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RESIN SALTS OF COUPLERS IN MIXED PACKET PHOTOGRAPHIC EMULSIONS

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8 Claims. (Cl. 95—2)

This invention relates to color photography and particularly to mixed packet photographic emulsions.

There have been many prior suggestions of mixed grain photographic emulsions, that is, photographic systems in which differently sensitized silver halide grains are incorporated in a single photographic emulsion layer and used to produce differently colored photographic images in the layer. Mixed grain systems have a number of advantages, chief among which is the simplicity of coating a single emulsion layer rather than several layers. Other advantages are the improved definition obtained by having the differently sensitized particles juxtaposed in a single layer, and the simplification of processing which is generally obtained.

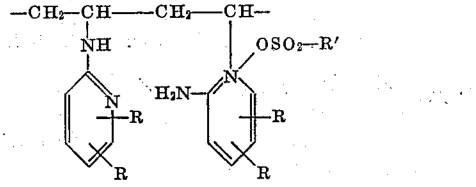
In Godowsky U. S. application Serial No. 156,066, filed April 15, 1950, a mixed packet process is described in which a color coupler is dissolved in a suitable coupler solvent and is mixed with a suitably sensitized silver halide emulsion, and packets caused to form enveloping the sensitized emulsion and associated coupler, leaving neither silver halide nor coupler free in the surrounding liquid or gelatin matrix. Another packet emulsion is made in like manner but containing a different coupler and an emulsion sensitized to a different portion of the spectrum. When these dispersions are mixed and coated on film, plates or paper, good color separation is achieved upon suitable exposure and development.

One of the disadvantages in processes such as that which is described in the Godowsky application is the presence in the dispersion of the coupler solvent which materially adds to the total volume of the finished emulsion. A second fault with the solvent system is the fact that the dye formed in the image is in solution in the solvent and is therefore in a more reactive state and is subject to more rapid fading and print-out than a dye in the solid state. A third difficulty with the solvent system is the fact that dispersing agents are used for dispersion of the coupler and these sometimes adversely affect the stability of the sensitized emulsion insofar as speed and contrast are concerned.

It is therefore an object of the present invention to provide a novel incorporated coupler emulsion. A further object is to provide a novel method of incorporating couplers in silver halide emulsions. A still further object is to provide a novel mixed packet emulsion. A further object is to provide a novel method of incorporating couplers in mixed packet emulsions. A further object is to provide mixed packet emulsions free of organic coupler solvent.

These objects are accomplished by the use of couplers having a sufficient number of solubilizing groups so that they can easily be put into aqueous solution, and precipitating the couplers with a polyvinyl resin containing pyridylamine nuclei, such as polyvinyl-N-(α-pyridyl)-amine, to give a precipitate completely insoluble in water even when the excess precipitant is washed out, but which is still sufficiently self-dispersible so that a satisfactorily fine dispersion can be made without recourse to dispersing agents. The fine dispersion of coupler salt is then added to a colloid-silver halide emulsion in the presence of a water-soluble salt of a polymer containing salt-forming acid groups, e. g. a methylmethacrylate-methacrylic acid copolymer, and a packet-forming component, e. g. a styrene-maleamic acid copolymer, to form particles of colloid, packet-forming component and silver halide containing the coupler salt.

The invention depends upon the use of polyvinyl resins containing pyridylamine nuclei. These compounds are N-substituted polyvinyl amines consisting of pyridylamine units and quaternized vinylsulfonate units along with some vinyl alcohol and cyclic ether units. Their preparation is described in Reynolds and Kenyon U. S. application 249,012, filed September 29, 1951. These compounds have the following recurring structure:

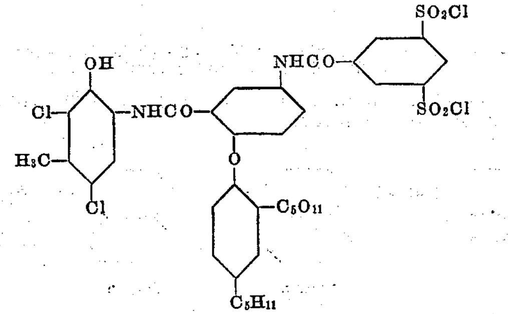


in which R represents hydrogen or an alkyl group containing from 1 to 5 carbon atoms and R′ represents an alkyl group containing from 1 to 5 carbon atoms and the resin contains from 6% to 24% by weight of vinylpyridyl amine units and from 40% to 60% by weight of vinylpyridinium quaternary salt units.

Couplers can be incorporated according to our invention to form an emulsion in which dye images are produced by color forming development, or dyes may be incorporated in an emulsion to form a system in which dye images can be produced by bleaching the dyes in the presence of the silver image as described in Christensen U. S. Patent 1,517,049.

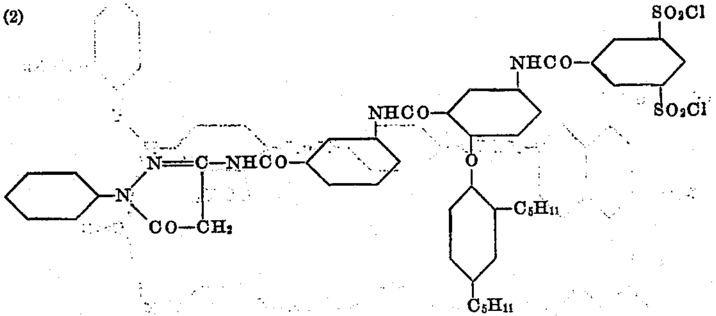
The following couplers are suitable for use according to our invention:

(1)



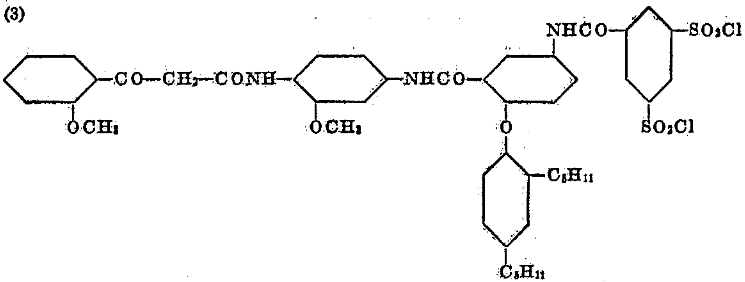
4,6 - dichloro - 5 - methyl - 2 - [2′(2′′,4′′ - diamylphenoxy)-5′-(3′′,5′′-dichlorosulfonyl) - benzamido} benzamido] - phenol.

(2)



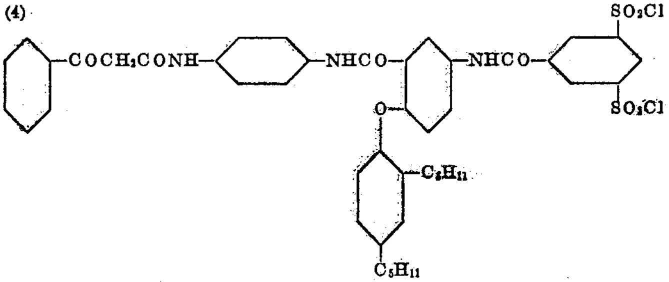
1 - phenyl - 3 - {3′ - {2′′- (2′′′,4′′′- diamylphenoxy) - 5′′-[3′′′,5′′′- dichlorosulfonylbenzamido] - benzamido} - benzamido}-5-pyrazolone.

(3)



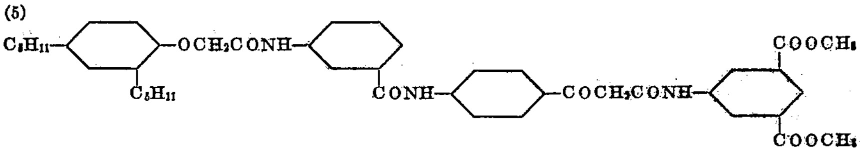
4′- (o - methoxybenzoylacetamido) - 3′- methoxy - 5 - (3″,5″-dichlorosulfonylbenzamido) - 2 - (2‴,4‴- di - tert - amylphenoxy)benzanilide.

(4)



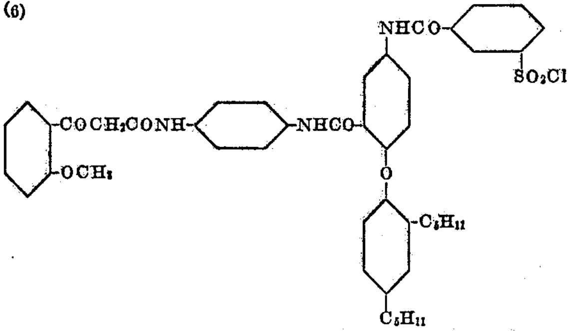
4′- (benzoylacetamido) - 2 - (2″,4″- di - tert - amylphenoxy)-5-(3‴,5‴-dichlorosulfonyl)-benzamido benzanilide.

(5)



Dimethyl - 5 - {4′- [3″(2‴,4‴- di - tert - amylphenoxyacetamido)benzamido]benzoylacetamido}isophthalate.

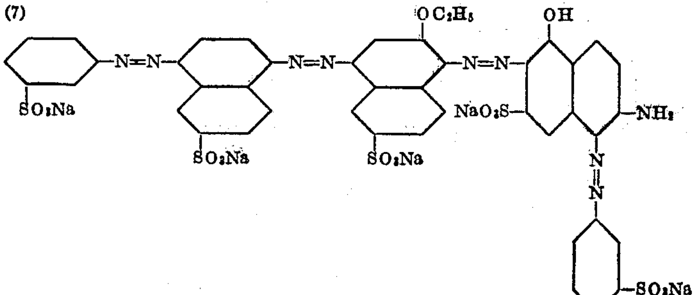
(6)



4′- (o - methoxybenzoylacetamido) - 2 - (2″,4″- di - tert - amylphenoxy)-5-(3‴-chlorosulfonylbenzamido)-benzanilide.

The following dyes may be incorporated in emulsions according to our invention:

(7)



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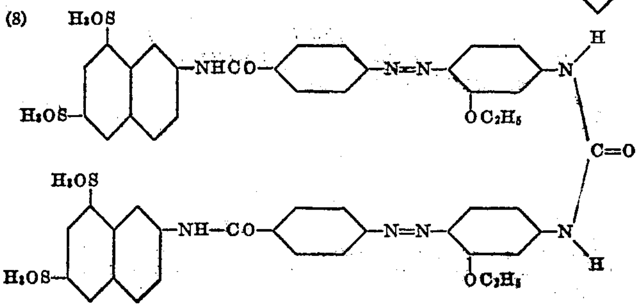

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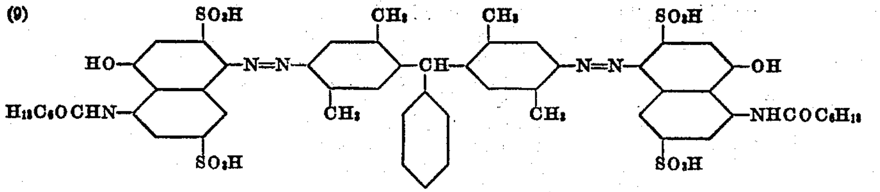


The silver halide emulsions in which these couplers or dyes are incorporated may be optically sensitized and ordinarily two or more emulsions sensitive to different regions of the visible spectrum will be employed and mixed.

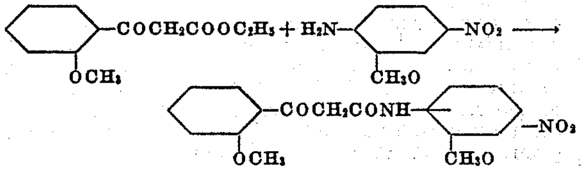
Compounds 1 to 6 were prepared as follows:

Compound 1 was prepared in the same way as Compound 11 of Salminen and Weissberger U. S. application Serial No. 344,884, filed concurrently herewith, using 3,5-dichlorosulfonylbenzoyl chloride instead of m-chlorosulfonylbenzoyl chloride in the next to the last step.

Compound 2 was prepared as described in Salminen and Weissberger U. S. application Serial No. 344,884.

COMPOUND 3

2-(2′-methoxybenzoylacetamido)-5-nitroanisole



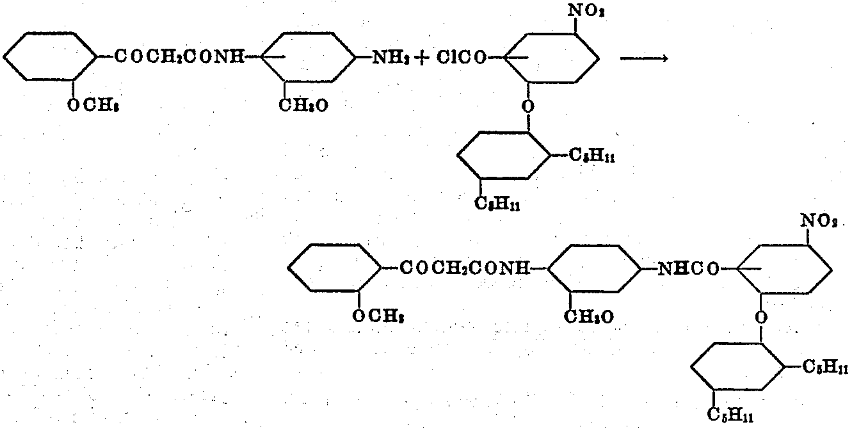
In a 2-l. three-necked flask, fitted with a stopper, stirrer, and a steam jacketed column terminating in a partial condensing still head which was connected to a water-cooled condenser set for distillation, was placed 240 cc. (1.2 moles) of ethyl o-methoxybenzoyl acetate and 300 cc. of histological xylene. One gram of anhydrous sodium acetate was added and the mixture was heated to boiling in an oil bath. Heating was then discontinued while one-half of 168.5 g. (1 mole) of 2-amino-5-nitroanisole was added. The flask was stoppered again and the mixture refluxed at such a rate as to maintain the temperature of the distilling vapors at 78–80° C. After about 30 mins. the elimination of alcohol became very slow, and the remaining half of the amine was added. It required a total heating time of 1.5–2.5 hrs. before all of the alcohol was eliminated; 40–50 cc. was collected. The reaction mixture was cooled with running water until 200 cc. of benzene could be added safely and was well stirred to prevent lumping while the mixture was cooled to 10° C. The yellow precipitate was filtered, washed with 500 cc. of cold ethyl alcohol diluted with 60 cc. of glacial acetic acid, finally washed with 100 cc. more of ethyl alcohol and dried. The yield was 228–270 g. (66–76%), M. P. 166–168°.

2-(2,4-di-tert-amylphenoxy)-5-nitrobenzoyl chloride

In a 12-liter wide mouthed flask equipped with a stirrer, thermometer, and condenser "stoppered" with a drying tube, were placed 1,200 g. (3 moles) of 2-(2,4-di-tert-amylphenoxy)-5-nitrobenzoic acid, to which was added with stirring 4.5 liters of thionyl chloride. The mixture was heated on a steam bath for 2 hours with stirring and permitted to stand over night. Excess thionyl chloride was taken off in vacuo and the residual amounts of hydrogen chloride, sulfur dioxide, and thionyl chloride were eliminated by two additions of 400-cc.-portions of dry benzene and distilling. The resulting light amber syrup was seeded with crystals from a previous run and permitted to stand. In a few hours the product began to crystallize and the following day was filtered.

After reduction of the 2-(2′-methoxybenzoylacetamido)-5-nitroanisole to the amine with iron and acetic acid as in the preparation of Compound 1, the amine was further treated as follows:

4′-(o-methoxybenzoylacetamido)-3′-methoxy-2-(2″,4″-diamylphenoxy)-5-nitrobenzanilide



A mixture of 20 g. (0.24 mole) of anhydrous sodium acetate and 62.8 g. (0.2 mole) of 4-(o-methoxybenzoylacetamido)-3-methoxyaniline was ground to a fine powder, and added with stirring to 700 cc. of glacial acetic acid at 30–35° C. To the resulting solution was added 83.5 g. (0.2 mole) of 2-(2′,4′-diamylphenoxy)-5-nitrobenzoyl chloride. The mixture became cloudy and after about five minutes set to a solid yellow mass. It was allowed to stand without heating or stirring for two hours. Then 100 cc. of water was added and the paste stirred thoroughly. After filtering and washing with 200 cc. of 50% acetic acid, and 400 cc. of water, the product was slurried with 1 l. of ethyl alcohol, filtered and dried thoroughly. The yield of light yellow material was 120 g. (85%), M. P. 130–132° C.

4′-(o-methoxybenzoylacetamido)-3′-methoxy-2-(2″,4″-diamylphenoxy)-5-aminobenzanilide

A copper bomb of 4500-cc. capacity was charged with 120 g. (0.18 mole) of 4′-(o-methoxybenzoylacetamido)-3′-methoxy-2-(2″,4″-diamylphenoxy)-5-nitrobenzanilide, 1800 cc. of anhydrous ethyl acetate and 20 g. of moist (alcohol) Raney nickel. The reduction was carried out at a maximum pressure of 60 lbs. and at 75–80° C. The calculated quantity of hydrogen was absorbed in 2 hrs and the mixture was shaken 1 hr. longer. After cooling, the solution was filtered to remove the catalyst, and the filtrate was concentrated at reduced pressure until all the ethyl acetate had distilled. The resulting syrup was taken up in 600 cc. of ethyl alcohol from which it rapidly crystallized. After thorough chilling to 10° C., the product was filtered and washed with 100 cc .of cold alcohol. The yield of cream colored amine was 82 g. (71%), M. P. 170–173°.

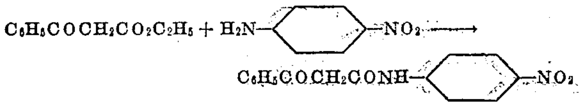
4′-(o-methoxybenzoylacetamido)-3′-methoxy-5-[3″,5″-di-(chlorosulfonyl)-benzamido]-2-(2‴,4‴-di-tert.-amylphenoxy)-benzanilde

A suspension of 10.2 g. (0.0152 mole) of powdered 4′-(o-methoxybenzoylacetamido)-3′-methoxy-5-

amino - 2 - (2'',4'' - diamylphenoxy) - benzanilide in 100 cc. of glacial acetic acid was warmed to 35° C. and 6.3 g. (0.0152 mole) of 3,5-dichlorosulfonylbenzoyl chloride was added with stirring. The reactants dissolved rapidly and the temperature rose 3–5°. Just as all the amine dissolved the complex separated as a thick, yellow slurry. This was stirred without external heating for 1 hr., and then 1.26 g. (0.0152 mole) of anhydrous sodium acetate was added. The color became lighter as the complex was decomposed and the product separated. After stirring for 1–2 hrs. longer the slurry was allowed to stand overnight. In the morning 10 cc. of water was added and after stirring for 15 mins. the yellow, crystalline solid was collected on a Büchner funnel. It was slurried with 100 cc. of 50% acetic acid, filtered again and washed with 100 cc. of water. It was dried overnight in the cabinet; yield 11.0 g. (75%), M. P. 210–212° (decomp.).

COMPOUND 4

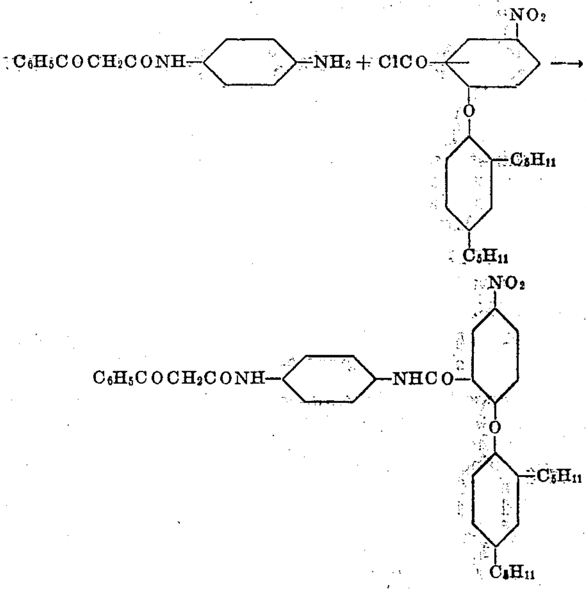
Benzoylacet-4-nitroanilide



In a 5-liter 3-necked round-bottom flask equipped with a partial condensing still-head were placed 10 g. of anhydrous sodium acetate, 1200 ml. of histological xylene, and 800 ml. (4.7 moles) of ethyl benzoyl acetate. The mixture was brought to a boil and 552 g. (4.0 moles) of p-nitroaniline was added portionwise (4) about 30 minutes apart. After 4–5 hours' reflux, ca. 200 ml. of ethyl alcohol had collected. The reaction mixture was then poured into a 4-liter beaker, diluted cautiously with 400 ml. of benzene, and allowed to stand at room temperature overnight. The product was filtered, slurried with 4 liters of ethyl alcohol, filtered, and dried. The yield was 855 g. (73%) of a yellow powder which melted at 178–180° C.

After reduction of the benzoylacet-4-nitroanilide to the amine with iron and acetic acid, the amine was treated as follows:

4'-(benzoylacetamido)-2-(2'',4''-di-tert-amylphenoxy)-5-nitrobenzanilide



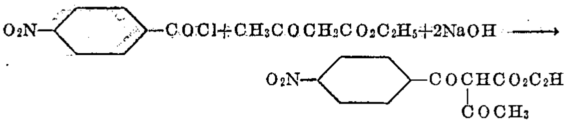
In a 100-ml. Erlenmeyer flask equipped with a stirrer were placed 5.08 g. (0.02 mole) of benzoylacet-4-aminoanilide, 1.62 ml. (0.02 mole) of pyridine, and 40 ml. of dioxane. With good stirring at 45–55°, 8.35 g. (0.02 mole) of 2-(2',4'-di-tert-amylphenoxy)-5-nitrobenzoyl chloride was added all at once. The gummy mixture was stirred for 1 hour and poured into 200 ml. of water containing 5 ml. of concentrated hydrochloric acid. Water was decanted from the gum several times, and upon titurating with ethyl alcohol, the product crystallized. The brilliant yellow needles were filtered, washed with alcohol, and dried to give 9.3 g. (73%) of product melting at 194–197°.

After reduction of the nitro compound to the amine with iron and acetic acid, it was further treated as follows:

In a 50-ml. Erlenmeyer flask equipped with stirrer and thermometer were placed 2 g. (0.0033 mole) of 4-(benzoylacetamido) - 2 - (2'',4'' - di - tert - amylphenoxy)-5-aminobenzanilide, 0.27 ml. of pyridine, and 25 ml. of dioxane. With good stirring at 50° C., 1.38 g. (0.0033 mole) of 3,5-dichlorosulfonylbenzoyl chloride was added. After 12–14 hours, the yellow solution was poured with vigorous stirring into 100 ml. of water containing 1–2 ml. of concentrated hydrochloric acid. The yellow solid was filtered, washed well with water, and dried. Three grams of crude material was recrystallized from 50 ml. of ethyl acetate. The yield of Compound 4 was 1.1 g. (37%) of tan powder which decomposed at 220–230° C.

COMPOUND 5

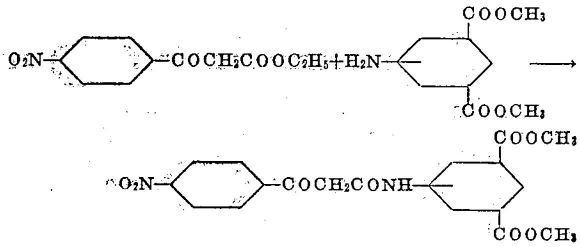
Ethyl α-(p-nitrobenzoyl)acetoacetate



In a 1-liter beaker was placed 33 g. (0.25 mole) of ethyl acetoacetate and 100 cc. of water. The mixture was cooled to 15° in running water. Then solutions of 46 g. (0.25 mole) of p-nitrobenzoyl chloride in 100 cc. of acetone and 20 g. (0.50 mole) of sodium hydroxide in 100 cc. of water were added simultaneously with stirring and cooling to keep the temperature below 23°. The additions required twenty minutes. The rates of addition were so adjusted that the alkaline solution was added slightly ahead of the acid chloride solution. Acidification of the reaction mixture with sulfuric acid caused an oil to separate. This was taken up in 300 cc. of benzene and washed with dilute sodium bicarbonate solution. Evaporation of the benzene from a steam-bath left a residue which crystallized. The solid was slurried with a little ethanol and collected to give 40 g. (57% yield), M. P. 52°–55° C.

To a solution of 28 grams of ethyl α(nitrobenzoyl)-acetoacetate in 200 cc. of ethyl alcohol was added 100 cc. of 20% ammonium hydroxide. The mixture was stirred in a bath at 40° C. for ten minutes. The solution became clear after five minutes and then salt separated. The mixture was left at room temperature for ninety minutes before it was chilled at 5° C. over night. The mixture was acidified with 100 cc. of glacial acetic acid in 250 cc. of ice water. The solid ethyl p-nitrobenzoyl acetate was collected and washed with water to give 21 grams. M. P. 66–68°. The product was purified by recrystallization from alcohol.

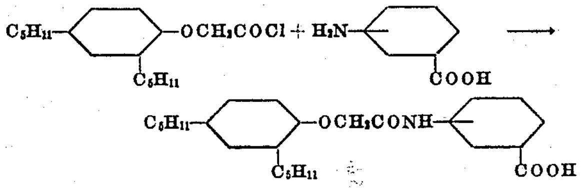
Dimethyl 5-(p-nitrobenzoylacetamido)-isophthalate



In a 2-l. 3-necked flask equipped with stirrer and reflux condenser was placed 95 g. (0.40 mole) of ethyl p-nitrobenzoyl acetate, and 680 cc. of xylene. The reaction mixture was brought to reflux and 2 g. of sodium acetate and 71 g. (0.34 mole) of dimethyl 5-amino isophthalate were added. After 10 minutes reflux the product began to crystallize and after an additional 5 minutes reflux, the reaction mixture was cooled to room temperature and filtered. The yellow solid was washed with 500 cc. of methyl alcohol and 500 cc. of petroleum ether. The yield was 111 g.–126 g. (81–93%) of a light yellow powder which melted at 213–215° C.

The nitro compound was reduced to dimethyl-5-(p-aminobenzoylacetamido)-isophthalate with iron and acetic acid in the usual way.

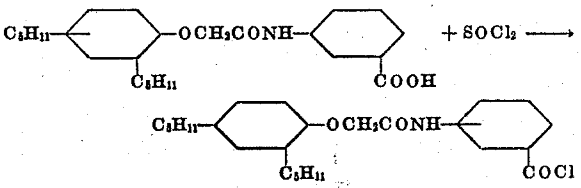
3-(2,4-diamylphenoxy)-acetamidobenzoic acid



In a 1-l. flask equipped with mechanical stirrer, condenser carrying a drying tube, and a dropping funnel was placed 43 g. (0.314 mole) of m-aminobenzoic acid, 40.5 g. (37 ml., 0.314 mole) of quinoline and 300 ml. of dioxane. The contents of the flask was heated on a steam bath and with stirring was added to it 98 g. (0.314 mole) of 2,4-diamylphenoxyacetyl chloride in about 30 min. Stirring and heating were continued for 30 min. longer and the reaction mixture was cooled.

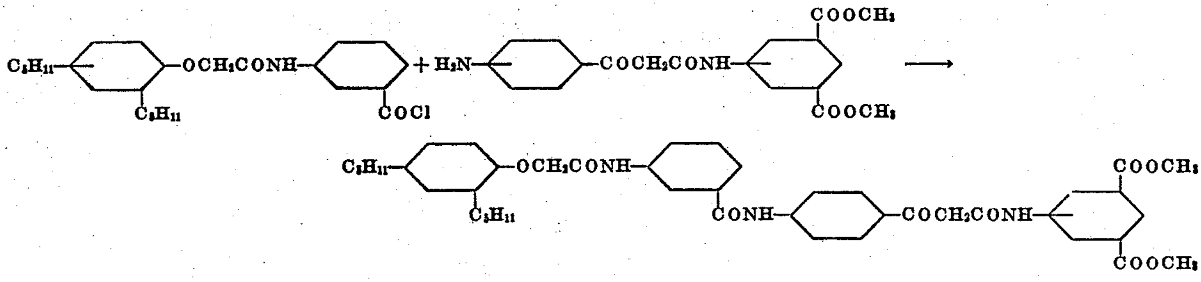
The cold solution was poured into 2 l. of cold water with hand stirring, and the solid formed was filtered, washed several times with cold water and dried. Yield=126 g. The dry 3-(2,4-diamylphenoxy)-acetamidobenzoic acid was crystallized from 1750 ml. of boiling ethyl alcohol and had a melting point of 208–209° C. The yield was 119 g. (92% of the theoretical 129 g.).

3-(2,4-di-tert.-amylphenoxyacetamido)-benzoyl chloride



In a 3-l., 3-necked flask equipped with an air condenser, drying tube, and stirrer was placed 411 grams (1.0 mole) of 3-(2'4'-diamylphenoxyacetamido)-benzoic acid and 2-l. (27.4 moles) of thionyl chloride. The reaction was stirred below 35° C. until solution was complete and then was allowed to stand for 17 hours. The excess thionyl chloride was removed in vacuo, temperature being kept below 35° C. Then 1500 cc. of dry chloroform were added and removed in vacuo below 35°. With good stirring, 1500 cc. of dry petroleum ether were added to the honey-like residue, stirred 15 minutes, chilled, filtered and dried. The yield was 358 grams (83%) of a white, crystalline solid which melted at 107–108° C.

Dimethyl 5-{p-[3'-(2",4"-di-tert.-amylphenoxyacetamido)-benzamido]-benzoylacetamido}isophthalate



In a 5-l. flask equipped with a stirrer was placed 118 g. (0.32 mole) of dimethyl 5-(p-aminobenzoylacetamido)-isophthalate, 32 g. (0.39 mole) of sodium acetate, and 2500 cc. of glacial acetic acid. The reaction mixture was heated to 60° C. on a steam bath and 137 g. (0.32 mole) of 3-(diamylphenoxyacetamido)-benzoyl chloride in 1 l. of glacial acetic acid at 60° was added all at once. When solution was complete, the reaction mixture was stirred an additional hour at 60° C., diluted with 400 cc. of hot water, chilled to 5°, and filtered. The white solid was washed well with 1 l. of 5% acetic acid, 1 l. of water, and dried. The yield was 160–190 g. (66–78%) of white material which melted at 213–215°.

Compound 6 was prepared as described in Salminen and Weissberger U. S. application Serial No. 344,884.

The coupler may be made in dispersion in gelatin or in solution in water, added to the silver halide emulsion or to the water-soluble salt such as the salt of methylmethacrylate-methacrylic acid copolymer, and then the remaining component, that is, either the water-soluble salt or the silver halide emulsion, added to the mixture.

The water-soluble salt of the polymeric material containing salt-forming acid groups which is employed in forming the emulsion may be a salt obtained from the copolymer of methacrylic acid and methyl-α-methacrylate (Minsk, Weyerts and McDowell U. S. Patent 2,391,181), algin (alkali metal salt of polymeric-d-mannuronic acid), carboxy methyl cellulose (Collings, Freeman and Anthonisen U. S. Patent 2,278,612), or cellulose sulfate (Belgian Patent 448,249). The water-soluble polymer when mixed with the gelatin of the dispersion acts as a modifying agent so that small packets containing appropriately sensitized silver halide and color-forming coupler can be formed.

The polymeric packet-forming component consists of a polymeric carbon chain having recurring phenyl groups and carboxylic acid groups and preferably also carboxylic acid amide groups or imide groups or both and is used as the water-soluble salt such as the ammonium, sodium, potassium or lithium salt. The polymeric packet-forming component is preferably an interpolymer of styrene and an α,β-unsaturated carboxylic acid, part of whose carboxyl groups have been converted to amide derivatives or both, such as interpolymers of styrene-maleic acid, styrene-acrylic acid, styrene-methacrylic acid, or styrene-itaconic acid.

Suitable polymers of styrene with maleic acid or its derivatives which may be used as the polymeric packet-forming component according to our invention are described in Godowsky U. S. application Serial No. 156,066, filed April 15, 1950. The polymers illustrated in Examples 2 and 3 of the Godowsky application are especially suitable for use according to our invention.

The packet emulsion in its single layer or single color form consists of particles or packets of gelatin associated with polymeric packet-forming component containing silver halide and coupler salt, the packets being dispersed in an aqueous medium containing additional gelatin or another film-forming water-soluble polymer.

The following example illustrates the production of a three-color mixed packet emulsion according to our invention:

A. To 3 grams of cyan coupler No. 1 there were added 15 cc. of ethyl alcohol and 7.5 cc. of 10% sodium hydroxide solution. The mixture was stirred at 40° C. for 15 minutes to hydrolyze the sulfonyl chloride groups to the sulfonic acid sodium salt and was then diluted to 200 cc. with water and the pH adjusted to 7.0 with citric acid. A solution of 60 cc. of 5% polyvinyl-N-(α-pyridyl)-amine resin in 1% acetic acid solution was then added producing a white precipitate. The mixture was stirred for 5 minutes, filtered, washed and dried to a moist cake. 20 cc. of water and 38 cc. of 10% gelatin solution were added and the mixture stirred at 40° C. until the lumps were broken down and finally dispersed by running through a colloid mill.

To the dispersion there was then added 55.8 grams of a red-sensitive emulsion (containing 1 mol of silver halide and 160 grams of gelatin in a total weight of 2790 grams). There was then added 81.4 cc. of a 10% solution of 1:1 copolymer of methylmethacrylate and methacrylic acid, 5 cc. of 5% sodium hexametaphosphate solution and 17.1 cc. of a 2% solution of styrene-maleic anhydride copolymer which had been aminated and converted to the ammonium salt. The mixture was stirred at moderate speed for 30 to 45 minutes when packet formation was complete with well defined packets and no free silver halide in the surrounding gelatin matrix. There were then added 5 cc. of 5% calcium acetate solution, 18 grams of 20% gelatin solution and 7 cc. of a 7.5% saponin solution making a total of about 275 grams.

B. A second set of packets was made as in A except that a green-sensitive emulsion and the magenta coupler No. 2 were used.

C. A third set of packets was made as in A except that a blue-sensitive emulsion and the yellow coupler No. 3 were used.

Film coatings were made by mixing the three components as follows and coating 25 cc. per square foot of surface:

80 g. packet dispersion A
80 g. packet dispersion B
80 g. packet dispersion C
38 cc. 10% gelatin solution
21 g. of a dispersion of 2.3 g. dioctyl hydroquinone dissolved in dibutyl phthalate and dispersed in gelatin
54 mg. of mucochloric acid in 5 cc. water

336 g. total

When exposed and processed in the following developing solution for 10 minutes at 68° F. good color separation was obtained.

	Grams
2-amino-5-diethylamino toluene HCl	2
Sodium sulfite (des.)	2
Potassium bromide	2
Potassium carbonate, monohydrate	20
Water to 1 liter.	

The coating was then placed in an acetic acid stop bath for 5 minutes and then washed, the reduced silver bleached and fixed in the usual manner.

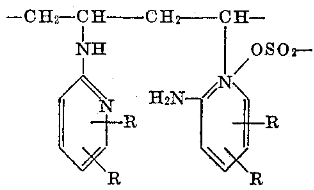
The azo dyes such as No. 7 and No. 8 are incorporated in an emulsion in a manner similar to that used by the couplers except that the hydrolysis step is omitted. Excellent packets containing the dyes are obtained and coatings containing these packets are processed by the silver dye bleach process.

Numerous modifications may be made in the packet systems within the scope of our invention. In a multilayer film one or more couplers may be incorporated in packets and the remaining coupler or couplers may be incorporated in separate layers in dispersion in a coupler solvent or directly incorporated in the gelatin of the emulsion. In a mixed system two packets of different couplers may be incorporated in a single gelatin layer and a third coupler incorporated in another layer either directly in the emulsion or in dispersion in a solvent for the coupler. In a single emulsion layer, all three couplers may be in packet dispersion or two of the couplers may be in packets and the third coupler incorporated in a surrounding silver halide emulsion in the same layer. Antistain agents other than dioctyl hydroquinone may be used in the emulsion such as diamylhydroquinone and didodecylhydroquinone.

It will be understood that the modifications and examples included herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

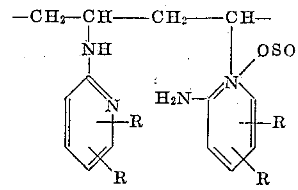
We claim:

1. The method of making a color-forming photographic emulsion which comprises dispersing in gelatin a salt of a coloring material selected from the class consisting of color couplers and polyazo dyes containing at least one salt-forming acid group with a polyvinyl resin containing pyridylamine groups and pyridinium quaternary salt groups and having the recurring structure:



where R is selected from the class consisting of hydrogen and alkyl groups containing from 1 to 5 carbon atoms and R' represents an alkyl group containing from 1 to 5 carbon atoms, said resin containing from 6% to 24% by weight of vinyl pyridylamine units and from 40% to 60% by weight of vinyl pyridinium quaternary salt units, mixing with the dispersion thus formed a gelatino-silver halide emulsion to form an emulsion of gelatin containing dispersed silver halide and coloring material-polyvinyl resin salt, adding to said last-mentioned emulsion a water-soluble salt of a polymer selected from the class consisting of methacrylic acid-methyl-α-methacrylate copolymer, algin, carboxymethyl cellulose and cellulose sulfate and a solution of a polymeric carbon chain compound having recurring phenyl groups, carboxyl groups and amide groups appended thereto and stirring to form a dispersion of particles of gelatin, polymeric carbon-chain compound, silver halide, and coloring material-polyvinyl resin salt in gelatin.

2. The method of making a mixed packet photographic emulsion which comprises dispersing in gelatin a salt of a coloring material selected from the class consisting of color couplers and polyazo dyes containing at least one salt-forming acid group with a polyvinyl resin containing pyridylamine groups and pyridinium quaternary salt groups and having the recurring structure



where R is selected from the class consisting of hydrogen and alkyl groups containing from 1 to 5 carbon atoms and R' represents an alkyl group containing from 1 to 5 carbon atoms, said resin containing from 6% to 24% by weight of vinyl pyridylamine units and from 40% to 60% by weight of vinyl pyridinium quaternary salt units, mixing with the dispersion thus formed a gelatino-silver halide emulsion sensitive to one region but less than all regions of the visible spectrum to form an emulsion of gelatin containing dispersed silver halide and coloring material-polyvinyl resin salt, adding to said last-mentioned emulsion a water-soluble salt of a polymer selected from the class consisting of methacrylic acid-methyl-α-methacrylate copolymer, algin, carboxymethyl cellulose and cellulose sulfate and a solution of a polymeric carbon chain compound having recurring phenyl groups, carboxyl groups and amide groups appended thereto and stirring to form a dispersion of particles of gelatin, polymeric carbon-chain compound, silver halide, and coloring material-polyvinyl resin salt in gelatin, in the same manner forming at least one other dispersion of particles in gelatin, polymeric carbon-chain compound, different coloring material-polyvinyl resin salt and silver halide sensitive to a different region of the visible spectrum than that to which said first-mentioned silver halide is sensitive, and mixing said dispersions of particles with a gelatin solution.

3. The method of making a color-forming photographic emulsion which comprises dispersing in gelatin a polyvinyl-N-(α-pyridyl) amine salt of a color coupler containing at least one salt-forming acid group, mixing with the dispersion thus formed a gelatino-silver halide emulsion to form an emulsion of gelatin containing dispersed silver halide and polyvinyl-N-(α-pyridyl) amine-coupler salt, adding to said last-mentioned emulsion a water-soluble salt of the copolymer of methyl methacrylate and methacrylic acid and a solution of a polymeric carbon chain compound having recurring phenyl groups, carboxyl groups and amide groups appended thereto and stirring to form a dispersion of particles of gelatin, polymeric carbon-chain compound, silver halide, and polyvinyl-N-(α-pyridyl) amine-coupler salt in gelatin.

4. The method of making a mixed packet photographic emulsion which comprises dispersing in gelatin a polyvinyl-N-(α-pyridyl) amine salt of a color coupler containing at least one salt-forming acid group, mixing with the dispersion thus formed a gelatino-silver halide emulsion sensitive to one region but less than all regions of the visible spectrum to form an emulsion of gelatin containing dispersed silver halide and polyvinyl-N-(α-pyridyl) amine-coupler salt, adding to said emulsion a water-soluble salt of the copolymer of methyl methacrylate and methacrylic acid and a solution of a polymeric carbon chain compound having recurring phenyl groups, carboxyl groups and amide groups appended thereto and stirring to form a dispersion of particles of gelatin, polymeric

carbon-chain compound, silver halide, and polyvinyl-N-(α-pyridyl) amine-coupler salt in gelatin, similarly forming at least one other dispersion of particles of gelatin, polymeric carbon-chain compound, different polyvinyl-N-(α-pyridyl)amine-coupler salt and silver halide sensitive to a different region of the visible spectrum than that to which said first-mentioned silver halide is sensitive, and mixing said dispersions of particles with a gelatin solution.

5. The method of making a mixed packet photographic emulsion which comprises dispersing in gelatin the polyvinyl N-(α-pyridyl) amine salt of 4,6-dichloro-5-methyl-2 - [2′{(2″,4″ - diamylphenoxy) - 5′-(3″,5″-dichlorosulfonyl)-benzamido}-benzamido]-phenol, mixing with the dispersion thus formed a red-sensitive gelatino-silver halide emulsion to form an emulsion of gelatin containing dispersed silver halide and coupler salt, adding to said emulsion the ammonium salt of styrene-maleic acid anhydride copolymer and a solution of the copolymer of methylmethacrylate and methacrylic acid and stirring to form a dispersion of particles of gelatin, styrene-maleic acid anhydride copolymer, silver halide and polyvinyl-N-(α-pyridyl) amine-coupler salt in gelatin, forming in the same way as said last-mentioned dispersion a second dispersion of particles of gelatin, styrene-maleic acid anhydride copolymer, polyvinyl N-(α-pyridyl) amine salt of 1-phenyl-3-{3′-{2″-(2‴,4‴-diamylphenoxy)-5″-[3‴, 5‴ - dichlorosulfonylbenzamido] - benzamido} - 5 - pyrazolone and green-sensitive silver halide, and forming in the same way as said last-mentioned dispersion a third dispersion of particles of gelatin, styrene-maleic acid anhydride copolymer, polyvinyl N-(α-pyridyl) amine salt of 4′ - (o-methoxy-benzoylacetamindo) - 3′ - methoxy - 5 - (3″,5″-dichlorosulfonyl benzamido)-2-(2‴,4‴-di-tert-amylphenoxy)-benzanilide and blue-sensitive silver halide, and mixing said dispersions of particles with a gelatin solution.

6. A light-sensitive mixed packet photographic emulsion comprising packets or discrete particles of gelatin reacted with a water-soluble salt of an interpolymer of styrene, said interpolymer containing at least a carboxylic acid group of the groups selected from the class consisting of carboxylic acid and carboxylic acid amide groups, said particles or packets containing a salt of polyvinyl-N-(α-pyridyl) amine and a color coupler containing at least one salt-forming acid group, and silver halide sensitive to at least one region but less than all regions of the visible spectrum, and at least one separate set of packets or discrete particles of gelatin reacted with said interpolymer, polyvinyl-N-(α-pyridyl) amine salt of a color coupler different from said first-mentioned color coupler, and silver halide sensitive to a region of the visible spectrum different from that to which said first-mentioned silver halide is sensitive.

7. The method of making a color-forming photographic emulsion which comprises dispersing in gelatin a polyvinyl-N-(α-pyridyl) amine salt of a polyazo dye containing at least one salt-forming acid group, mixing with the dispersion thus formed a gelatino-silver halide emulsion to form an emulsion of gelatin containing dispersed silver halide and polyvinyl-N-(α-pyridyl) amine-dye salt, adding to said last-mentioned emulsion a water-soluble salt of a polymer containing salt-forming acid groups and a solution of a polymeric carbon chain compound having recurring phenyl groups, carboxyl groups and amide groups appended thereto and stirring to form a dispersion of particles of gelatin, polymeric carbon chain compound, silver halide, and polyvinyl-N-(α-pyridyl) amine-dye salt in gelatin.

8. A light-sensitive mixed packet photographic emulsion comprising packets or discrete particles of gelatin reacted with a water-soluble salt of an interpolymer of styrene, said interpolymer containing at least a carboxylic acid group of the groups selected from the class consisting of carboxylic acid and carboxylic acid amide groups, said particles or packets containing a salt of polyvinyl-N-(α-pyridyl) amine and a polyazo dye containing at least one salt-forming acid group, and silver halide sensitive to at least one region but less than all regions of the visible spectrum, and at least one separate set of packets or discrete particles of gelatin reacted with said interpolymer, polyvinyl-N-(α-pyridyl) amine salt of a polyazo dye different from said first-mentioned polyazo dye, and silver halide sensitive to a region of the visible spectrum different from that to which said first-mentioned silver halide is sensitive.

No references cited.