooled to 40° C. and the precipitated sodium chloride was removed by suction. The filtrate was cooled in the refrigerator and the desired product then precipitated. After removal by suction, the parent liquid was concentrated by evaporation to 1 liter solution. M.P. 51–52° C.; total yield: 440 g.

Stage 2.—β-(Pentadecylphenoxy)-ethylchloroformate

This chloroformic acid ester was formed analogously to the manner in Stage 2 of Example 1. Instead of 460 g. of phenol, there were used 435 g. of the phenoxyethanol obtained in Stage 1 of the present example. The yield was 450 g.

Stage 3.—Making of the purple component

277.5 g. of 1 - (2',4',6' - trichlorophenyl)-3-(4''-aminoanilino)-pyrazolone-(5) were dissolved in 1.5 l. pyridine and added in one batch at 40° C. to 330 g. of the chloroformic acid ester formed in Stage 2 while stirring. Subsequently, stirring was continued for another 30 minutes at 60° C., and the solution was then poured while stirring into a mixture of 6 l. of ice water and 2 l. of hydrochloric acid. The precipitate that formed was removed by suc-

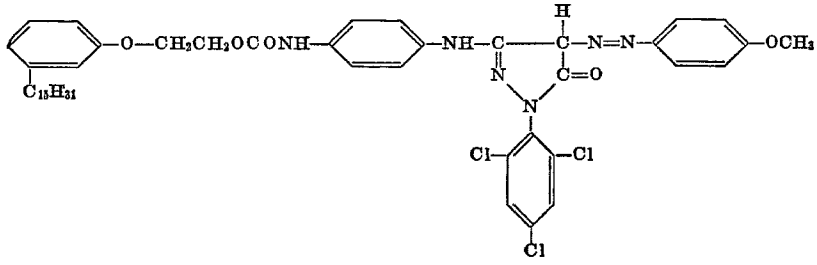
tion and thoroughly washed with dilute hydrochloric acid and water.

The dried crude product was dissolved in 1.75 l. of acetic acid ethyl ester and the solution was reacted with 2 l. of methanol. After 24 hours, suction was applied. M.P. 153–155° C.; yield: 400 g.

This purple coupler can be used as in Example 1. With 2-amino-5-diethylaminotoluene it will furnish a color material with an absorption maximum of 535 mμ.

EXAMPLE 4

This example illustrates the making of a yellow colored masking coupler of the formula



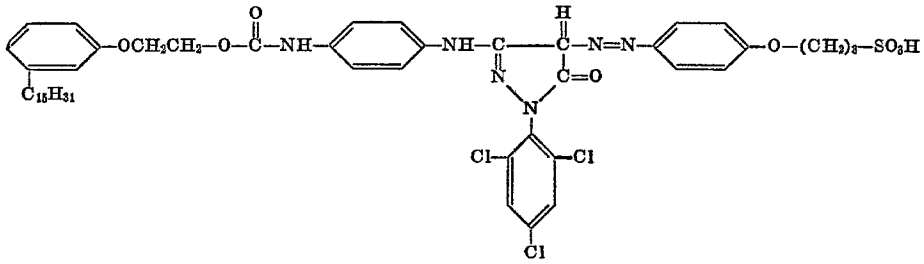
3.08 g. of p-anisidine in 37.5 ml. 2 N hydrochloric acid and 15 ml. water were diazotized at 0° C. with a solution of 1.73 g. of $NaNO_2$ in 5 ml. water at a temperature of 0° C. The diazonium salt solution was then added at 0° C. to a solution of 18 g. of the purple component formed in Example 3 dissolved in 350 ml. pyridine. Stirring was continued at room temperature for another 30 minutes and the mass was subsequently poured while stirring into a mixture of 2 liters ice water and 500 ml. concentrated hydrochloric acid. The formed precipitate was removed by suction and washed with dilute hydrochloric acid and water. The dried crude product was recrystallized from ligroine. M.P. 66–70° C.; yield: 18 g.

The component, an azo dye, had an absorption maximum of 425 mμ.

The yellow colored coupler, a so-called masking coupler, was incorporated in the form of a dispersion in a green sensitive negative emulsion. The emulsion was cast, dried and photographically exposed. Upon developing with a negative color developer (developer: N-ethyl-N-β-methane-sulfonamide-ethyl - 3-methyl-4-aminoaniline-sulfate, a negative purple image was obtained, absorption mam 533 mμ. At the same time, there was left a positive yellow image which therefore was opposed to the gradation of the purple image which yellow image could be used for masking the blue absorption of a purple color material.

EXAMPLE 5

This example illustrates the making of another masking coupler of the formula



15 g. of 4-amino-ω-sulfopropyl-phenylether were dissolved in 30 cc. concentrated hydrochloric acid and 50 cc. water and diazotized at 0–5° C. with a solution of 5 g. of sodium nitrite and 25 cc. water. The diazonium salt solution was added in the course of half an hour to a solution of 35 g. of the purple coupler obtained in Example 3 and dissolved in 250 cc. pyridine. After stirring for 6 hours, the solution was precipitated in 225 cc. concentrated hydrochloric acid and 1000 cc. ice water. The final pH was 1 to 2.

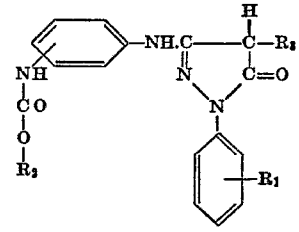
The formed precipitate was eliminated by suction and dried. It was dissolved hot in methanol for purification and adjusted to a pH of 5 to 6 with a 20% sodium hydroxide solution. The precipitated coupler was removed by suction, washed with methanol and dried. M.P.: decomposition starting at 240° C.

The yellow colored coupler was incorporated in a green sensitive negative emulsion. The emulsion was cast, dried and photographically exposed. It was subjected to the negative color development process using N,N-diethyl-p-phenylenediamine as developer and potassium ferricyanide in the bleaching bath. A negative purple image was obtained was an absorption maximum of 526 mμ.

Significant was smooth conversion coupling of the masking couplers and the excellent stability of the mask in the bleaching bath.

We claim:

1. A suspension or dispersion for incorporation in a photosensitive halogen-silver emulsion, the said suspension or dispersion comprising a carrier material having suspended or dispersed therein an acyl-amino-anilino-pyrazolone having the formula



wherein R_1 is hydrogen, alkyl, halogen or an acid group; R_2 is alkyl, cycloalkyl, aryl, aryloxyalkyl or a substituted alkyl, cycloalkyl, aryl or aryloxyalkyl group, wherein said substituent is halogen; R_3 is hydrogen, halogen or a SO_3H or COOH acid group or a phenylazo group; and wherein at least one of R_1 and R_2 is or includes an antidiffusion straight-chain or branched hydrocarbon group having from 8 to 20 carbon atoms.

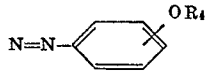
2. The suspension or dispersion of claim 1, wherein R_1 is chlorine or a sulfonic acid group.

3. The suspension or dispersion of claim 1, wherein R_2 is alkyl having 8 to 20 carbon atoms.

4. The suspension or dispersion of claim 1, wherein R_2 is chlorophenyl, phenyl being further substituted by said 8 to 20 carbon hydrocarbon group.

5. The suspension or dispersion of claim 1, wherein R_2 is alkylphenoxy, the phenyl group of phenoxy being further substituted by said 8 to 20 carbon hydrocarbon group.

6. The suspension or dispersion of claim 1 wherein R_3 is a phenylazo group of the following structure

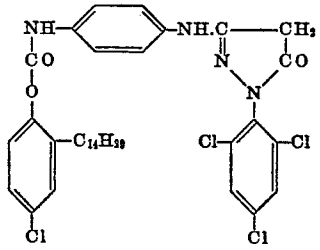


R_4 being alkyl or substituted alkyl, wherein said substituent is lower alkyl or a sulfo lower alkyl group.

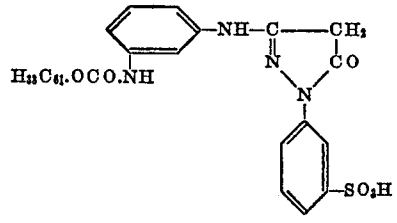
7. The suspension or dispersion of claim 6, wherein R_4 is methyl.

8. The suspension or dispersion of claim 6, wherein R_4 is sulfo-propyl.

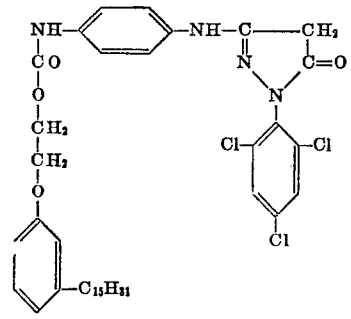
9. The suspension or dispersion of claim 1, wherein said pyrazolone is



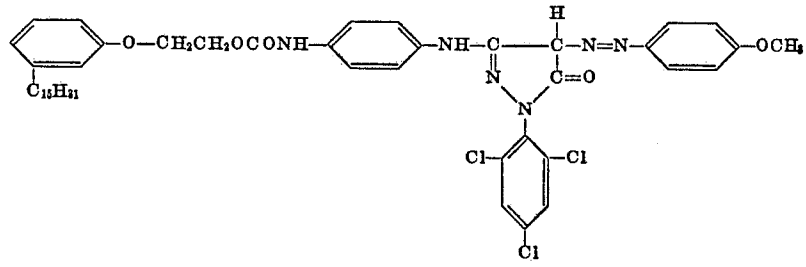
10. The suspension or dispersion of claim 1, wherein said pyrazolone is



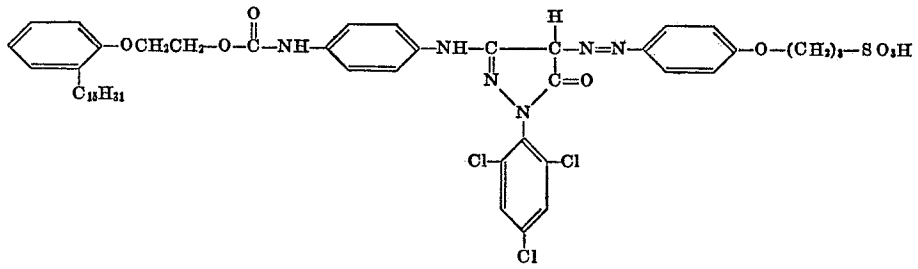
11. The suspension or dispersion of claim 1, wherein said pyrazolone is



12. The suspension or dispersion of claim 1, wherein said pyrazolone is



13. The suspension or dispersion of claim 1 wherein the color coupler is



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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—9, 56.5