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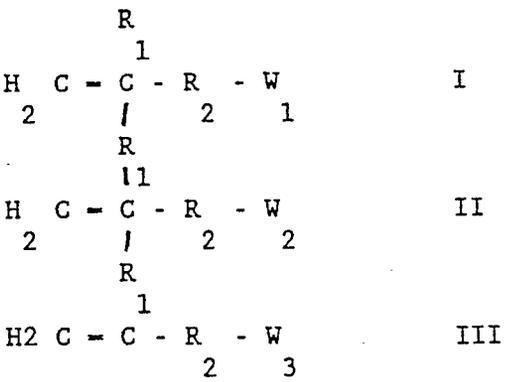
(54) Polymeric colour couplers.

(57) A polymeric colour coupler which comprises the residue of three monomeric colour couplers of the formulae



EMI ID=00/1 HE=55 WI=100 TI=CHE

where R_1 is hydrogen, alkyl, chlorine or bromine, R_2 is a divalent organic radical and W_1, W_2 and W_3 are each an active colour former moiety capable of forming upon chromogenic development of exposed silver halide material with a primary aromatic amine colour developing agent a dye, W_1 forming a yellow dye, W_2 forming a magenta dye and W_3 forming a cyan dye.

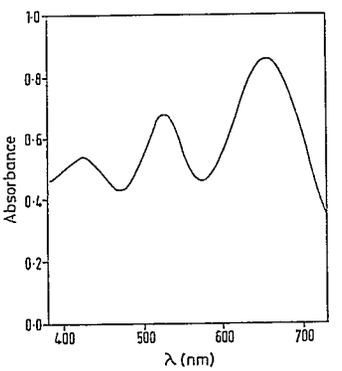


FIG.1

EP 0 321 401 A2

Description

POLYMERIC COLOUR COUPLERS

This invention relates to new polymeric colour couplers and to their use in photographic materials.

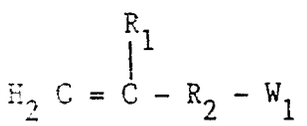
There is currently on the market camera speed film material which comprises silver halide and colour couplers in a silver halide emulsion layer which yields on colour development a so-called monochromatic dye image. This material has some advantages over the conventional black and white camera speed film material in that the dye images are virtually grainless compared with the silver image obtained using high-speed film material. Furthermore film material of this type can be processed using conventional colour film processing chemistry. Most processing houses are now set-up to process only colour film and thus it is a great convenience to be able to process the monochromatic camera speed film material in a colour film processing system.

However in order to obtain a negative which is sufficiently dense to inspect visually and has sufficient light absorbing range to print all classes of black and white paper therefrom including variable contrast paper, it has been found necessary to include in the silver halide emulsion yellow, cyan and magenta colour couplers. As these can only be incorporated in the silver halide emulsion as oil solutions this has required that a lot of oil has to be present in the photographic material in order to dissolve and keep in solution all the colour couplers.

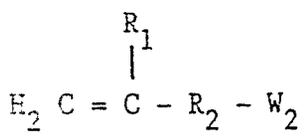
This has led to grave disadvantages. For example when the film is cut-up oil deposits are left on the cutting equipment. Additionally as the silver halide layer is required to be thick the presence of oil droplets reduces sharpness. Further a soft layer is produced which can lead to mechanical damage.

We have found a method of incorporating cyan, magenta and yellow colour couplers in a single silver halide emulsion layer which does not require the use of oil as a solvent therefor.

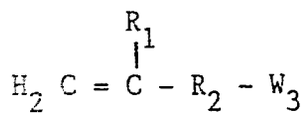
According to the present invention there is provided a polymeric colour coupler which comprises the residue of three monomeric colour couplers of the formulae :-



I



II



III

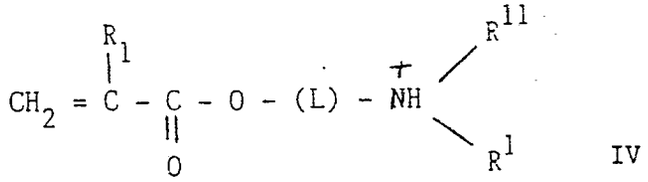
where R_1 is hydrogen, alkyl, chlorine or bromine, R_2 is a divalent organic radical and W_1, W_2 and W_3 are each an active colour former moiety capable of forming upon chromogenic development of exposed silver halide material with a primary aromatic amine colour developing agent a dye, W_1 forming a yellow dye, W_2 forming a magenta dye and W_3 forming a cyan dye.

Preferably the three moieties W_1, W_2 and W_3 are present in the polymer in such a ratio that a black or blackish dye is obtained upon colour development.

W_1, W_2 and W_3 can be any coupler moiety known in the art such as those described below. Preferably R_1 is hydrogen or methyl. Preferably R_2 the divalent organic radical may be the residue of a urethane, a urea, a carbonate, an ester, an ether, a ketone or an amide. More preferably however it is a simple amido linkage -C(O)-NH-.

The polymeric colour coupler of the type described may be formed as a polymer latex which is not isolated but is used as such. Or it may be formed as a water-soluble solid. If it is formed as a polymer latex there is preferably present in the polymer unit at least one other simple, non-colour-coupling photograhically inert comonomer. The presence of other monomers in the polymer is particularly desirable if the polymer is to be incorporated in photographic material as a latex. In which case it is desirable that a latex polymer is produced having optimum physical properties, such as glass transition temperature, compatibility with the gelatin used in preparing coating solutions, suitable refractive index, as well as beneficial rates of copolymerisation between the coupler monomers and the photographically inert comonomers and the ability to confer lowered viscosity and reasonable miscibility with the mixture of coupler monomers.

When the polymeric colour coupler of the type described is formed as a water-soluble solid there is present in the polymer from 40 - 60% by weight of the residue of a monomer which has the formula IV

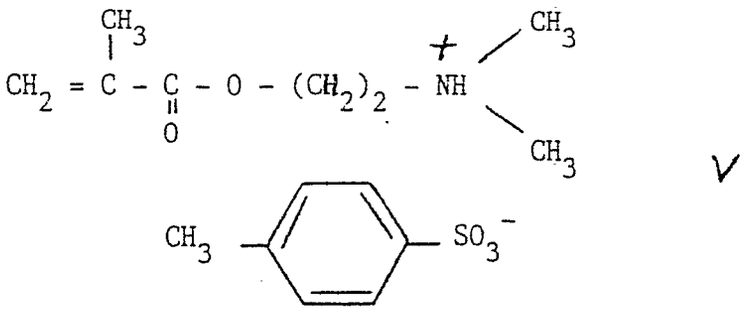


IV

where R_1 has the meaning assigned to it above, L is an alkylene or interrupted alkylene linking group and R^1 and R^{11} are alkyl groups having 1 to 4 carbon atoms and X is an anion.

L is preferably an alkylene chain having from 2 to 6 carbon atoms or is an interupted alkylene chain having from 2 to 6 carbon atoms there being an oxygen from or an -NH- group in the chain.

A particularly suitable monomer residue of this type has the formula V :-



V

Suitable comonomers which may be present when the polymeric colour coupler is formed as a polymer latex or as a water soluble polymer include methyl acrylate, ethyl acrylate, butyl acrylate, ethyl hexyl acrylate, vinyl acetate; hydroxyethyl methacrylate, hydroxypropylmethacrylate; methacrylic acid, acrylic acid, itaconic acid, 2-carboxyethyl acrylate and the salts thereof, acrylamide, methacrylamide, N-hydroxymethyl acrylamide, styrene, N-vinyl pyrrolidone, 1-vinyl imidazole; 4-vinylpyridine, dimethylaminoethyl methacrylate, tetrahydrofurfuryl methacrylate; sulfphoethyl methacrylate, vinyl sulphonic acid and salts thereof, acrylonitrile and vinylidene chloride, although this list is not intended to be comprehensive.

In addition, crosslinking monomers may be present such as divinyl benzene, ethylene dimethacrylate, trivinyl cyclohexane and trimethylol propane triacylate.

The surface active agents used in the preparation of the polymer latex may be any of those well known in the art, for example nonionic wetting agents including alcohol ethoxylates, sorbitan esters, aryl phenol alkoxylates, alkyl alkanolamides, anionic wetting agents including alkyl sulphates and sulphonates, sulphosucciniates, aryl sulphonates, polyalkoxy sulphates, alkyl phosphates, aryl phenol phosphates, alkyl taurates, sarcosinates, and copolymerisable surfactants such as allyl sulphosuccinates, again this list is not intended to be exhaustive.

The initiators and initiator systems used for the preparation of the latices may be persulphates, azo compounds, peroxides or any of the other well known initiators used for emulsion polymerisation, including redox systems. Examples of these initiator systems may be found in the book "Emulsion Polymerisation" by D. Blackely, Applied Science Publishers, 1975 especially pages 155 to 250.

The methods for the preparation of the latices may make use of techniques such as "seed" polymerisation and core-shell techniques, as well as "power-feed" procedures and other methods well known in the art. Latices may be prepared in bulk, semi-continuously or continuously using any of the known designs of apparatus.

According to another apsect of the present invention there is provided photographic material having at least one gelatino silver halide emulsion layer which comprises a polymeric colour coupler of the type described. More preferably, the photographic material comprises a polymeric colour coupler which comprises the residues of monomers A, B and C shown below.

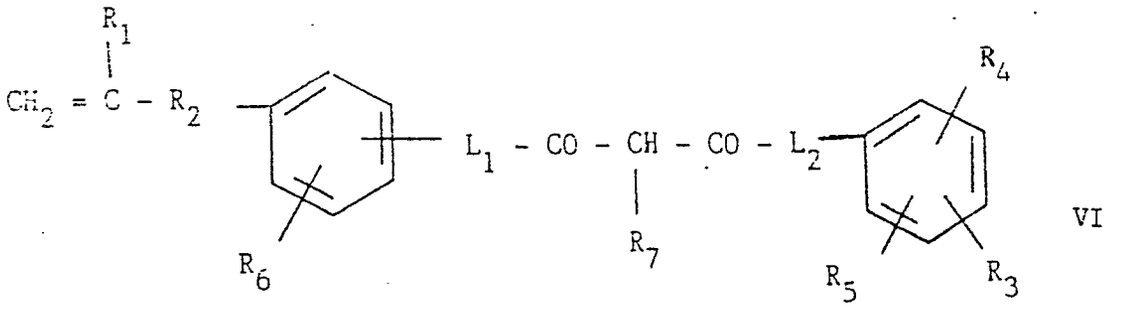
In one embodiment the polymeric colour coupler of the type described is present in the silver halide emulsion layer as a polymer latex.

In another embodiment the colour coupler of the type described is added to the silver halide emulsion layer as an aqueous solution.

Any of the monomeric colour couplers described in the prior art may be used in the polymeric colour coupler

of the present invention. The colour coupler portion of the monomer may comprise ballasting groups or leaving groups for example so that the colour coupler may act as a two equivalent coupler.

Examples of the yellow dye forming monomeric colour couplers include couplers of the general formula VI-

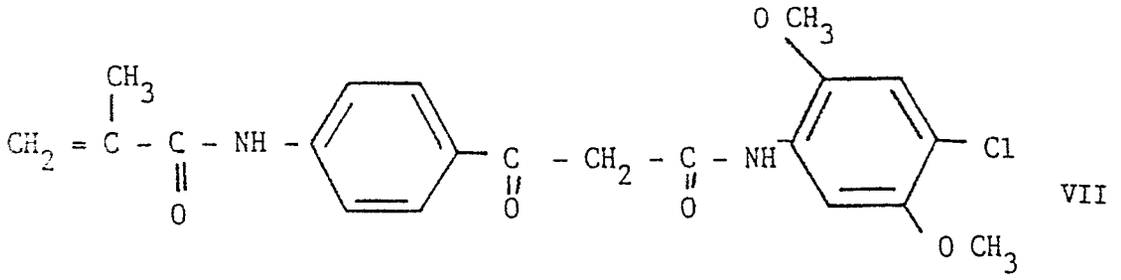


VI

wherein each of R_3, R_4, R_5 and R_6 are hydrogen, halogen, alkoxy, sulphoxy or sulphonamido, R_1 and R_2 are as defined above, R_7 is hydrogen or a leaving group and L_1 and L_2 are direct linkages or -NH-.

Particularly useful linking groups R_2 are -CO-NH- and -O-CH_2-CH_2-NH SO_2-

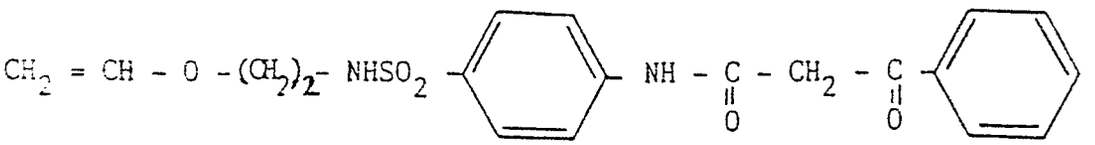
Preferably one of L_1 and L_2 is a direct linkage. An example of such a monomer is Monomer B which is used in the Examples which follow. This monomer has the formula VII :



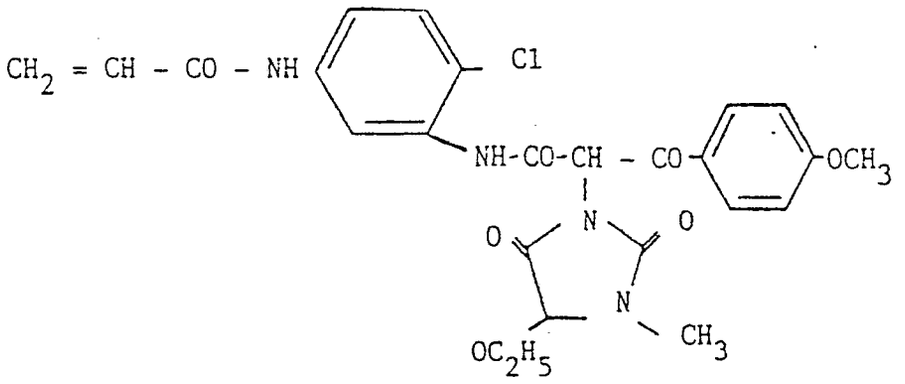
VII

Another example of a monomer of general formula VI has the formula VIII :

VIII



A further example of a monomer of general formula VI which has a leaving group in the monomer of the formula IX :-

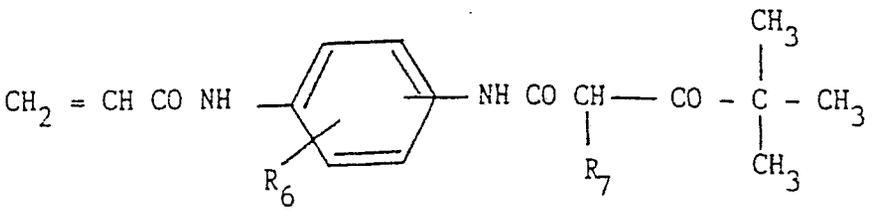


IX

Monomeric yellow colour couplers of formula VI are described in U.S. 4,080,211.

Another class of yellow dye forming monomeric colour couplers have a pivaloyl end group rather than a benzoyl and group.

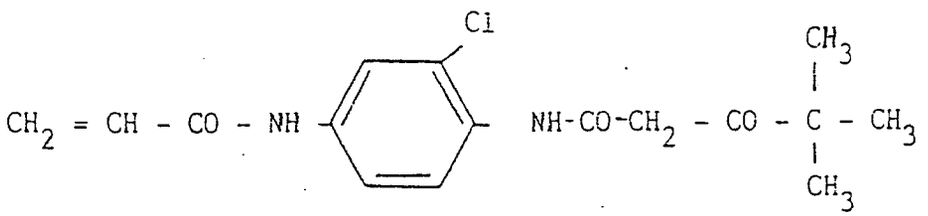
Such colour couplers have the general formula X :-



X

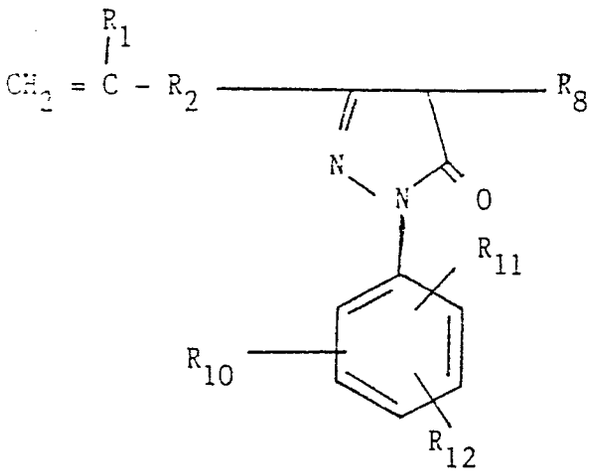
where R_1, R_2, R_6 and R_7 have the meanings assigned to them above.

An example of such a coupler has the formula XI :-



XI

Examples of magenta dye forming monomeric colour couplers include couplers of the general formula XII :-



XII

where R_1 and R_2 are as defined above, R_8 is hydrogen or a leaving group and R_{10} R_{11} and R_{12} are each hydrogen, halogen or alkoxy. Preferably the alkoxy group comprises an alkyl moiety having up to six carbon atoms.

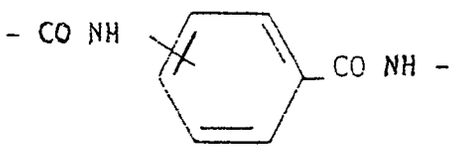
Preferably R_1 is hydrogen or $-CH_3$

Preferably R_2 is -CO NH -

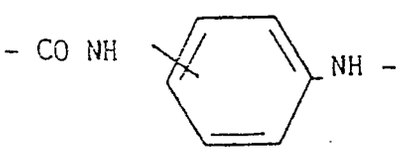
However other useful linking groups R_2 include

$-CO\ NH(CH_2)_x$ -O-CO-NH

where x is 2 to 6,



and

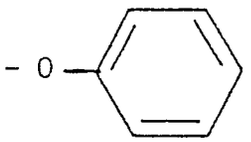


where in the above two formulae the phenylene group is optionally substituted by chlorine alkyl having 1 to 4 carbon atoms.

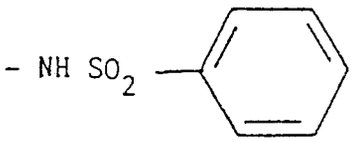
Particularly useful monomers of formula XII are those wherein at least two of R_{10}, R_{11} and R_{12} are chlorine atoms.

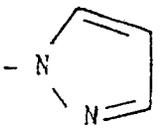
Examples of leaving groups R_7 or R_8 includes the group -S- R_9 where R_9 is a long chain alkyl group having over 10 carbon atoms or is a substituted phenyl group having at least one alkyl or alkoxy group. Preferably R_9 when an alkyl group has from 12 to 30 carbon atoms or the chain.

Other examples of the leaving group R_7 or R_8 include

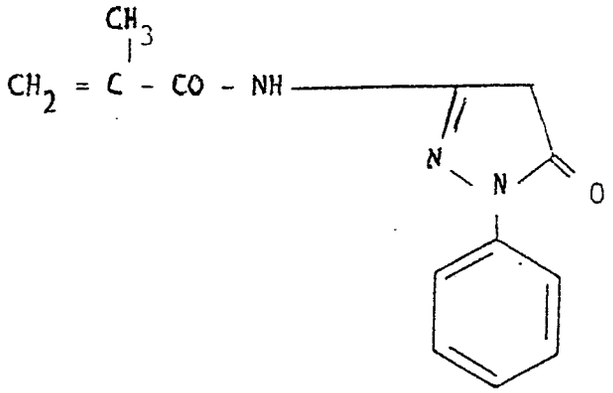


,

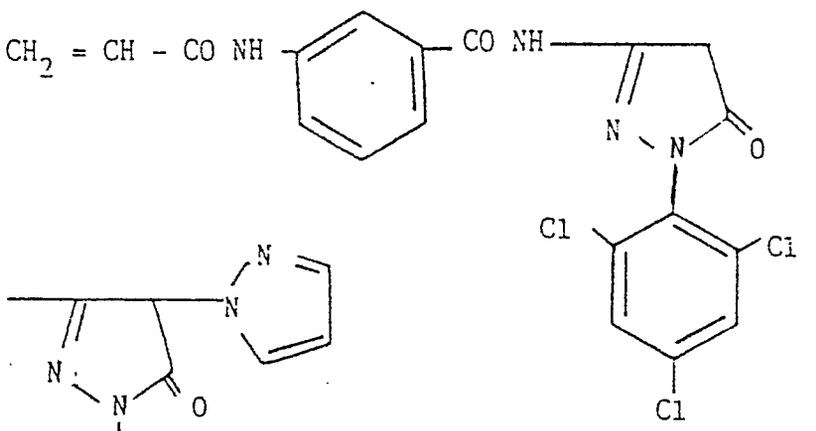




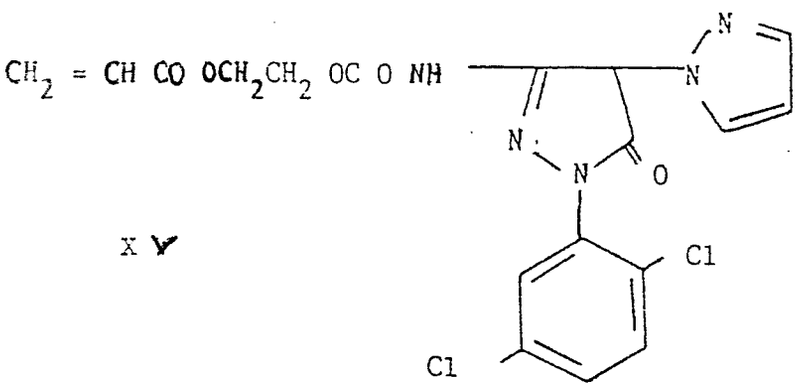
Examples of monomers of formula XII are :-



XIII

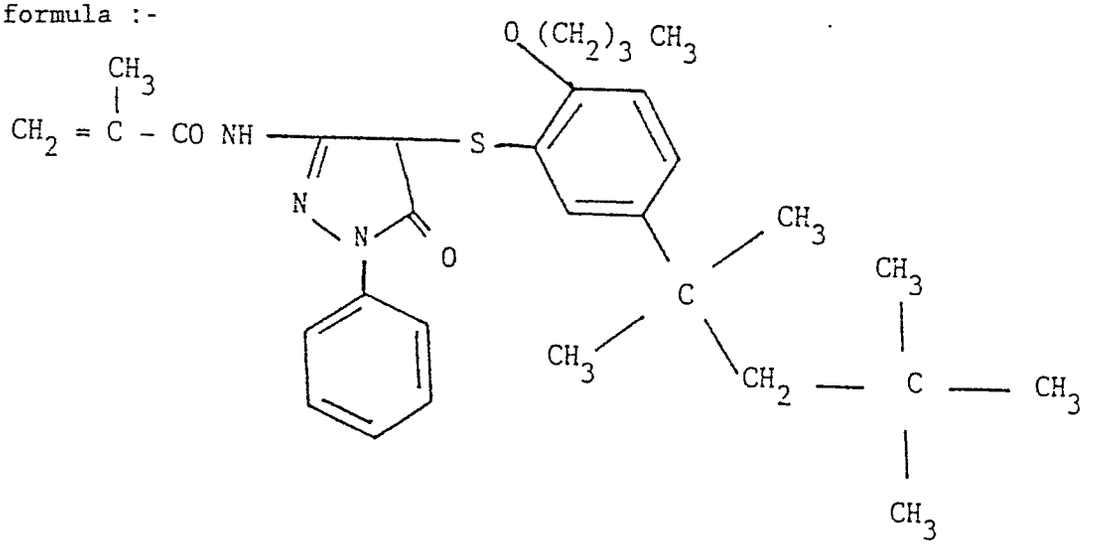


XIV

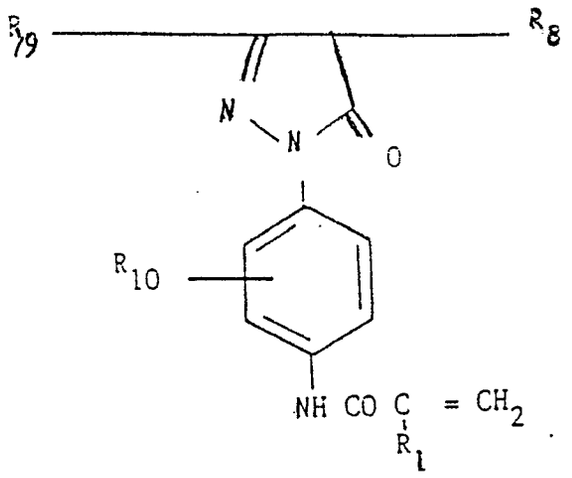


XV

and Monomer A which is used in the Examples which follow and which has the formula :-



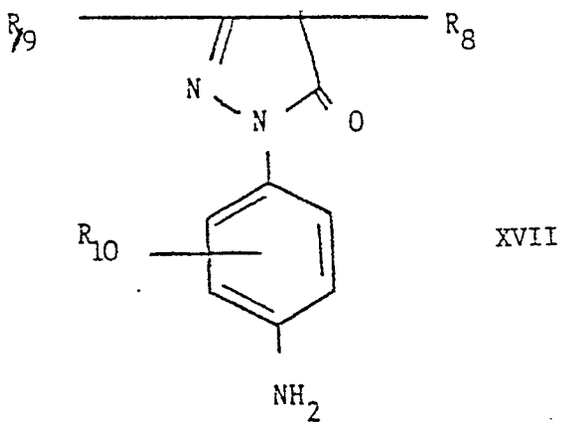
Monomeric magenta colour couplers of formula XII are described in EP 133262.
Another type of magenta dye forming monomeric colour couplers are those of general formula XVI :-



XVI

wherein R_1, R_8 and R_{10} are as defined above and R_{19} is alkyl, dialkyl amino, optionally substituted phenyl and optionally substituted acylamino. Substituents in the phenyl or ecylamino group include alkyl groups having 2 to 6 carbon atom and chloric.

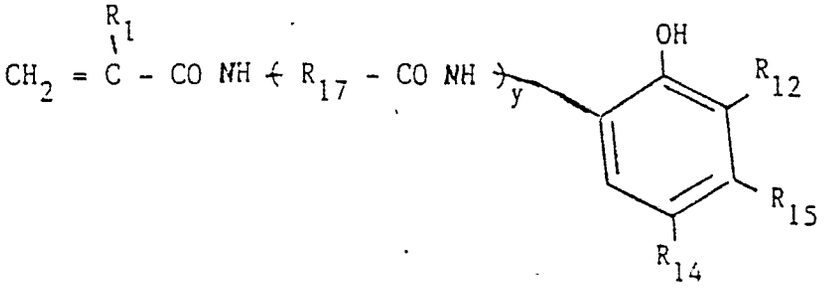
These couplers may be prepared by reacting magenta colour couplers of the formula



XVII

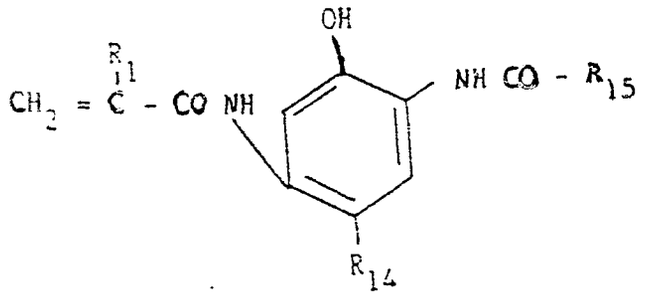
with acryloyl or methacryloyl chloride

Examples of cyan dye forming monomeric colour couplers include phenol couplers of the general formula XVIII :-

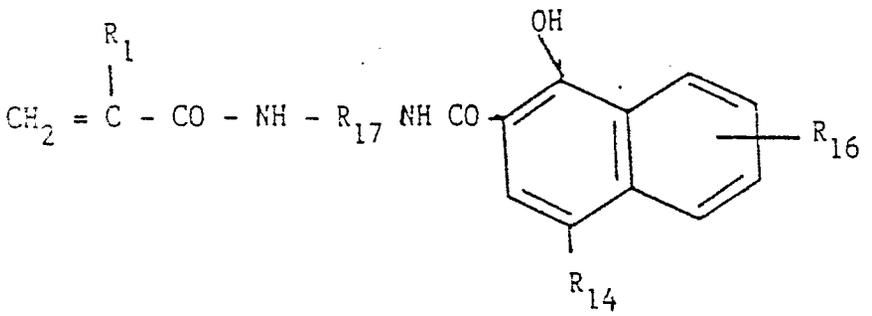


XVIII

and of general formula XIX :



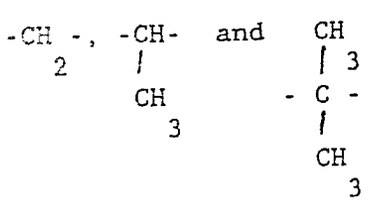
and a naphthol coupler of the general formula XX :-



wherein the above three formulae R_1 and R_{12} are as defined above, R_{14} is hydrogen or a leaving group such as a halogen atom or a substituted alkoxy group, R_{13} is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, R_{15} is an optionally substituted alkyl or acylamino group and R_{17} is a linking group and y is 0 or 1, and R_{16} is an alkoxy, amino, amido or sulphonamido group or hydrogen atom.

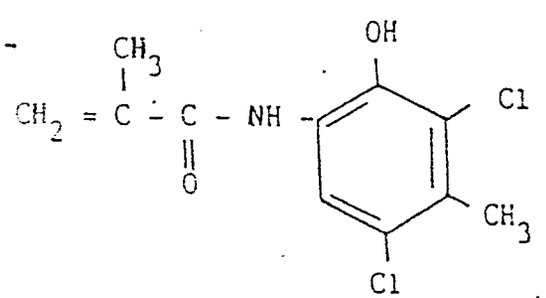
Preferably R_1 is hydrogen or methyl.

Examples of the linking groups R_{17} include alkylene chains of 2 to 6 carbon atoms including interrupted alkylene chains and an alkyl group for example

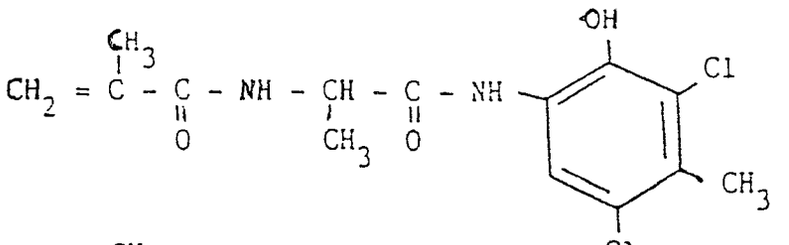


Preferably interupted chains have from 2 to 6 carbon atoms and - O - or - NH - group in the chain.

Examples of monomers of formula XVIII are :-

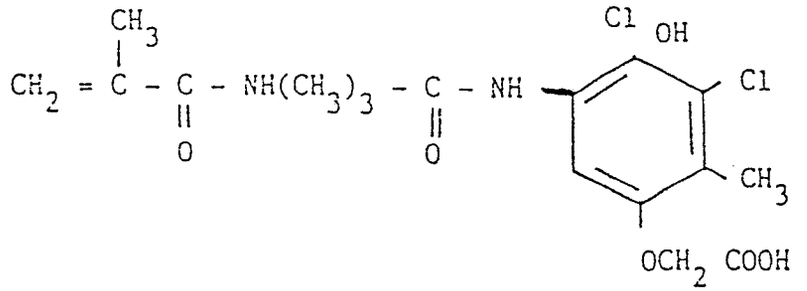


This Monomer C which is used in the Examples which follow, further examples of monomers of formula XVIII are of the formula



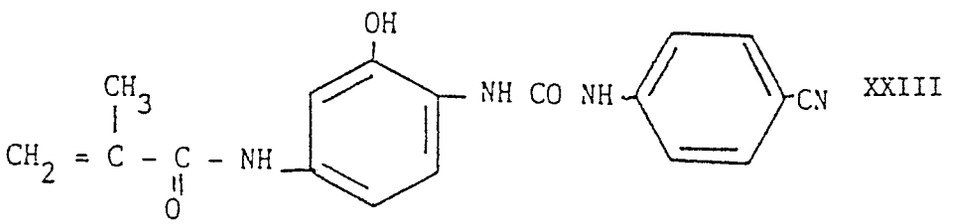
XXI

and



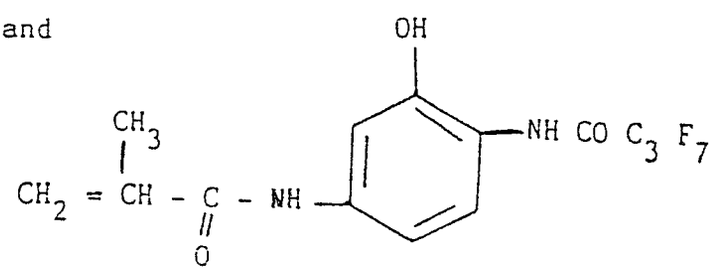
XXII

Examples of monomers of formula XIX are those of formulae :-



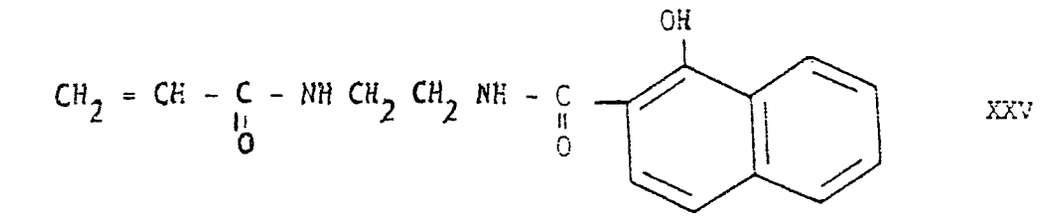
XXIII

and



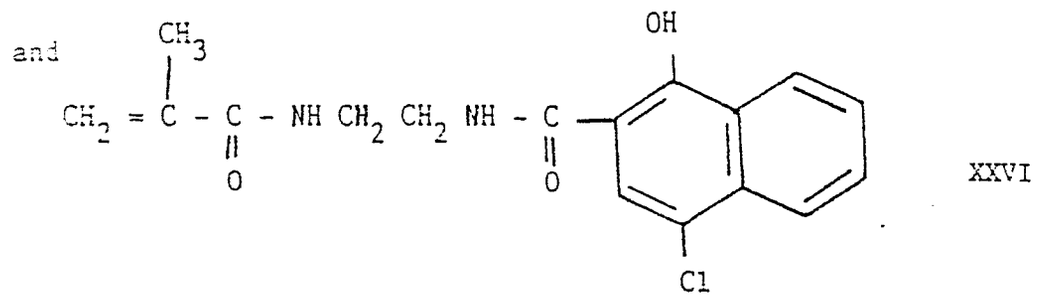
XXIV

Examples of monomers of formula XX are those of formulae :-



XXV

and



XXVI

Monomeric colour couplers of general formula XX are described in B.P. 2133170.

The colour couplers of the type described are of particular use in monochromatic camera speed silver halide film material. The photographic material after imagewise exposure is developed in a colour developing bath by use of a para - phenylene diamine developing agent to yield a developed silver image and black dye image. The material is then subjected to a bleach fix treatment which removes the developed silver image and then unexposed silver halide leaving the black dye negative image which can be used to print all types of black and white paper including variable contrast paper.

The colour couplers of the type described can also be used to prepare monochromatic paper. That is to say paper which can be processed using colour processing chemistry to yield a black dye image instead of a silver image. Paper of this type is of particular use from which to prepare proof prints.

The colour coupler of the type described can also be used to reinforce silver halide images at such time that, as occurred some years ago, the price of silver becomes too prohibitive to use in photography when a very dense silver image is required.

The photographic material of the present invention preferably comprises gelatin as the binder in the silver halide emulsion layer.

The halide used can be any of the silver halides normally used in photography e.g. silver bromide, silver iodobromide, silver chloride, silver chlorobromide and silver iodochlorobromide. The silver halide grains may be both optically and chemically sensitised. The silver halide emulsion may contain stabiliser, bacteriocides and any of the other additives commonly found in photographic silver halide emulsions. The gelatin may have been hardened and may contain coating aids as usual when preparing coated silver halide emulsions.

For camera speed film material the base can be any of the usual transparent bases used in photography for example subbed polyester, polycarbonate or polystyrene base, or may be a cellulose triacetate or cellulose acetate - butyrate base. If the material is to be used for proof prints the base may be any opaque base in common use for photographic print material for example baryta coated paper base or polyethylene laminated paper base.

The accompanying Examples will serve to illustrated the invention.

Example 1

To a solution of sodium oleyl methyl taurate which comprised 0.16 g in 15.8 ml of water maintained at 80° C in a 100 ml reaction vessel there was added under a nitrogen atmosphere and mechanical stirring 70 mg of potassium persulphate and 10 mg of sodium metabisulphite.

A monomer solution was made by dissolving in 2.00 g hydroxy propyl methacrylate and 3.00 g butyl acrylate 0.34 g Monomer A, (magenta monomer), 0.34g Monomer B (yellow monomer) and 0.34 g Monomer C (cyan monomer). The vessel containing this solution was maintained at about 30 to 40° C. A surfactant solution was prepared by dissolving in 5.80 g water sodium oleylmethyl taurate 0.16 g and potassium persulphate 40 mg.

The surfactant and monomer solutions were then fed slowly into the 100 ml vessel which comprised the initiator solution first set forth. These additions were made over 2 hours. The resultant latex formed in the 100 ml vessel was maintained at 80° C for 1 $\frac{1}{2}$ hours. The contents were then cooled and filtered.

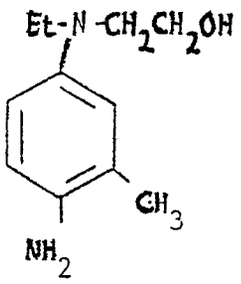
After isolation a latex having 22 % solids content was obtained with particle size of 72 nm. A total of only 0.04 g of coagulum was present in the vessel.

The latex as just prepared was used to prepare colour photographic material. To 2.2 ml of an undyed twinned crystal iodobromide gelatino emulsion there was added 0.4 ml of the latex and 7 ml of water. To this emulsion there was added 0.4 ml. of water. To this emulsion there was added 0.4 ml of a 3% solution of a triazine hardener. The emulsion was then coated on clear cellulose triacetate base to provide a silver coating weight of 12 mg/dm^2. The coating was dried and inspected in green light to show a clear, glossy coating. This photographic material was then exposed to a white light source for 10 seconds and processed in a colour developing solution for 3.25 minutes at 38°C.

The formula of the developing solution used as in follows :-

Potassium Carbonate	37.5 g
Sodium Sulphite	4.5 g
Nitrilotriacetate (complexing agent)	2 g
Sodium hydroxide	0.6 g
Sodium bromide	0.9 g
Hydroxylamine sulphate	2.8 g
Developing agent of the formula below	5.25 g
Water	1 litre

The formulae of the developing agent used is :-



The photographic material was then passed to a bleach bath for 6.5 minutes at 35°C.

The formula of the bleach bath used is as follows :-

ammonium bromide	150 g
ferric EDTA 1.8 M	150 ml
sodium nitrate	20 g
water to	1 litre

The material was then passed to a fixing bath at 35°C for 6 1/2 minutes of the formula :-

ammonium thiosulphate (80% w/v)	190 ml
sodium sulphite	19 g
sodium EDTA	1.5 g
water to	1 litre

The material was then washed for 3 minutes in water at 30°C and then dried. A neutral grey image was present on the photographic material. This image has the visible absorption spectrum shown in the accompanying Figure 1. This shows that the material has good absorption in the blue, green and red regions of the visible spectrum.

Two other samples of photographic material as just prepared were prepared except that the silver halide emulsion comprised a green sensitising dye and a red sensitising dye. Thus the material was panchromatically sensitised.

Both samples were imagewise exposed in a plate camera and then processed as just described.

One of the negatives obtained thereby was placed in a photographic enlarger and was used to print normal non-optically sensitised black and white paper. After processing the exposed paper a bright image having

clear highlights and dark shadows was obtained.
The other of the negatives obtained was placed in a photographic enlarger provided with a filter to enable variable contrast photographic paper to be printed. An inspection of the image on the enlarger baseboard indicated that a No. 2 contrast filter should be used. This was placed in position with a sheet of variable contrast material below it and was printed using the negative. After processing the print was examined. As before a bright print having clear highlights and dark shadows was obtained.

The shows that the photographic material of the present invention can be used to provide negatives which can be used to print ordinary black and white paper material as well as variable contrast black and white photographic papers.

Example II

Water-soluble polymeric colour coupler of the type described.

p-Toluene sulphonic acid (4g) was dissolved in industrial alcohol (30 ml). Sufficient of the monomer dimethyl-aminoethyl methacrylate was added with stirring to raise the pH to 7. This required 5.2 g. This solution was placed in a 50 ml flask to which were added 1 g of Monomer A (the magenta monomer), 0.5 g of Monomer B (the yellow monomer) and 0.5 g of Monomer C (the cyan monomer). The flask was equipped with a condenser, nitrogen inlet, oil bath and magnetic stirrer. Nitrogen was bubbled through for 10 minutes at room temperature. The flask was then heated to 70°C and maintained at that temperature.

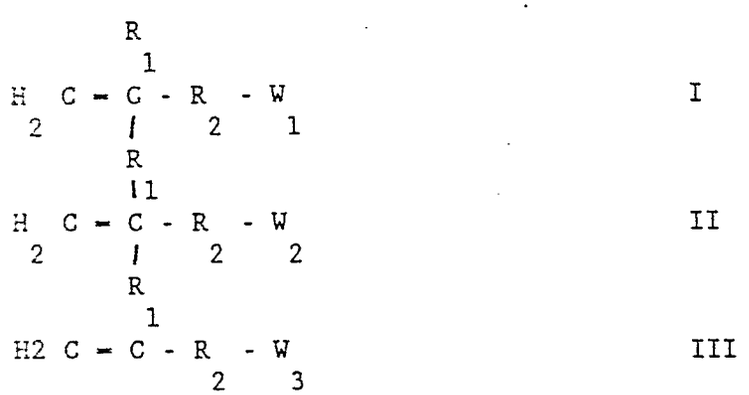
A free radical initiator solution was prepared which comprised 0.5 g azobis(isobutyronitrile) in 50 ml of industrial alcohol. 4.8 ml of this solution was added to the flask. After 2 hours a further 1.2 ml of the initiator solution was added and this was repeated after a further 2 hours. After 7 hours reaction time the contents of the flask were added to ether (500 ml) and a tacky brown solid precipitated. This solid was dissolved in industrial alcohol and reprecipitated in ether to give a free flowing white powder. Yield 7.13 g (67.3 %). This powder was found to be completely water soluble.

0.1g of this solid was then added to an emulsion as prepared in Example 1. A clear glossy coating was used in Example 1. A clear glossy coating was found on inspection in green light. As in Example 1 the coating was exposed to white light for 10 seconds and then was processed as set forth in Example 1.

A greyish image was obtained which was sufficiently dense and had sufficient absorption throughout the visible region to be used as a negative from which to print black and white photographic material as shown in Figure 2.

Claims

1. A polymeric colour coupler which comprises the residue of three monomeric colour couplers of the formulae :-



I

II

III

where R_1 is hydrogen, alkyl, chlorine or bromine, R_2 is a divalent organic radical and W_1, W_2 and W_3 are each an active colour former moiety capable of forming upon chromogenic development of exposed silver halide material with a primary aromatic amine colour developing agent a dye, W_1 forming a yellow dye, W_2 forming a magenta dye and W_3 forming a cyan dye.

2. A polymer according to claim 1 wherein the three moieties W_1, W_2 and W_3 are present in the polymer in such a ratio that a black or blackish dye is obtained upon colour development.

3. A polymer according to claim 1 wherein R_1 is hydrogen or methyl.

4. A polymer according to claim 1 wherein R_2 is the residue of a urethane, a urea, a carbonate, an ester, an ether, a ketone or an amide.

5. A polymer according to claim 4 wherein R_2 is - C (O) - NH -.

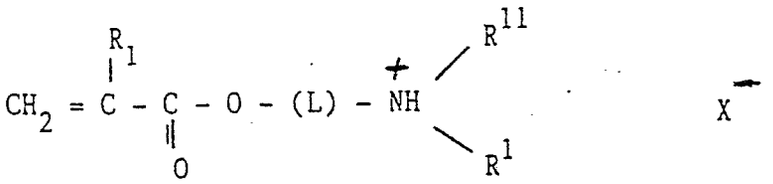
6. A polymer according to claims 1 wherein the polymer is formed as a latex which is not isolated but which is used as such.

7. A polymer according to claim 6 wherein the polymer comprises units derived from at least one non-colour coupling, photographically inert comonomer.

8. A polymer according to claim 7 wherein the photographically inert comonomer is methyl acrylate, ethyl acrylate, butyl acrylate, ethyl hexyl acrylate, vinyl acetate; hydroxyethyl methacrylate, hydroxypropylmethacrylate; methacrylic acid, acrylic acid, itaconic acid, 2-carboxyethyl acrylate and the salts thereof, acrylamide, methacrylamide, N-hydroxymethyl acrylamide, styrene, N-vinyl pyrrolidone, 1-vinyl imidazole; 4-vinylpyridine, dimethylaminoethyl methacrylate, tetrahydrofurfuryl methacrylate; sulfphoethyl methacrylate, vinyl sulphonic acid and their salts thereof, acrylonitrile and vinylidene chloride.

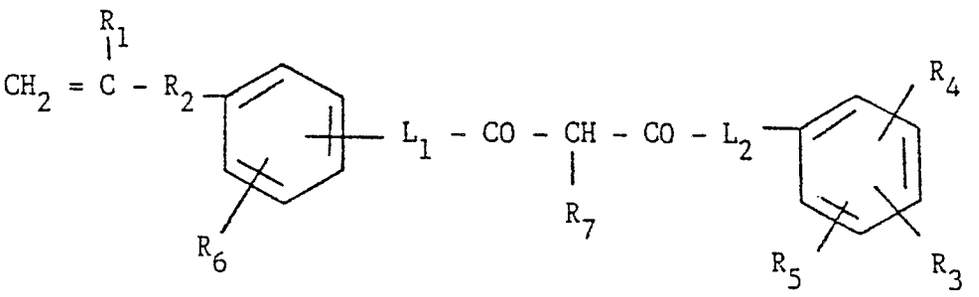
9. A polymer according to claim 1 wherein the polymer is formed as a water-soluble solid.

10. A polymer according to claim 9 wherein there is present in the polymer from 40 - 60 % by weight the residue of a monomer which has the formula



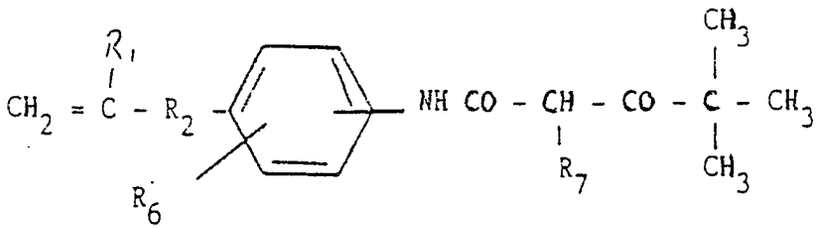
wherein R_1 has the meaning assigned to it in claim 1, L is an alkylene or interupted alkylene linking group R^1 and R^{11} are alkyl groups having 1 to 4 carbon atoms and X is an anion.

11. A polymer according to claim 1 which comprises the residue of a yellow dye forming monomeric colour coupler of the general formula :-



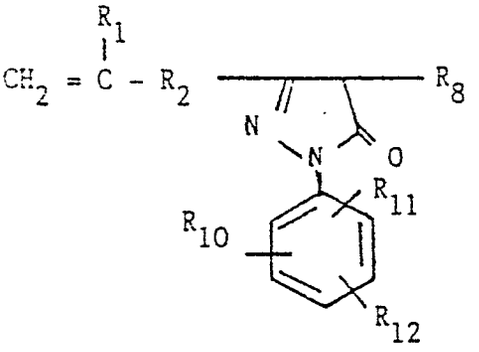
wherein each of R_3, R_4, R_5 and R_6 are hydrogen, halogen, alkoxy, sulphoxy or sulphonamido, R_1 and R_2 are as defined in claim 1, R_7 is hydrogen of a leaving group and L_1 and L_2 are direct linkages or -NH-.

12. A polymer according to claim 1 which comprise the residue of a yellow dye forming monomeric colour coupler of the general formula :-



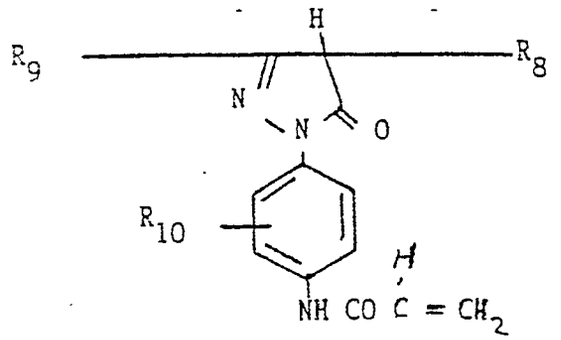
wherein R_1 and R_2 are as defined in claim 1 and R_6 and R_7 are as defined in claim 11.

13. A polymer according to claim 1 which comprises the residue of a magenta dye forming monomeric colour coupler of the general formula :-



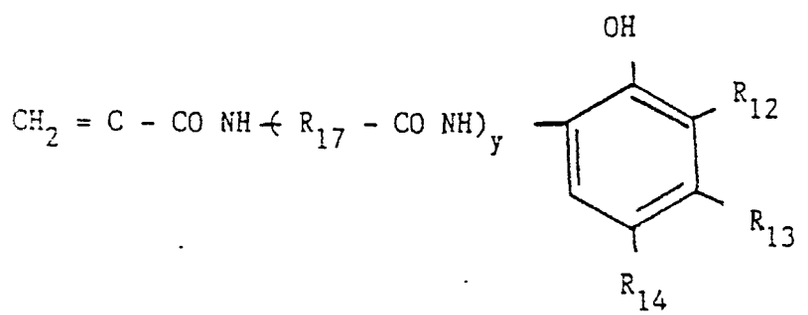
where R_1 and R_2 are as defined in claim 1, R_8 is hydrogen or a leaving group and R_{10}, R_{11} and R_{12} are each hydrogen halogen or alkoxy.

14. A polymer according to claim 1 which comprises the residue of a magenta dye forming monomeric colour coupler of the general formula

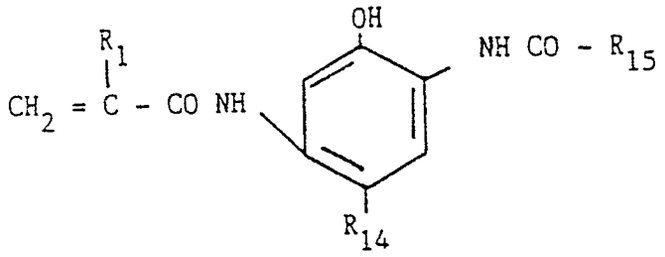


wherein R_1 is as defined in claim 1, R_8 and R_{10} are as defined in claim 13 and R_9 is alkyl, dialkylamino, operationally substituted aryl and optionally substituted acylamino.

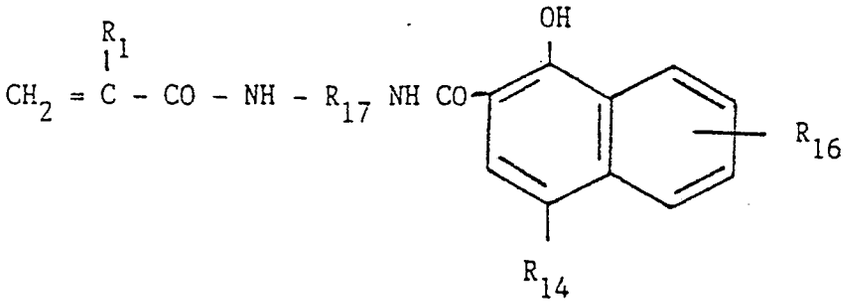
15. A polymer according to claim 1 which comprises the residue of a cyan dye forming monomeric colour coupler which is a phenol coupler of the general formula :-



or is a phenol coupler of the general formula :-



or is a naphthol coupler of the general formula



wherein the above three formulae R_1 and R_{12} are as defined in claim 13, R_{14} is hydrogen or a leaving group such as a halogen atom or a substituted alkoxy group, R_{13} is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, R_{15} is an optionally substituted alkyl or acylamino group and R_{17} is a linking group and y is 0 or 1, and R_{16} is an alkoxy, amino amido, sulphonamide group.

16. A polymer according to claim 1 which comprises the residue of Monomer A, or Monomer B and of Monomer C.

17. Photographic material having at least one gelatino silver halide emulsion layer which comprises a polymeric colour coupler as claimed in claim 1.

18. A photographic material according to claim 17, which comprises a polymeric colour coupler comprising the residues of Monomer A, of Monomer B and of Monomer C.

19. A photographic negative film which comprises a black negative image, which dye image has been obtained from the imagewise exposure and development of the photographic material as claimed in claim 17.

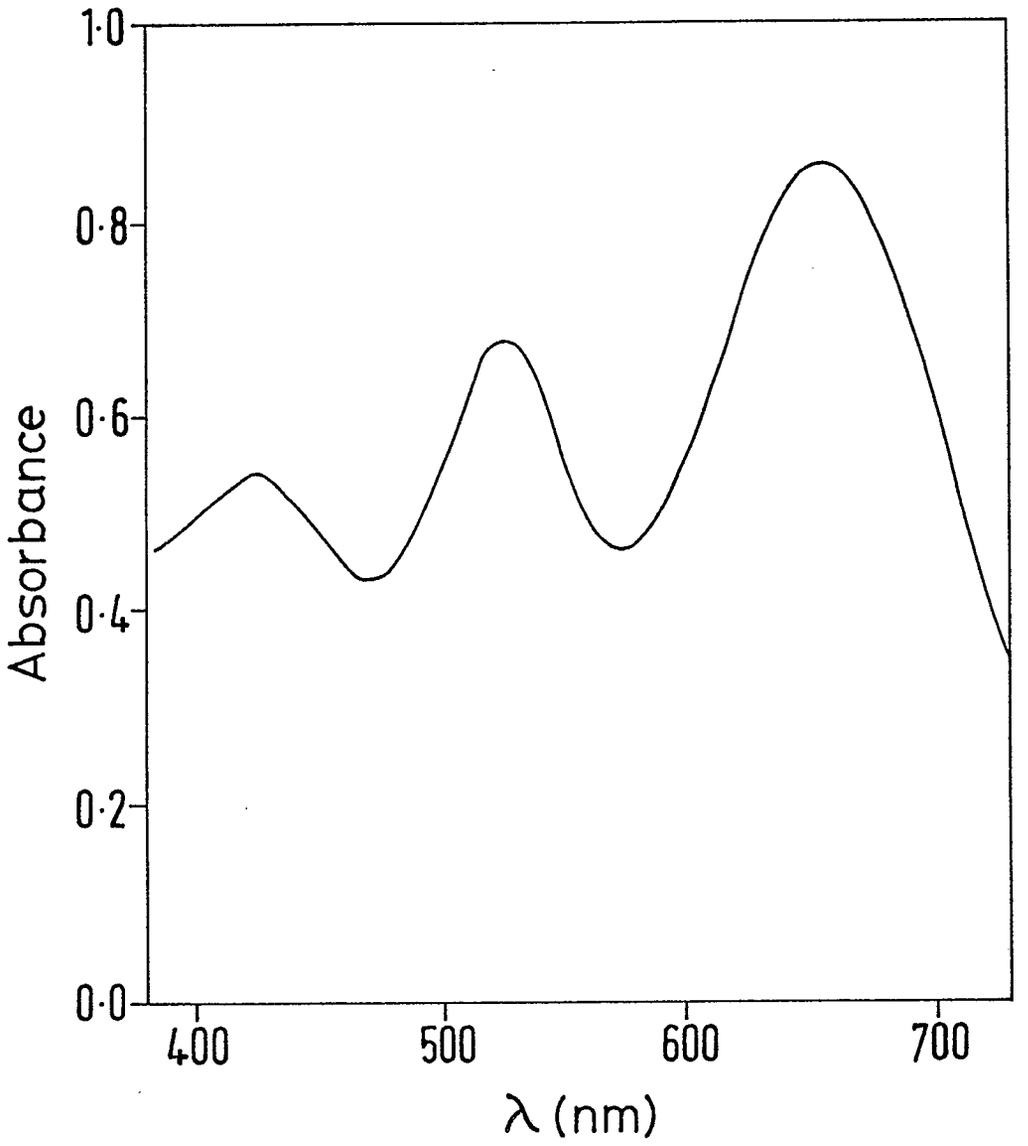


FIG.1

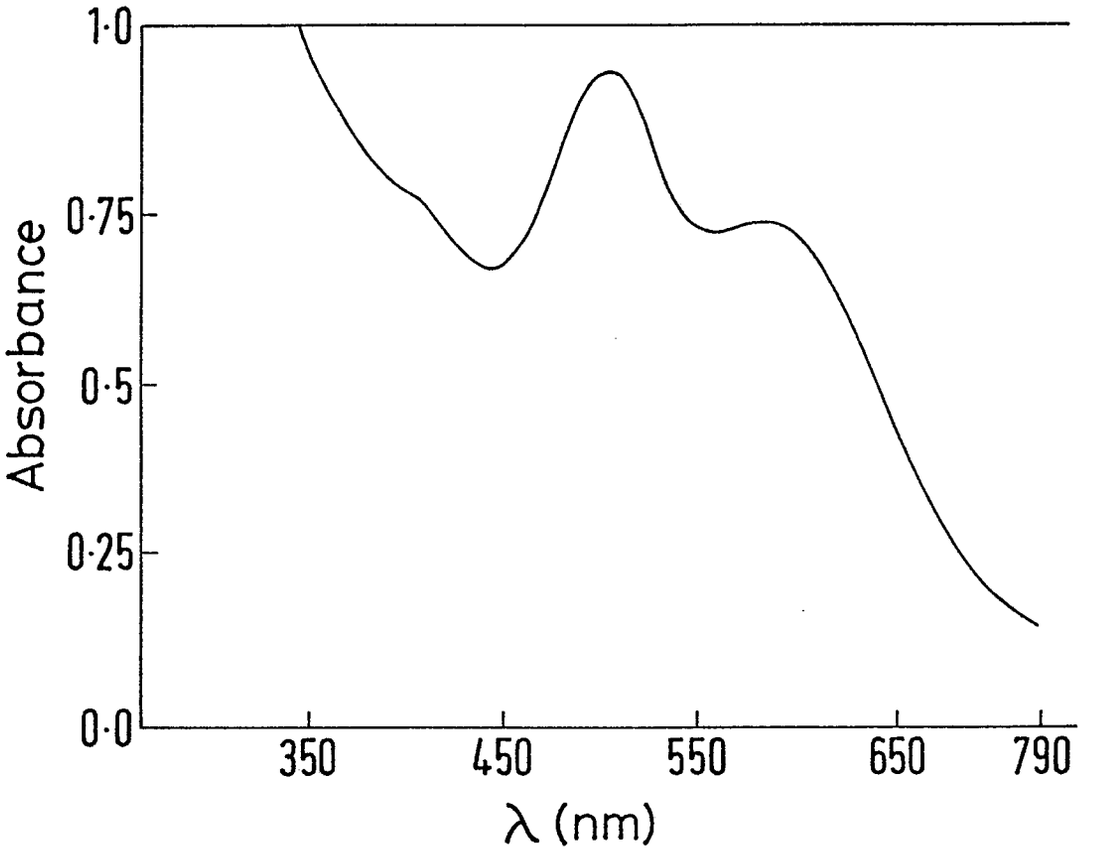


FIG. 2