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3,758,308

**SILVER HALIDE EMULSION CONTAINING  
PARA-FLUORO PHENOLS**

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9 Claims

**ABSTRACT OF THE DISCLOSURE**

A group of para-fluoro substituted phenols having substituted carbonamido moieties in ortho and meta position thereon, the described compounds and materials incorporating the same having particular advantages in efficiently producing stable cyan dyes in excellent yield when reacted with an oxidized phenylene diamine, particularly in the capacity of a 2-Equivalent Color Photographic Coupler Compound.

This invention relates to a unique group of para-fluoro substituted phenols and their utilization, the compounds having both

- (1) 2-substituted aryl-alkyl- or halalkyl carbonamido or 2-aryl ureido; and
- (2) 5-substituted phenoxy lower alkyl-carbonamido groups attached to carbon atoms of the phenol ring.

More specifically, the present invention relates to a group of phenolic compounds which have been found to particularly favor reaction with oxidized primary aromatic amines such as phenylene diamines to obtain stable cyan dyes in excellent yield.

The group of compounds within this invention enjoy an unusual spectrum of additional functional characteristics which uniquely qualify them as 2-Equivalent Cyan Dye-Forming Color Photographic Couplers.

By way of background, colored photographic images are obtained in the photographic art by coupling the development product (i.e., oxidized primary aromatic amino developing agents) with a color-forming or coupling compound. The subtractive process of color formation is ordinarily employed and the resulting image dyes are usually of the complementary primary colors such as cyan, magenta or yellow.

Coupler compounds employed to produce the above three dyes generally contain color-forming groups of the phenolic hydroxyl, pyrazolone or benzoyl acetamide classes, capable of reacting with the oxidation product of the primary aromatic amino developing agent on photographic development.

Conventional color-forming coupler compounds containing acetoacetanilides, 5-pyrazolones, phenolic or naphtholic configuration also customarily have active methylene groups which will react with an oxidized color developer during color development to produce a dye. A majority of color photographic couplers of the above types are known and described as "4-Equivalent" couplers and are characterized in requiring the development of four light-exposed silver halide molecules in order to ultimately produce one molecule of dye by a coupling reaction with oxidized developer.

There are other classes of coupler compounds, however, including "2-Equivalent" couplers in which non-chromophoric coupling off groups are substituted in coupling positions. Such couplers are functionally characterized by requiring the development of only two exposed silver halide molecules during development to obtain one molecule of dye.

Compounds of this type vary substantially in overall structure, depending upon the particular dye product desired. Known 2-Equivalent Couplers and methods for their utilization are disclosed, for instance, in U.S. Pats. 3,458,315 and 3,277,155 of Loria and Loria et al. respectively.

Modern photographic products and the underlying technology still utilize 4-Equivalent Couplers despite the fact that 2-Equivalent Couplers offer increased reactivity (i.e., high dye density) and partial avoidance of some stability problems such as "print out." This is so because of the fact that present day photographic couplers must have a constantly increasing and changing spectrum of ancillary characteristics.

It is now important to obtain thinner, more durable photographic elements containing stable couplers which, in turn, produce stable photographic dyes having precise spectral absorption characteristics.

Of equal importance is the need for couplers which may be homogeneously incorporated into silver halide emulsions in carefully controlled amounts without adversely affecting viscosity, adhesion, or the unity of any particular emulsion layer during modern high speed multilayer application onto a film backing. Undesired changes in viscosity of melted gelatin photographic emulsions may be caused by additives such as wetting agents, color components, etc., and these changes directly affect the coating characteristics of a photographic emulsion. This fact is indicated, for instance, on page 250 of the text by Zelikman and Levi, entitled "Making and Coating Photographic Emulsions"; The Focal Press.

Including antihalation and gelatin interlayers, up to eight or more separate layers may now be applied to a film base to obtain a modern color photographic element (ref. Kirk-Othmer, vol. 5, pp. 812-845, Encyclopedia of Chemical Technology). For this reason, any major coupler-induced changes in the adhesion or coating characteristics of a photographic layer are unacceptable.

The order of application of a coupler-containing layer in such an element is also important, and depends upon the absorption properties of the particular dye to be obtained upon reaction of coupler and oxidized developer. For this reason, an optimal spectrum of characteristics for yellow, cyan and magenta dye-producing couplers may differ to some extent. Also to be considered, in this connection, is the fact that a cyan dye is generally not required in the same amount as a yellow photographic dye to effect color balance.

A further desired characteristic of a coupler compound is substantial solubility in high- and/or low-boiling organic solvents as described and utilized, for instance, in Julian, U.S. Pat. 2,949,360, in the light of earlier disclosures in Mannes, U.S. Pat. 2,304,939; Jelley et al., U.S. Pat. 2,322,827; Vittum, U.S. Pat. 2,801,170; and Fierke, U.S. Pat. 2,801,171. It is much to be desired that a modern coupler require only minimal amounts of solvent since the thickness, durability and optical opacity of the resulting photographic element is substantially affected by the amount required. This, in turn, affects image definition and resolution properties of the resulting photographic element. Limitation in the use of competing couplers also helps, to a lesser extent, provided cyan dye couplers in the existing solvent or vehicle produce a  $D_{max}$  value commensurate with good color balance and having a lower parameter of not less than about 1.8 for reflective photographic purposes.

The above-listed advantages are not necessarily compatible, or are otherwise matched by disadvantages since the color photographic technology of recent years is complex and functionally interrelated. In fact, some coupler

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characteristics considered advantageous in earlier photographic art may now even be considered undesirable. Moreover, with few exceptions, it is not possible to predict a particular desirable combination of functional coupler characteristics from molecular structure alone.

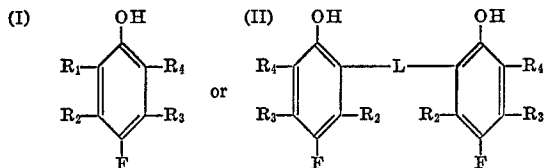
It is an object of the present invention to obtain a group of cyan dye-producing 2-Equivalent Color Coupler compounds which will readily and efficiently convert into stable dyes having a precise, desirable light absorption spectrum upon exposure to small amounts of oxidized aryl diamines, such as phenylene diamine color photographic developer compounds.

It is a further object to obtain new highly reactive cyan dye-producing 2-Equivalent Coupler compounds without the sacrifice of coupler or dye stability, diffusibility of resulting emulsion, image definition, resolution characteristics of the resulting photographic element, or effect undesirable viscosity changes prior to or during application onto a film base.

It is a still further object to find new stable cyan dye-producing coupler compounds which can, if desired, be successfully incorporated into a silver halide emulsion and applied to a film base, using minimal amounts or substantially no coupler solvent in the resulting photographic element.

These and other objects are accomplished by means of our invention as hereinafter described.

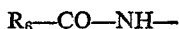
Compounds, as well as silver halide emulsions and photographic elements within the present invention and their method of use are characterized by the following formulae:



wherein

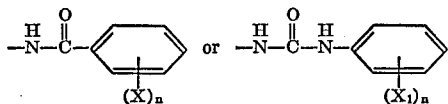
$R_1$  and  $R_3$  are individually defined as hydrogen or alkyl of 1-4 carbon atoms;

$R_2$  is defined as an aryloxy-substituted alkylcarbonamido group such as a phenoxy alkyl carbonamido and including alkyl- and dialkyl-substituted phenoxy-alkylcarbonamido groups. Such substituents may be conveniently and specifically expressed in formula form as follows:



wherein  $R_6$  is defined as (1) an alkyl-substituted phenoxy-lower alkyl in which the alkyl group of the "alkyl-substituted" phenoxy contains about 1-20 carbon atoms and (2) as a di-alkyl substituted phenoxy-lower alkyl, preferably a (t)-alkyl phenoxy-lower alkyl in which the (t) alkyl group contains up to 10 carbon atoms.  $R_6$  is exemplified as di-tertiary pentyl phenoxy propyl, di-tertiary pentyl phenoxy butyl, di-tertiary pentyl-phenoxy pentyl, n-octadecyl phenoxy propyl, n-pentadecyl phenoxy propyl, and n-pentadecyl phenoxy ethyl group;

$R_4$  is defined as an aryl- or alkyl-carbonamido group, such as polyfluoro phenyl carbonamido, a fluoroalkyl carbonamido, an alkyl substituted phenoxy-lower alkyl carbonamido, also an aryl ureido group such as a chlorophenyl ureido, and may be conveniently expressed, for instance, as



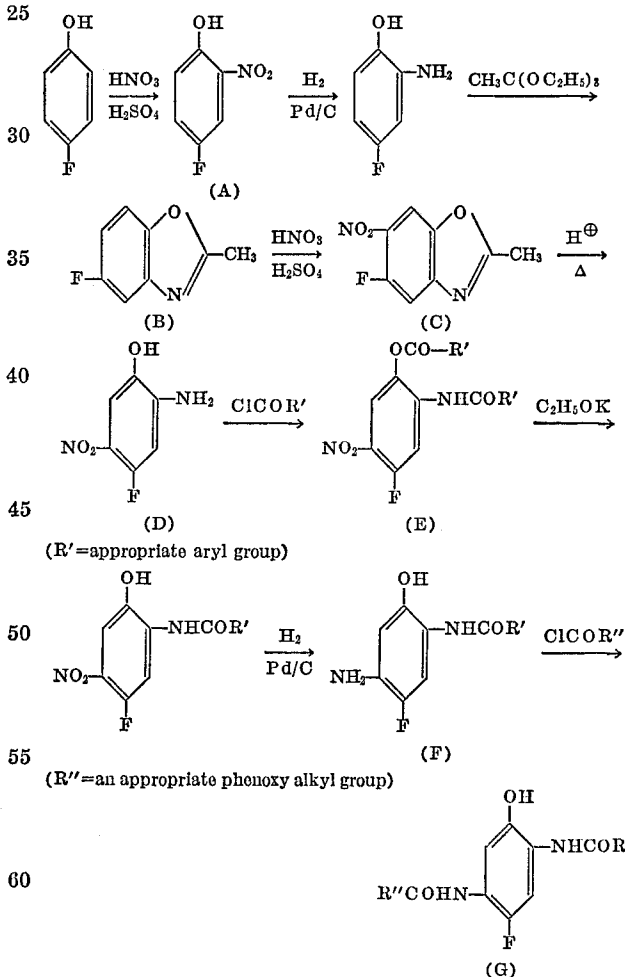
wherein X and  $X_1$  are defined as halo radicals, inclusive of chloro and fluoro groups, and  $n$  is an integer of 0-5, 75

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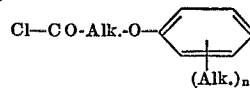
$n$  preferably being 5 when X is defined as fluoro, and 1 when  $X_1$  is defined as chloro; and

L is defined as a linking group exemplified, for instance, The above compounds may be obtained from commercially available para-fluoro phenols obtainable, for instance, from the corresponding p-amino phenols.

The p-fluoro phenol may then be converted into a 2-nitro derivative by adding  $HNO_3$  in glacial acetic acid, and this intermediate converted to the corresponding 2-methyl-5-fluorobenzoxazole by catalytic reduction followed by cyclization with triethylorthoacetate. The resulting 2-methyl-5-fluoro benzoxazole is then nitrated with a  $HNO_3$  and  $H_2SO_4$  acid mixture and hydrolyzed to obtain 2-amino-4-fluoro-5-nitro phenol. This intermediate is dissolved in quinoline and dioxane and reacted with an equimolar amount of pentafluorobenzoyl chloride in dioxane for 1 hour at room temperature, the mixture poured into a dilute solution of HCl at about  $0^\circ C.$  and the resulting product precipitated, washed and recrystallized. The resulting 2-acylamido-4-fluoro-5-nitro phenol is then finally converted to the 2-(2,3,4,5,6-pentafluoro benzamido)-5-amino-4-fluorophenol by catalytic hydrogenation at about  $40^\circ C.$  The above multi-step process may be demonstrated as follows:



65 Where the  $R_4$  substituent of Formula I is a phenyl ureido radical, steps (A) through (D), as above described, may be followed by reaction with a meta chlorophenyl isocyanate to obtain a corresponding o-ureido substituted intermediate, the meta-substituent group being then added by reaction of the meta amino group with a suitable acid chloride such as



wherein Alk. is defined as an alkyl or lower alkyl group, and  $n_1$  is an integer of 1-2.

The corresponding bis compound of Formula II may be obtained, for instance, by treating the product of step (D) supra with phosgene to obtain a ureido linkage under conditions permitting further reaction with a compound having the desired para-fluoro phenol moiety.

Compounds having the above-defined configurations are generally of the ballasted non-diffusing type and are usefully incorporated into photographic silver halide emulsion layers as part of single- or multi-layer color photographic materials by methods (i.e., the solvent and Fisher fat-tail methods) described earlier in part, for instance, in Mannes et al. in U.S. Pat. 2,304,939/40; and Jelley et al. U.S. Pat. 2,322,027 (June 1943), in which high-boiling organic solvents are used to dissolve the coupler. A further procedure is also described in Vittum et al. U.S. Pat. 2,801,170; Fierke et al. U.S. Pat. 2,801,171 (July 1957); and Julian U.S. Pat. 2,749,360 (August 1960), whereby low-boiling or water soluble organic solvents are used with or in place of a high-boiling solvent. In the case of multi-layer photographic materials or elements, the present compounds, as couplers, may be incorporated into a layer adjacent to a red-sensitive silver halide emulsion layer and/or within such layer and may optimally utilize no high boiling solvent.

Compounds of the present invention may also be utilized as chromophores in polymeric couplers such as described, for instance, in U.S. Pat. 2,698,797.

The term "incorporating" is herein used to describe the introduction or inclusion of one or more coupler compounds initially in a color photographic element either with an emulsion layer or as part of an adjacent layer, and may be introduced in the manner described in the above patents.

Hydrophilic colloid-silver halide emulsion layers suitable for purposes of incorporating the instant group of 2-Equivalent Couplers include silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc., within gelatin, colloidal albumin, a cellulose derivative or synthetic resin such as described in U.S. Pat. 2,286,215 or 2,327,808, a water-soluble ethanol amine cellulose acetate as described in U.S. Pat. 2,322,085, a suitable polyacrylamide having a combined acrylamide content of 30-60% and a specific viscosity of .25-1.5 on an imidized polycrylamide of similar acrylamide content and viscosity as described in U.S. Pat. 2,541,474, Zeil as described in U.S. Pat. 2,563,791, a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in U.S. Pat. 2,768,154, or one containing cyano-acetyl groups, such as vinyl alcohol-vinyl cyano-acetate copolymers as described in U.S. Pat. 2,808,331, a polymeric material from a protein polymerisate or a saturated, acylated protein with a monomer having a vinyl group described in U.S. Pat. 2,852,382.

Emulsions utilized in the present invention may also include those chemically or optically sensitized by known means as demonstrated, for instance, in U.S. Pats. 1,574,944, 1,623,499, 2,410,689, 2,448,060, 2,566,245, 2,566,263, 2,399,083, 2,597,856, 2,597,915, 2,487,850, 2,518,698, 2,521,926, 1,942,854, 1,990,507, 2,493,748, 2,519,001, 2,666,761, 2,734,900, 2,739,149 and British Pat. 450,958.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium and polyethylene glycol type as found in U.S. Pats. 2,271,623, 2,288,226, 2,334,864 and 2,708,162.

The terms "support layer" and "film base," as used herein, constitute a layer suitable for purposes of coating photographic emulsions thereon within the scope of the present invention. Such layers include cellulose nitrate film, cellulose acetate film, polyvinylacetal film, polystyrene film, polyethylene terephthalate film, polyethylene

film, polypropylene film and related films of resinous materials as well as paper, glass, and others. The terms also include paper or other fibrous material coated with a hydrophobic film or surface which repels and does not absorb or adsorb water. A support layer having a hydrophobic surface also may include hydrophobic resin layers which have been electron bombarded as described, for instance, in British Pats. 971,058, 1,060,526 and U.S. Pats. 2,864,755 and 2,864,756 to improve adhesion of hydrophilic colloid layers coated over them. Such resin layers or films may be either self-supporting or may be coated over another support layer. Specific supports having useful hydrophobic surfaces include polyethylene terephthalate films electron-bombarded to have a contact angle less than 45° C. (U.S. Pat. 2,220,842), an electron-bombarded surface comprising a chromium halide (U.S. Pat. 2,117,865), or electron-bombarded hardened gelatin coated papers (Belgian Pat. 671,661), etc.

A support layer may also contain various functional additives such as titanium dioxide pigments and an anti-static agent as described, for instance, in U.S. Pat. 3,253,922.

Usually photographic emulsions within the present invention are coated on support layers in the form of multi-layer color photographic elements wherein at least three differently sensitized emulsion layers are coated over one another on the support. The support is usually coated in succession with a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer, either with or without a Carey Lea filter layer between the blue- and green-sensitive layers. The three differently color sensitized layers may be arranged in any other order over one another on the same side of the support layer.

As a matter of preference, the above light-sensitive layers are arranged on the same side of the support layers.

This invention is further described, although not limited, by the following examples:

#### EXAMPLE 1

(A) 2-nitro-4-fluorophenol: To a stirred solution of 22.4 g. (0.2 mole) of p-fluorophenol in 100 ml. of glacial acetic acid is added at room temperature 14 ml. (0.22 mole) of concentrated nitric acid. The obtained mixture is stirred for 30 minutes, then poured into 500 ml. of ice-water. A yellow precipitate is formed, collected, washed with water, and dried. Yield 20 g. (64%); M.P. 72-74° C.

(B) 2-methyl-5-fluorobenzoxazole: A solution of 15.7 g. (0.1 mole) of 2-nitro-4-fluorophenol from step (A) in 200 ml. of dioxane is reduced catalytically (Pd/C) under a hydrogen pressure of 40 p.s.i. at 40° C. After the theoretical uptake of hydrogen (25 p.s.i.), the mixture is filtered through Super-Cel, transferred to 500 ml. round-bottomed flask, and the solvent removed by distillation under reduced pressure. To the residue is added 32.4 g. (0.2 mole) of triethyl orthoacetate and a few drops of concentrated sulfuric acid. This mixture is heated in an oil-bath until the bath temperature reaches 185-190° C. Ethanol begins to distill at 115° C. and distillation is completed at 185°. The resulting dark brown residue is vacuum distilled, and the fraction boiling at 51-53° C. (2.0 mm.) collected. Yield is 11.2 g. (74%).

(C) 2-methyl-5-fluoro-6-nitrobenzoxazole: To 23 ml. of concentrated sulfuric acid in a 500 ml. beaker is added, with stirring, 9.8 g. (0.065 mole) of 2-methyl-5-fluorobenzoxazole from step (B) the temperature being kept below 30° C. The reaction mixture is cooled to -10° C. and a precooled (-10° C.) nitrating mixture consisting of 9 ml. of concentrated sulfuric acid and 6.5 ml. (0.1 mole) of concentrated nitric acid is added slowly from a dropping funnel. The reaction temperature is maintained at 20-25° C., and after being stirred at this temperature for 1.5 hrs., the mixture poured into 200 ml. of ice-water. The resulting precipitate is removed, washed with water,

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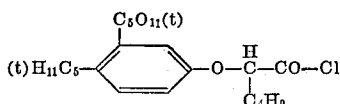
and dried. Yield is 12 g. (95%); M.P. 95–97° C. Recrystallization from ethanol gave 9.8 g. of light yellow platelets, with no change in melting point.

(D) 2-amino-4-fluoro-5-nitrophenol: A suspension of 49 g. (0.25 mole) of 2-methyl-5-fluoro-6-nitrobenzoxazole from step (C) in 600 ml. of concentrated hydrochloric acid and 600 ml. of water is treated, with stirring, on a hot plate for 2 hrs. The mixture is filtered and the filtrate neutralized with sodium acetate. Upon cooling to room temperature, long black needles crystallize from solution. The solid is collected and dried, giving 30.1 g. (70%) of product, M.P. 211–212° C.

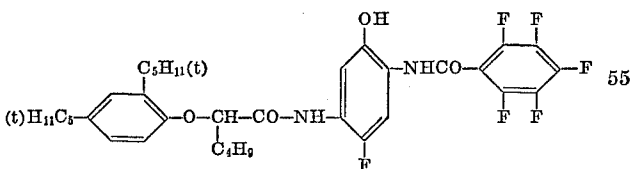
(E) 2 - (2,3,4,5,6 - pentafluorobenzamido) - 4-fluoro-5-nitrophenol: To a solution of 0.1 mole of 2-amino-4-fluoro-5-nitrophenol from step (D) and 0.2 mole of quinoline in 300 ml. of dioxane are added, with stirring, a solution of 0.2 mole of pentafluorobenzoyl chloride in 100 ml. of dioxane. The reaction mixture is stirred at room temperature for 1 hr., then poured into 1 liter of ice-water containing 10–15 ml. of concentrated hydrochloric acid. The precipitated solid or gum is removed, washed with water, and treated for 30–40 mins. in 100 ml. of 10% aqueous alcoholic potassium hydroxide solution. The mixture is then carefully neutralized with cold dilute hydrochloric acid, solid product was collected, washed with water, and finally recrystallized from aqueous alcohol.

(F) 2-(2,3,4,5,6 - pentafluorobenzamido) - 5 - amino-4-fluorophenol: A solution of 0.05 mole of the above intermediate 2-acylamido-4-fluoro-5-nitrophenol in 200 ml. of dioxane containing a teaspoonful of palladium-on-charcoal is placed in a Parr bottle and reduced under hydrogen at 40 p.s.i. at 40° C. After the theoretical uptake of hydrogen (about 30 min.), the mixture is filtered through Super-Cel, and the solution of the amine used directly for preparation of the desired coupler.

(G) To the solution of 2 - acylamido - 5 - amino-4-fluorophenol obtained in the previous step is added, with stirring, 0.1 mole of quinoline and 0.05 mole of ballasted acid chloride of the formula

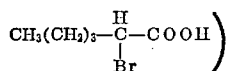


The reaction mixture is stirred for 5 hours, then poured into 1 liter of ice-water containing 10–15 ml. of concentrated hydrochloric acid. The solid is removed, washed with water, and recrystallized from acetonitrile to obtain a compound having the formula



having a melting point of 194–5° C.

The acid chloride reactant of step (G) is prepared, for instance, by reacting the sodium salt of the corresponding alkyl-substituted phenol and an appropriate  $\alpha$ -bromophenoxy alkanic acid (i.e.,



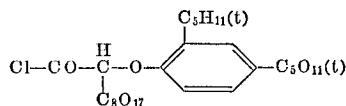
and, thereafter, further reacting the product with thionyl chloride to obtain the desired acid chloride.

#### EXAMPLE 2

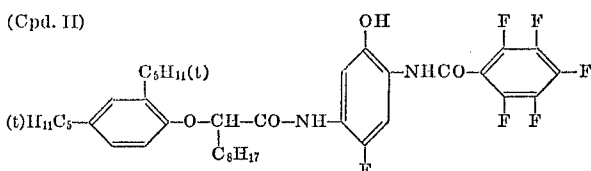
.2 mole of p-fluorophenol is reacted in accordance with steps (A)–(F) of Example 1 and the resulting product

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reacted with .05 mole of a ballasted acid chloride of the formula



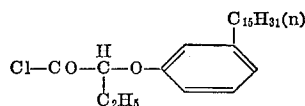
prepared in the manner of Example 1, and the resulting product recovered as in step (G) of Example 1



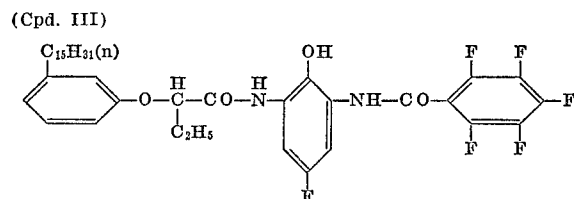
having a melting point of 152°–153° C.

#### EXAMPLE 3

.2 mole of p-fluorophenol is reacted in accordance with steps (A)–(F) of Example 1 and the resulting product reacted according to step (G) with a ballasted acid chloride of the formula



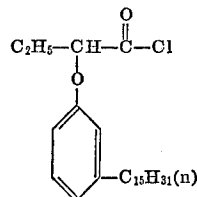
prepared in the usual manner from  $\alpha$ -bromo butyric acid to obtain the compound



having a melting point of 133°–134° C.

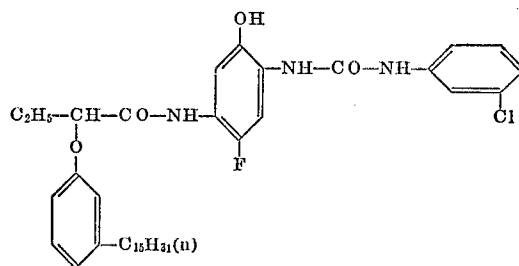
#### EXAMPLE 4

Para-fluoro phenol is reacted as in steps (A) through (D) of Example 1, the resulting 2-amino-4-fluoro-5-nitrophenol is then reacted with meta-chlorophenyl isocyanate to obtain the corresponding 2-(m-chlorophenyl)-4-fluoro-5-nitrophenol, and this compound is then hydrogenated and reacted with .05 mole of ballasted acid chloride of the formula



to obtain a compound of the formula

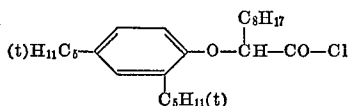
(Cpd. IV)



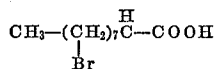
having a melting point of 170°–171° C.

**9**  
**EXAMPLE 5**

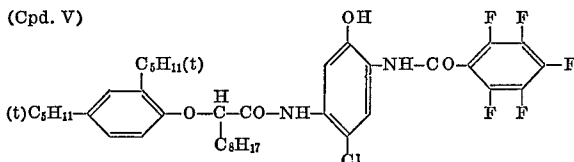
Para-chloro phenol is reacted in accordance with steps (A)-(F) of Example 1, the product being reacted with an acid chloride of the formula



prepared from



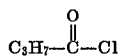
and step (G) carried out to obtain a compound of the formula



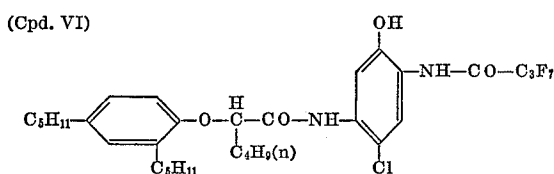
having a melting point of 159-160° C.

**EXAMPLE 6**

Para-chloro phenol is reacted in accordance with steps (A)-(E) of Example 1, using



as the acid chloride, to effect placement of the o-substituent on the phenol ring. The remaining steps (F)-(G) of Example 1 are then followed, using o,p-ditertiary pentyl as the ballasted phenoxy hexanoic acid chloride as the acid chloride of step (G). A compound of the formula

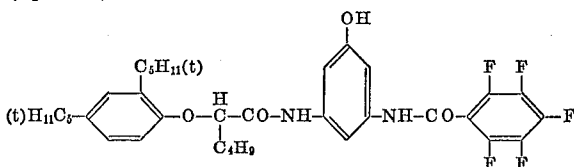


is obtained having a melting point of 170-171° C.

**EXAMPLE 7**

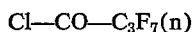
Phenol is reacted in accordance with steps (A)-(G) of Example 1 to obtain a compound of the formula

(Cpd. VII)



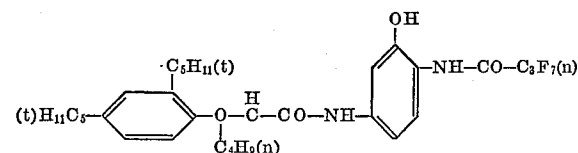
**EXAMPLE 8**

Phenol is reacted in accordance with steps (A)-(G) of Example 1 wherein step (E) is effected with



and step (G) effected with di(t)-pentyl phenoxy-hexanoic acid chloride to obtain a compound of the formula

(Cpd. VIII)

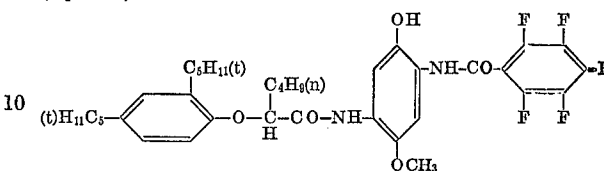


having a melting point of 154-155° C.

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**EXAMPLE 9**

Para-methoxy phenol is reacted in accordance with steps (A)-(G) of Example 1 to obtain a compound of the formula

(Cpd. IX)

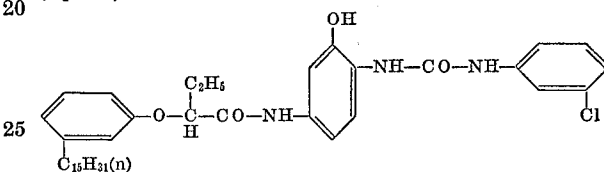


having a melting point of 234-5° C.

**EXAMPLE 10**

Phenol is reacted in accordance with Example 4 to obtain a compound of the formula

(Cpd. X)



having a melting point of 144-6° C.

**EXAMPLE 11**

Photographic test strips are coated with standard gelatinous silver bromo-iodide emulsion coating to obtain 136 mg. silver, 450 mg. gelatin, 78 mg. of one of the above-described coupler compounds 1-10, and 39 mg. di-n-butyl phthalate as coupler solvent in accordance with the technique described in the Example 1 of U.S. Pat. 2,949,360.

The coated strips are sensitometrically exposed through a graduated-density test object and processed in the usual manner at 20° C., one duplicate being treated with Color Developing Solution A, as hereinafter described. The strips are then stop-fixed, washed, silver bleached, washed, fixed, washed, stabilized and dried in the usual manner, thereafter tested as explained below, and evaluated to determine their maximum image dye density, also light and heat fading characteristics, and the results set forth in Table I.

**Color developing solution A**

H <sub>2</sub> O	-----ml---	800
Calgon	-----g---	0.5
Na <sub>2</sub> SO <sub>3</sub>	-----g---	2.0
4-amino-3-methyl - N,N - diethyl aniline hydrochloride	-----g---	2.0
Na <sub>2</sub> CO <sub>3</sub> · H <sub>2</sub> O	-----g---	20.0
50% NaBr solution	-----ml---	3.46
H <sub>2</sub> O	to 1 liter.	

(pH 10.86)

**Light fading tests**

The extent to which the image dyes fade under the influence of light is determined by subjecting processed coatings to a simulated 21-day north skylight exposure (SANS) and determining the resulting decrease in dye density in an area having an initial dye density of approximately 1.2. The resulting "Light Fade" is recorded as density units.

The extent to which unreacted coupler causes unwanted stain under the influence of light is determined by exposing processed coatings to SANS, as above described, and recording the resulting increase in density to blue light (420 mμ) in a D<sub>min</sub> area of the coating. This increase is termed "Print Out" (PO) and is recorded in terms of percent density increase in Table I infra.

**Heat fading tests**

The extent to which the image dyes fade under the influence of heat and humidity is determined by subjecting

coatings to a temperature of 60° C. at a relative humidity of 70% for 1 week. The resulting decrease in image dye density is termed "Heat Fade" (H.F.) and is measured in terms of decrease in dye density in density units.

The effect of heat on unreacted coupler is determined by subjecting coatings to the above heat and humidity conditions, and determining the increase in density (i.e. yellowing) in a  $D_{min}$  area (420  $m\mu$ ) of the coating, and recording this in terms of percent density increase.

TABLE I

Compound No.	Developer solution	$D_{max}$	$\tau_{max}$	SANS 21 day (light fade)	Heat fade (HF) (1 week)	Yellowing percent density increase	Print out, percent
I.....	A	3.40	6.77	.09	+.02	6	3
II.....	A	3.32	6.70	.06	+.03	4	2
III.....	A	3.20	6.54	.08	+.03	5	1
IV.....	A	3.53	6.70	.13	+.02	6	3
V.....	A	2.36	6.73	.07	+.01	2	3
VI.....	A	2.98	6.74	.24	+.03	4	3
VII.....	A	2.86	6.76	.16	+.02	1	2
VIII.....	A	3.00	6.57	.14	+.01	7	2
IX.....	A	2.26	6.66	.08	+.01	1	4
X.....	A	2.86	6.64	.....	+.06	5	1

TABLE II.—AVERAGE VALUES

Compound No.	Developer solution	$D_{max}$	$\tau_{max}$	SANS 21 day (light fade)	Heat fade (HF) (1 week)	Yellowing percent density increase	Print out, percent
I-IV.....		3.36	.....	.090	.025	5.3	2.3
V-X.....		2.73	.....	.138	.023	3.3	2.5

## EXAMPLE 12

Photographic test strips corresponding to Example 11 are prepared utilizing, as coupler compound, yellow dye-producing compounds of the following formula prepared in accordance with U.S. Pats. 3,369,895 and 3,409,439.

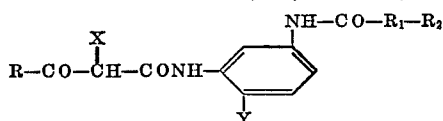
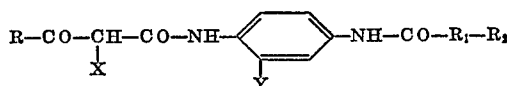


TABLE III

Compound No.	R	X <sup>1</sup>	Y	R <sub>2</sub>	R <sub>1</sub>
XII, A.....	(t)-Butyl	Cl	Cl	1,3di(t) pentyl-phenoxy.	-(CH <sub>2</sub> ) <sub>3</sub> -
XII, B.....	(t)-Butyl	F	Cl	.....do.....	-(CH <sub>2</sub> ) <sub>3</sub> -

<sup>1</sup> Coupling position substituent.

TABLE IV



Compound No.	R	X <sup>1</sup>	Y	R <sub>2</sub>	R <sub>1</sub>
XII, C.....	o-Methoxy phenyl.	Cl	H	1,3di(t) pentyl-phenoxy.	H   -C-CH <sub>2</sub> CH <sub>3</sub>
XII, D.....	.....do.....	F	H	.....do.....	Same as above.

The test strips were exposed, developed and  $D_{max}$  values determined as in Example 11.

TABLE V

Compound No.	$D_{max}$	$\lambda_{max}$
XII, A.....	2.94	448
XII, B.....	2.08	448
XII, C.....	2.00	433
XII, D.....	1.90	434

## EXAMPLE 13

(A) Five grams of Compound 1 of Example I are dissolved in a solution of 2.5 grams of di-n-butyl phthalate

and 7.5 grams of B-ethoxyethyl acetate at 138° C. A gelatin solution is prepared containing 34 grams of 10% gelatin solution in water, 5 ml. of 7.5% alkanol B solution and 10 grams of B-ethoxyethyl acetate dissolved at 49° C. The coupler solution is poured into the gelatin solution, stirred for about one minute and passed through a colloid mill five times. The dispersion was set up on a chill plate at 5° C., noodled and washed for 6 hours in cool water to substantially remove all auxiliary solvent

in the manner of U.S. Pat. 2,949,360. After remelting, the coupler is incorporated into a gelatino-silver halide emulsion coated onto test strips as in Example 11. A cyan dye image having a  $D_{max}$  value of 3.40 is obtained.

(B) Five grams of Compound 1 of Example I are incorporated in a system free of high-boiling coupler solvent and substantially free of low-boiling coupler solvents, obtained by initially dissolving into 10 grams of a 1:1 mixture of B-ethoxyethyl acetate and methyl-n-propyl ketone. The resulting solution is then dispersed in a 10% gelation solution, chilled, noodled, washed and dried as described above and thereafter melted and incorporated into a gelatino-silver halide emulsion. The resulting emulsion is applied to test strips as before, the concentration of silver, gelatin and coupler being identical, to obtain a cyan dye image having suitable  $D_{max}$  value of 1.92 for reflective purposes. The thickness of the test strips is observed to be about  $\frac{3}{4}$  of the test strip of Example 13A and also substantially more resistant to scratching and abrasion.

## EXAMPLE 14

(A) Five grams of Compound VII of Example 7 are dissolved, incorporated into a gelatino-silver halide emulsion and coated onto a test strip as in Example 13A to obtain a cyan dye having a  $D_{max}$  value of 2.85.

(B) Five grams of Compound VII are initially dissolved in auxiliary solvents and dispersed into a 10% gelatin solution followed by chilling, noodling and washing as described in Example 13. Extensive crystallization of the coupler is evidenced by the fact that the washed noodles cannot be melted or reconstituted in the usual manner, crystals of the coupler being directly observed under low microscopic power. No coating or  $D_{max}$  determination is obtained.

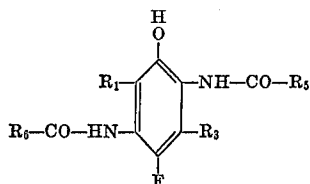
This invention has been described in detail with particular reference to a preferred embodiment thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A color photographic element having a film base, a light-sensitive silver halide emulsion applied thereto,

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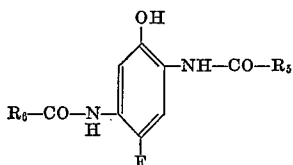
and containing as cyan dye-forming coupler compound a compound having the formula



wherein

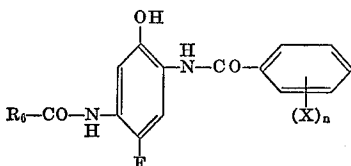
R<sub>1</sub> is hydrogen or an alkyl group of 1-4 carbon atoms;  
R<sub>3</sub> is hydrogen or an alkyl group of 1-4 carbon atoms;  
R<sub>5</sub> is a halophenyl, a halo-phenylamino or a phenylamino group; and  
R<sub>6</sub> is an alkyl-substituted- or dialkyl-substituted-phenoxy-lower alkyl group.

2. A light-sensitive silver halide photographic emulsion containing as cyan dye-forming coupler a compound of the formula

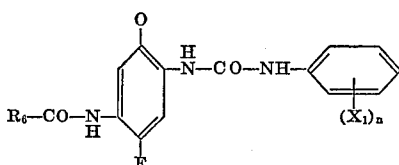


wherein R<sub>5</sub> is defined as a halophenyl, a halo-phenylamino or phenylamino group; and R<sub>6</sub> is an alkyl substituted- or dialkyl-substituted-phenoxy-lower alkyl group.

3. A light-sensitive silver halide photographic emulsion containing a compound of the formulae



or



wherein R<sub>6</sub> is defined as an alkyl substituted aryloxy-lower alkyl group; X is fluoro, X<sub>1</sub> is chloro and n is 0,

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1, or 5, n being defined as 5 when X is fluoro and as 1 when X<sub>1</sub> is defined as chloro.

4. A light-sensitive silver halide photographic emulsion containing a compound of claim 2 wherein R<sub>5</sub> is pentafluorophenyl and R<sub>6</sub> is a di-tertiary-lower alkyl-substituted phenoxy-lower alkyl.

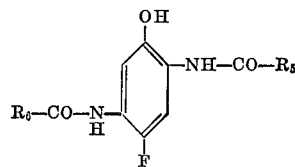
5. A light-sensitive silver halide photographic emulsion containing a compound of claim 2 wherein R<sub>5</sub> is pentafluorophenyl and R<sub>6</sub> is a 2,4-di-tertiary pentyl substituted phenoxy-lower alkyl.

6. A light-sensitive silver halide photographic emulsion containing a compound of claim 2 wherein R<sub>5</sub> is 2-chlorophenyl amino and R<sub>6</sub> is an n-alkyl-phenoxy-lower alkyl.

7. A light-sensitive silver halide photographic emulsion containing as cyan dye-forming coupler 2-(pentafluorophenylcarbonamido) - 4-fluoro-5-(di-tertiarypentyl-phenoxy-pentyl carbonamido)-phenol.

8. A light-sensitive silver halide photographic emulsion containing as cyan dye-forming coupler 2-(2-chlorophenyl)ureido-5-(pentadecyl phenoxy propyl carbonamido)-phenol.

9. A color photographic element having a film base, and light-sensitive silver halide emulsion applied thereto and having incorporated therein as cyan dye forming coupler compound a compound of the formula



wherein R<sub>5</sub> is defined as a halophenyl, a halo-phenyl-amino or phenylamino group; and R<sub>6</sub> is an alkyl substituted- or dialkyl-substituted-phenoxy-lower alkyl group.

#### References Cited

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2,772,162	11/1956	Salminen et al.	96—100
3,369,895	2/1968	Loria et al.	96—100
3,516,831	6/1970	Wolf et al.	96—100

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1,099,418	1/1968	Great Britain	96—100
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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—55, 56; 260—623

# CERTIFICATE OF CORRECTION

Patent No. 3,758,508 Dated September 11, 1973

Inventor(s) Leo E. Beavers, Philip T. S. Lau and Ilmari F. Salminen

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 26, "halalkyl" should read ---haloalkyl---;

Column 3, line 16, "resoltuion" should read ---resolution---;

Column 4, line 3, after "instance," insert ---by a acyl-amido ureido or -CH=CH- group.---;

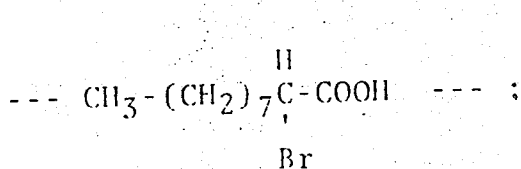
Column 6, line 17, "2,117,865" should read ---3,117,865---;

Column 6, line 33, delete "layers are arranged on the same side of the support layer" and insert ---another that is desirable with the exception that Carey Lea filter cannot be placed over a blue-sensitive layer---;

Column 6, line 61, "drak" should read ---dark---;

Column 8, line 6, that part of the formula " $C_8O_{17}$ " should read --- $C \begin{matrix} 8 \\ 17 \end{matrix} H$ ---;

Column 9, lines 11-14; " $CH_3-(CH_2)_7 \overset{C}{H}-COOH$ " should read





UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

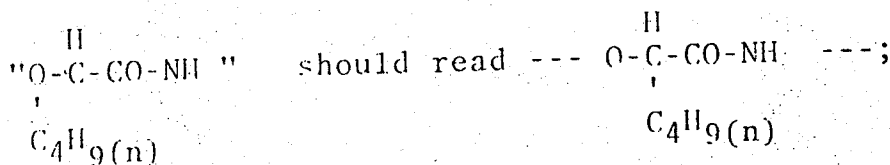
Patent No. 3,758,308 Dated September 11, 1973

Inventor(s) Leo E. Beavers, Philip T. S. Lau and Ilmari F. Salminen

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

PAGE - 2

Column 9, lines 68-74, that part of the formula,



Column 11, Tables I and II, the column headings "D<sub>ma</sub>" should read ---D<sub>max</sub>---

Column 11, line 24, "2.26" should read ---2.22---

Column 12, line 43, "gelation" should read ---gelatin---

Column 11, Tables I and II, the column heading "λ<sub>max</sub>" should read ---λ<sub>max</sub>---

Signed and sealed this 5th day of March 1974.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents