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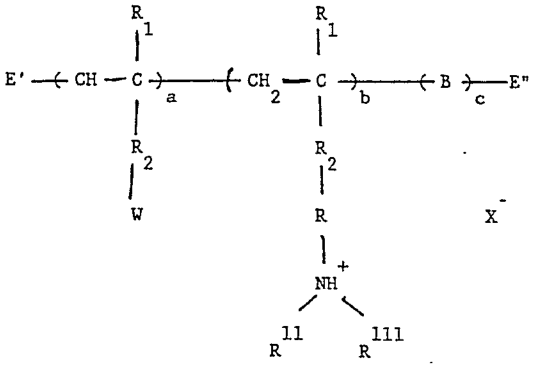
(54) Polymeric colour couplers.

(57) A polymeric colour coupler of the formula I :-



wherein E′ and E″ represent the end groups of the polymer chain, R_1 is methyl, hydrogen, chlorine or bromine, R_2 is a divalent organic radical, R^{11} and R^{111} are each lower alkyl groups having 1 to 6 carbon atoms, or together represent the atoms required to form a five or size-membered heterocyclic ring, R^1 is an alkylene chain or an interrupted alkylene chain, W is the residue of a colour coupler which can react with an oxidised colour developer to yield a dye and B is the residue of an ethylenically unsaturated monomer which comprises no colour coupling residue nor a water solubilising group, a is from 10 to 60% by weight of the polymer, b is from 40 to 90% by weight of the polymer and c is from 0 to 20% by weight of the polymer, at least 10% by weight of the polymer being derived from the monomer which comprises the colour coupler residue and X is an anion.

Bundesdruckerei Berlin

Description

POLYMERIC COLOUR COUPLERS

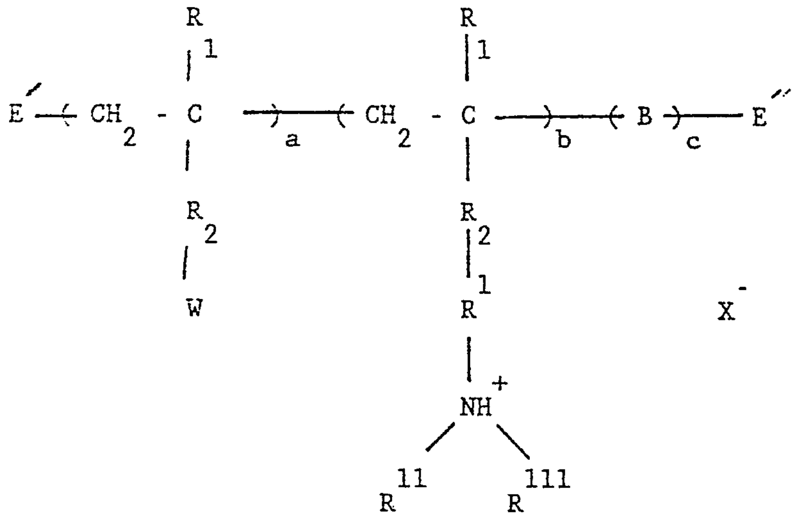
This invention relates to new polymeric colour couplers and to a process for their production. Polymeric colour couplers are finding increasing use in photographic material instead of colour couplers which require to be incorporated in photographic layers dissolved in an oil. The presence of the oil leads to several disadvantages including rendering the layer which comprises it soft and thus liable to mechanical deformation. Furthermore photographic material in which the colour couplers are present as a polymer latex can be much thinner than material in which the colour couplers are dissolved in oil. This decrease in thickness leads to sharper images being obtained.

However it has been found to be difficult to produce latexes of polymeric colour couplers easily and economically. One reason is that owing to the high melt point of most monomeric colour couplers and their limited solubility in most of the suitable comonomers and/or inert solvents, there is a marked tendency for the couplers to crystallise out of the monomer feed during the time over which the monomer feed is introduced to the reaction vessel. This necessitates keeping the monomer solution hot to prevent crystallisation. However it is known that it is inadvisable to maintain bulk solutions of monomers at elevated temperatures for prolonged periods of time owing to the serious risk of spontaneous thermally-induced polymerisation of the monomer mixture occurring rapidly and exothermically.

Because of the difficulties in preparing polymeric colour couplers as polymer latexes some effort has been made in trying to prepare colour couplers which are water-soluble polymers. However the difficulty is to find a polymeric colour coupler which whilst being water soluble is also layer substantive when coated in photographic material.

We have found a polymeric colour coupler which is readily water soluble but which when incorporated in a gelatino silver halide emulsion layer remains substantive to this layer.

Therefore according to the present invention there is provided a polymeric colour coupler of the general formula I:-

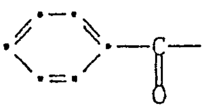


$$E'\!-\!\left(CH_2-\underset{\underset{W}{|}}{\underset{R_2}{\underset{|}{\overset{R^1}{\overset{|}{C}}}}}\right)_a\!-\!\left(CH_2-\underset{\underset{R^{11}\;\;NH^+\;\;R^{111}}{|}}{\underset{R^1}{\underset{|}{\underset{R^2}{\underset{|}{\overset{R^1}{\overset{|}{C}}}}}}}\right)_b\!-\!\left(B\right)_c\!-\!E''\qquad X^-$$

I

wherein E′ and E″ represent the end groups of the polymer chain, R_1 is methyl, hydrogen, chlorine or bromine, R_2 is a divalent organic radical, R^{11} and R^{111} are each alkyl having 1 to 6 carbon atoms, or together represent the atoms required to form a five or six-membered heterocyclic ring such as R^1 is an alkylene chain or an interupted alkylene chain, W is the residue of a colour coupler which can react with an oxidised colour developer to yield a dye and B is the residue of an ethylenically unsaturated monomer which comprises no colour coupling residue nor a water solubilising group, a is from 10 to 60% by weight of the polymer, b is from 40 to 90% by weight of the polymer and c is from 0 to 20% by weight of the polymer and X is an anion.

With reference to the E′ and E″ end-groups, as is well-known to anyone experienced in the art, the end-groups of polymer molecules formed by free radical initiation are generally incapable of determination with any degree of certainty, however it may be expected that at least one of the end-groups may either be an initiator residue or a group formed by disproportionation or chain transfer reactions during the preparation of the polymer of the claimed structure. Initiator residues may generally include those from alkyl or aryl peroxides, azo compounds, peroxydisulphates, peresters and peroxy carbonates, and specific examples may include the following radicals: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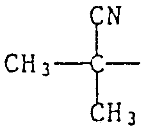
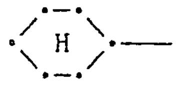
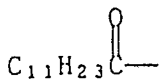
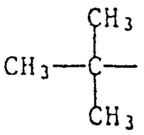


$CH_3-C(CN)(CH_3)-$,


,



$C_{11}H_{23}C(O)-$ and



$CH_3-C(CH_3)(CH_3)-$.

Further examples of commonly used initiators may be found in Polymer Handbook, Second Edition, John Wiley Publishers N.Y., 1975. Editors E.H. Immergut and J. Brandrup, Chapter II.1.

End-groups formed by disproportionations reactions may be saturated or unsaturated units from M or the initiating agent. Examples of such units may be found in Principles of Polymer Chemistry, Cornell U.p., P.J. Flay, p. 111.

It is not believed that the end-groups play any significant part in the photopolymerisation process described hereinafter.

R^1 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 atom or an -NH- group in the chain.

Suitable five or six membered rings include pyrolidine, piperidine, or morpholine.

Preferably R_1 is hydrogen or methyl. 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. Preferably however it is a simple amido linkage -C (O) - NH -.

Preferably in the quaternary ammonium residue in the polymer colour coupler R_1 is methyl or hydrogen and R_2 is -CO-O-, R^1 is an alkylene group and R^{11} and R^{111} are each methyl groups.

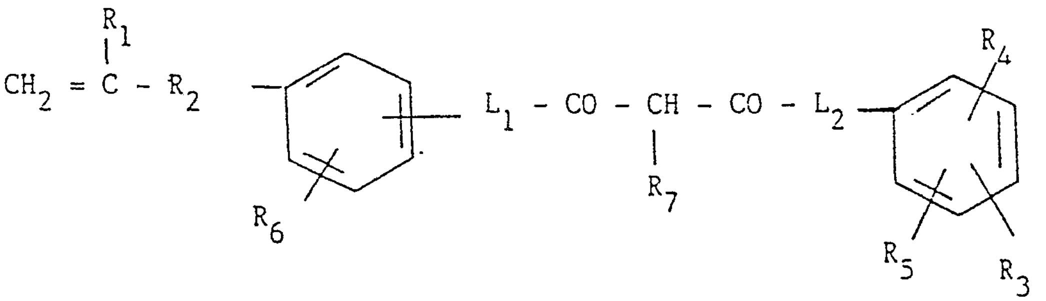
Most preferably R^1 is $-CH_2-CH_2-CH_2-$ or$-CH_2CH_2CH_2CH_2-$.

Most preferably the anion X is paratoluene sulphonate.

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

The residue of a single colour coupler may be present in the polymer or the residue of more colour couplers may be present. When the residues of a yellow, a cyan and a magenta colour coupler are present a black or blackish dye is formed on colour development.

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

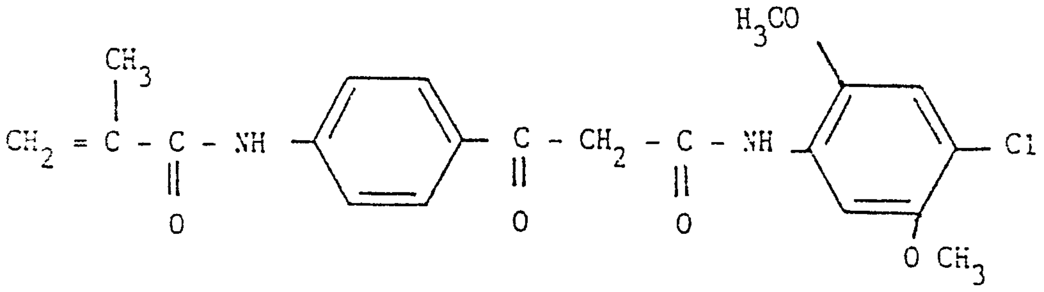


II

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-.

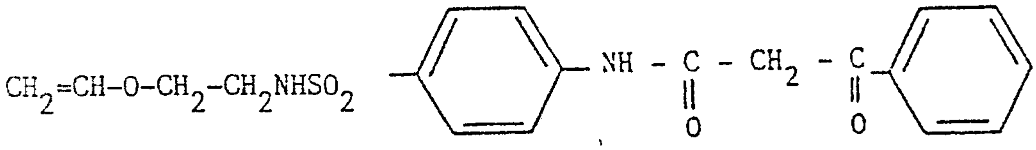
Particularly useful linking groups R_2 are -CO-NH-
and $-O-CH_2-CH_2-NHSO_2-$
Preferably one of L_1 and L_2 is a direct linkage. An example of such a monomer is Monomer B which is used in the Examples which follow.

This monomer has the formula III :



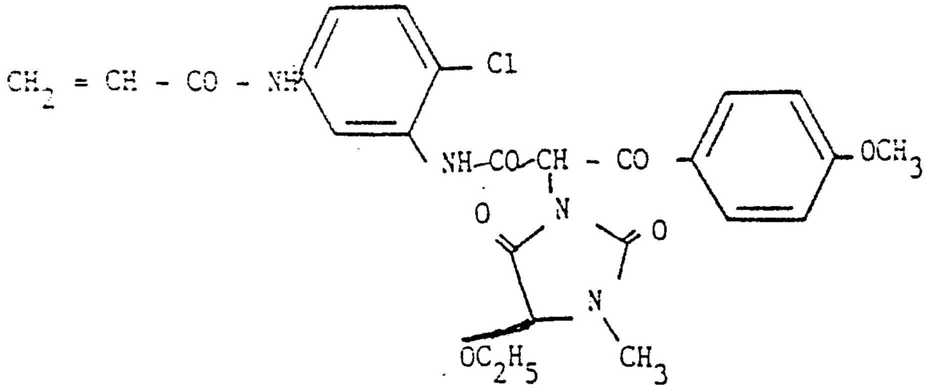
III

Another example of a monomer of general formula II has the formula IV



IV

A further example of a monomer of general formula II which has a leaving group is the monomer of the formula V :-

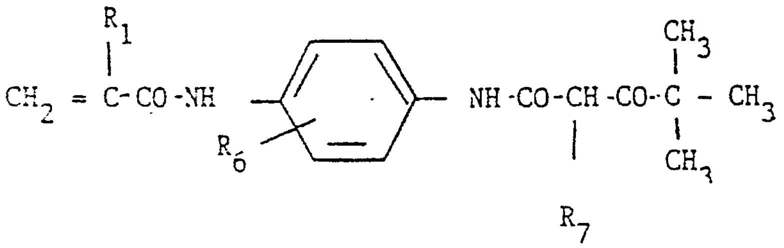


V

Monomeric yellow colour couplers of formula II 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 end group.

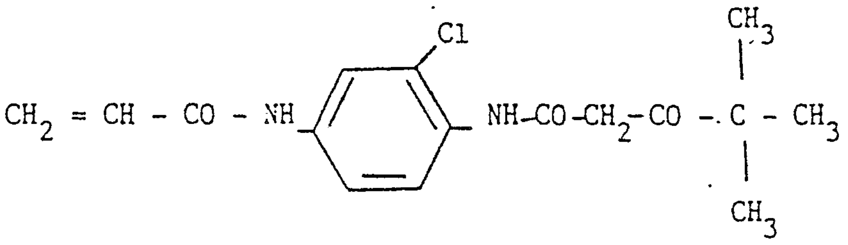
Such colour couplers have the general formulae VI:-



VI

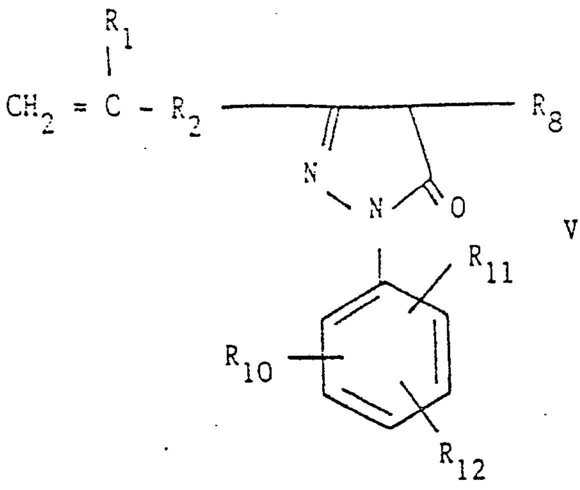
where R_1, R_6 and R_7 have the meanings assigned to the above.

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



VII

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



VIII

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 having 1 to 6 carbon atoms.

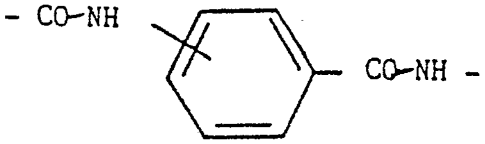
Preferably R_1 is hydrogen or $-CH_3$

Preferably R_2 is -CO NH-

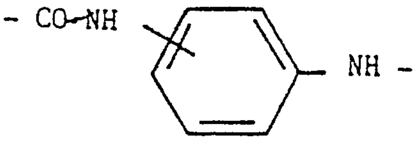
However other useful linking groups R_2 include

-CO NH (CH_2) -O-CO-NH

where x 2 - 6,



and



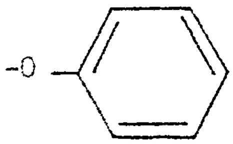
where in the above two formulae the phenylene group is optionally substituted.

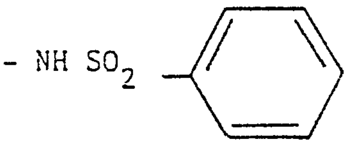
Examples of such substitution include halogen, alkyl and alkoxy.

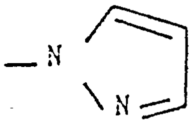
Particularly useful monomers of formula V are those wherein at least two of R_{10}, R_{11} and R_{12} are chlorine atoms.

Examples of leaving groups R_7 and R_8 include 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 has from 12 to 20 carbon atoms in the chain.

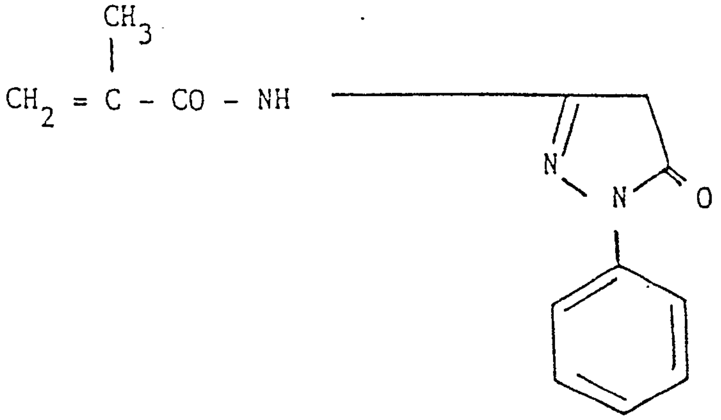
Other examples of the leaving group R_8 include



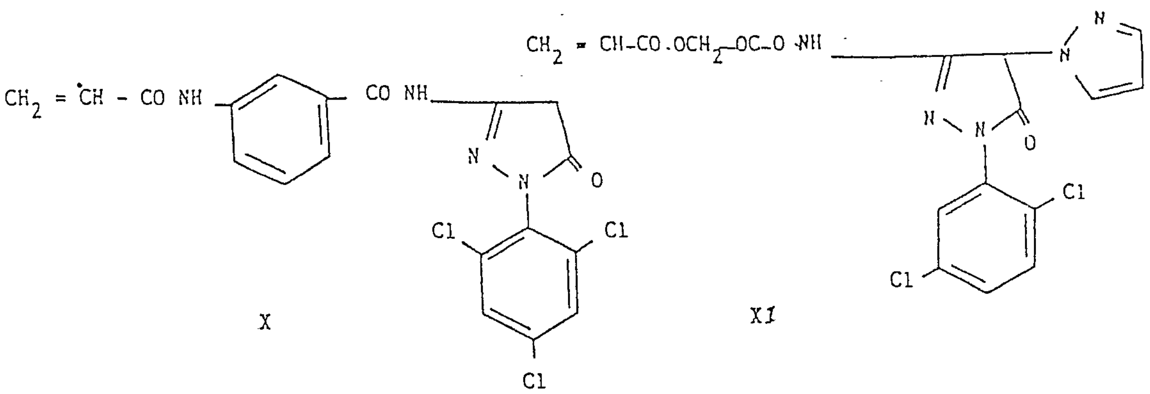




Examples of monomers of formula VIII are :-



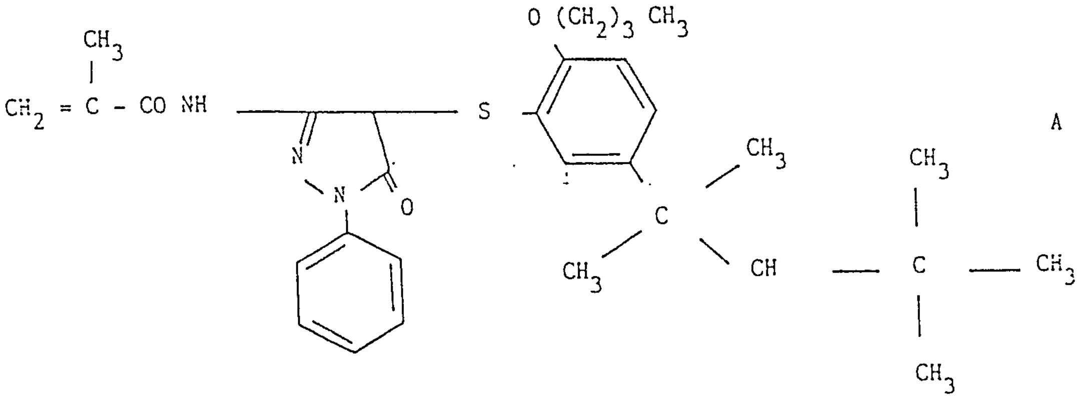
IX



X

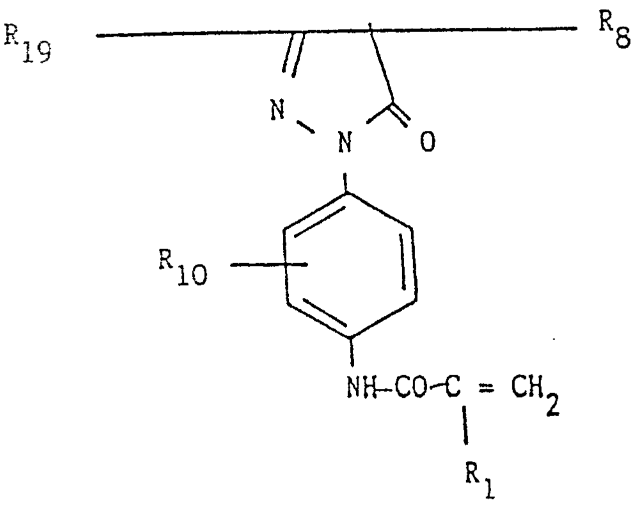
XI

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



A

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

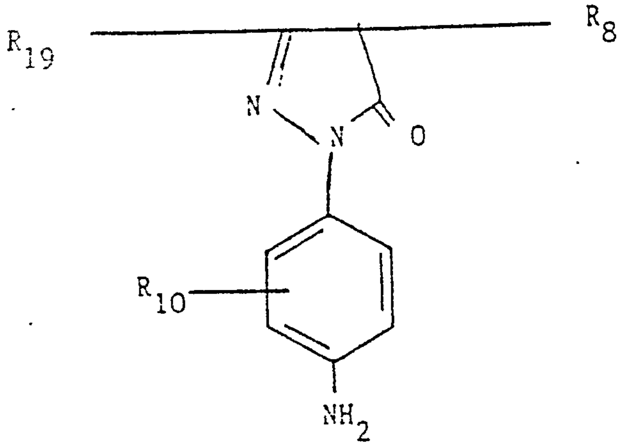


XII

wherein R_1, R_8 and R_{10} are as defined above and R_{10} is alkyl, dialkyl amino, optionally substituted phenyl and optionally substituted acylamino.

Substituents in the phenyl or acylamino group include alkyl groups having from 2 to 6 carbon atoms and chlorine atoms.

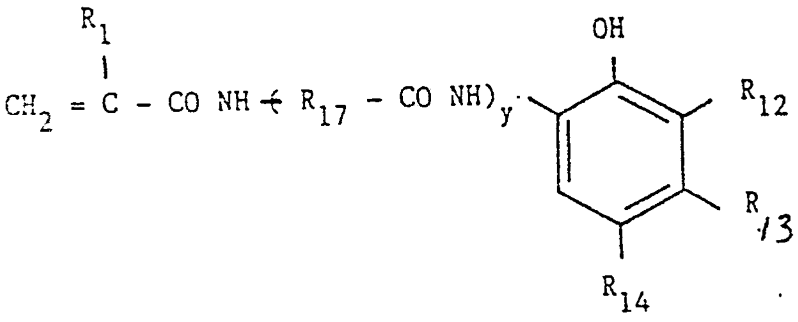
These couplers may be prepared by reacting magenta colour couplers of the formula XIII :



XIII

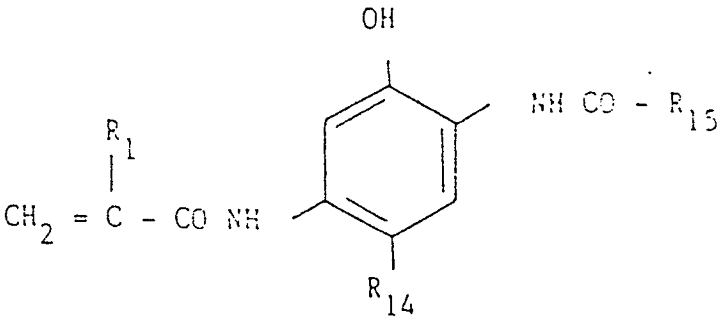
with acryloyl or methacryloyl chloride.

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



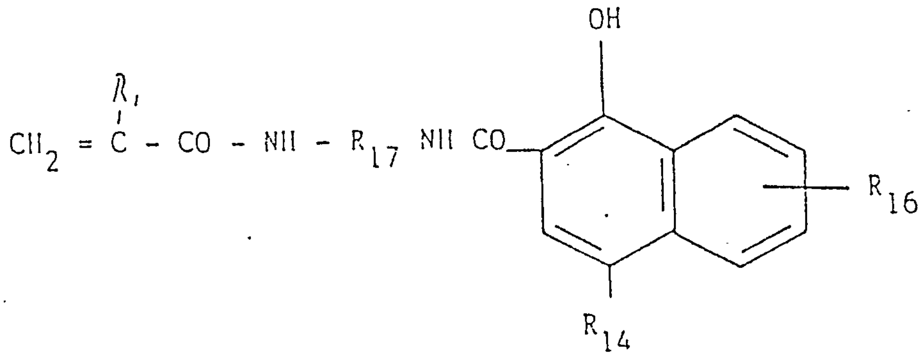
XVI

and of general formula X V :



XV

and a naphthol coupler of the general formula XVI :



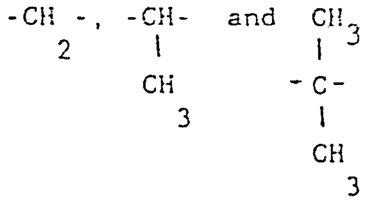
XVI

where in the above three formulae R₁ is as defined above, R_{12} is hydrogen or halogen, R_{14} is hydrogen or a leaving group such as a halogen atom or substituted alkoxy, R_{13} is hydrogen or alkyl having 1 to 5 carbon atoms, R_{15} is an alkyl group having 1 to 6 carbon atoms or acylamino or arylamino, and R_{17} is a linking group and y is 0 or 1, and R_{16} is hydrogen, alkoxy having 1 to 4 carbon atoms or an amino, amido or sulphonamido group.

Suitable substituents in the alkoxy group R_{14} include alkyl sulphonyl and alkylthio.

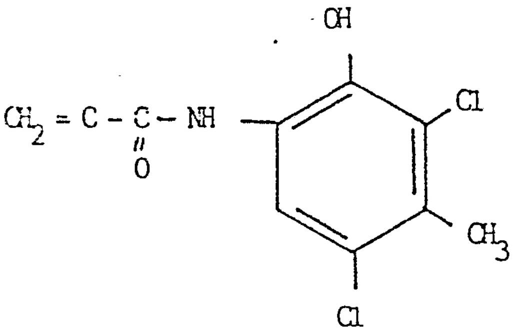
Preferably R_1 is hydrogen or methyl.

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

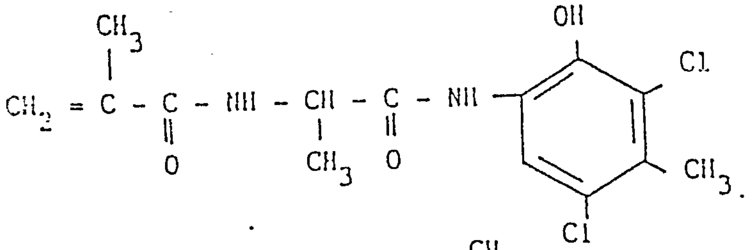


$-CH_2-$, $-CH(CH_3)-$ and $-C(CH_3)_2-$

Examples of monomers of formula XIV are

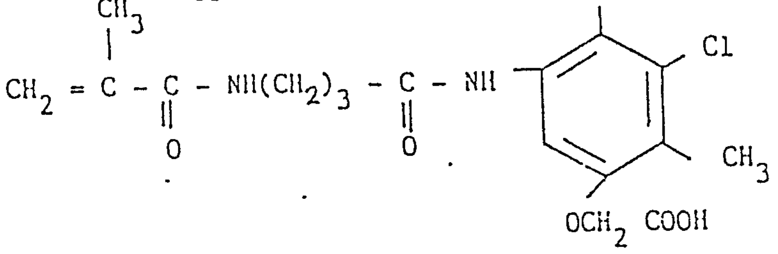


this is Monomer C which is used in the Examples which follow,



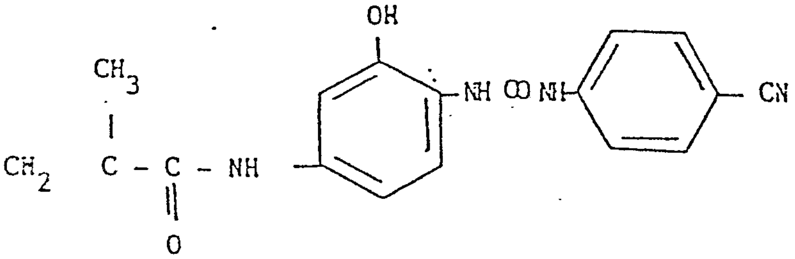
XVII

and



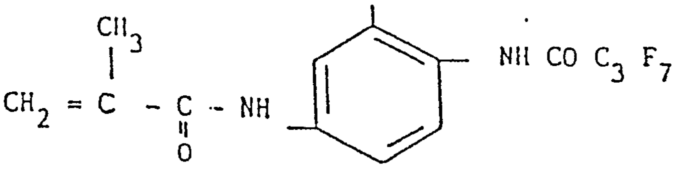
XVIII

Examples of monomers for formula X V are :



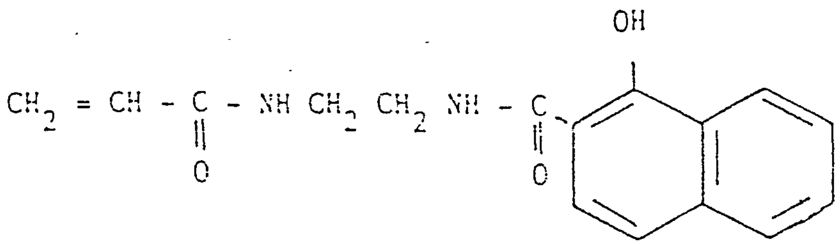
XIX

and



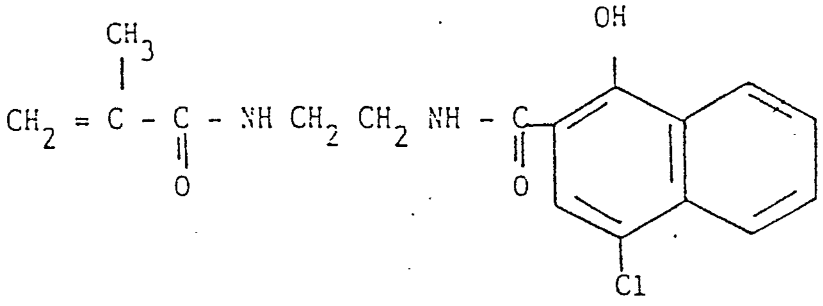
XX

Examples of monomers of formula XVI are :-



XXI

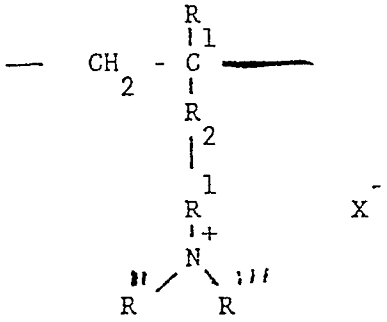
and



XXII

Monomeric colour couplers of general formula XVI are described in B.P. 2,133,170.

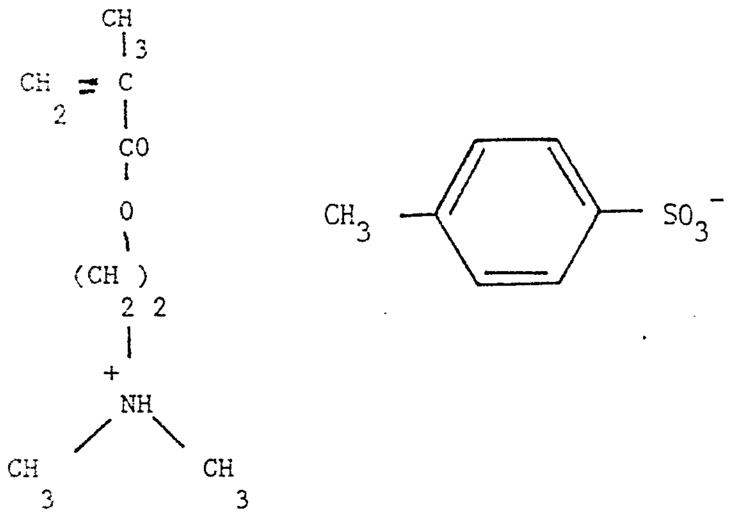
In the quaternary ammonium residue of the polymeric colour coupler of formula I,



$$-CH_2-\overset{\displaystyle R_1}{\underset{\substack{\displaystyle R_2\\ \displaystyle R^1\\ \displaystyle N^+\\ \displaystyle R'' \quad R'''}}{C}}- \qquad X^-$$

R_1 is preferably methyl or hydrogen and R_2 is preferably - CO - O -
R^1 is preferably an alkylene group and most preferably $-CH_2-CH_2-$or $-CH_2-CH_2-CH_2-$ R^{11} and R^{111} preferably are each methyl groups, X is Cl or Br or preferably is an organic anion such as para-toluene-sulphonate.

A particular useful quaternary ammonium residue is derived from dimethylaminoethyl methacrylate and has the formula :-



In order to improve the physical characteristics of the polymer of formula I it is sometimes advantageous to include up to 20% by weight of a non-coupling, non-water solubilising monomer in the coupler.

Suitable for component B comonomers include methyl acrylate, ethyl acrylate, butyl acrylate, ethyl hexyl acrylate, vinyl acetate; hydroxymethyl methacrylate, hydroxypropylmethacrylate; methacrylic acid, acrylic acid, itaconic acid, 2-carboxyethyl acrylate and the salt thereof, acrylamide, methacrylamide, N-hydroxymethyl acrylamide, styrene, N-vinyl pyrrolidone, 1-vinyl imidazole; 4-vinylpyridine, dimethylaminoethyl methacrylate, vinyl sulphonic acid and the salts thereof, acrylonitrile and vinylidene chloride.

According to another aspect of the present invention there is provided a process for the production of a polymer of formula I which comprises dissolving in a water-miscible organic solvent a monomeric colour coupler, a monomer which comprises the quaternary ammonium group and optionally another monomer in the ratio a, b and c as hereinbefore set forth, heating the solution and adding a solution of free radical polymerisation initiating agent and precipitating the polymer by addition of a water immiscible organic solvent.

The resultant polymer is water soluble. It is compatible with gelatin and when added to a silver halide emulsion yields a clear dry coating.

The polymer is layer substantive and thus when the polymer is incorporated in a gelatino silver halide emulsion and after exposure and colour development a coloured dye image is obtained in the layer in which the polymer is coated.

It is surprising that the quaternary ammonium residue when incorporated into the polymer provides water-soluble colour couplers because when various other water-soluble monomers were tried either they did not copolymerise at all with the monomeric colour couplers or they yielded a polymer which was water insoluble.

Examples of comonomers that did not copolymerise included :-

1. Vinyl sulfonic acid
2. Maleic anhydride
3. Sodium allyl sulfonate
4. acrylamido propane sulfonic acid.

Monomers that did copolymerise but did not provide water soluble colour coupler polymers included :-

1. N-vinyl pyrrolidone
2. Acrylamide
3. hydroxymethyl N-vinyl acetamide
4. tetrahydrofurfuryl methacrylate
5. N-vinyl acetamide
6. vinyl imidazole
7. vinyl imidazole-p-toluene sulfonic acid salt

According to a further feature of the present invention there is provided a method of preparing colour photographic material which comprises forming a colour coupler polymer as just described, mixing this polymer with an aqueous gelatino silver halide emulsion and coating the emulsion on a photographic base.

Such photographic material may comprise one gelatino silver halide emulsion layer comprising a colour coupler polymer of the present invention, two such silver halide emulsion layers or three such layers. In the last case the three layers will most likely be a silver halide layer in which the polymeric colour coupler yields a yellow dye, a layer in which the polymeric colour coupler yields a cyan dye and a layer in which the polymeric colour coupler yields a magenta dye.

In another embodiment the colour coupler polymer of the present invention may comprise the residue of a monomeric yellow colour coupler, the residue of a monomeric magenta colour coupler and the residue of a monomeric cyan colour coupler.

Polymeric colour couplers of this type are of particular use in monochrome camera speed silver halide 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 the 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 former of this type can also be used to prepare monochrome 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 former of this type 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 stabilisers bactericides 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 illustrate the invention.

Example 1

Para-toluene sulphonic acid (1g) was dissolved in 5cm^3 of industrial alcohol. Sufficient of the monomer dimethyl aminoethyl methacrylate was added with stirring to raise the pH to 7. This required 1.3 g. This solution was placed in a 25 cc round bottom flask to which 0.5 g of a monomeric colour coupler was added. The flask was fitted with a magnetic stirrer, condenser and nitrogen inlet. The flask was immersed in an oil bath at 75° C and nitrogen was bubbled through. A solution of azobisisobutyronitrile in industrial alcohol (1.2 cm^3 of a 1% solution) was added. After 2 hour a further 0.3 cm^3 of the same solution was added, then left for a further two hours when a further 0.3 cm^3 of the solution was added. After hours reaction time the contents of the flask were poured into 200 cm^3 of ether whereupon the polymer precipitated as a solid. Yield = 2.30 g (82.1%) when the polymeric colour coupler used was yellow colour coupler Monomer B.

Yield = 1.97g (70.3%) when the monomeric colour coupler used was the magenta colour coupler Monomer A.

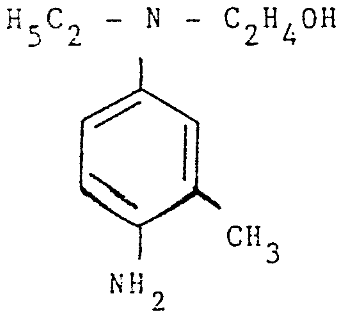
Both solids were found to be completely water soluble.

These solids were used to prepare colour photographic material. To 2.2 cm^3 of an undyed twinned crystal iodobromide gelatino emulsion there was added 0.1 g of the solid and 7 cm$_3$ of water. To this emulsion there was added 0.4 cc 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 is as follows :-

Potassium Carbonate	35.5 g
Sodium Sulphite	4.5 g
Nitrilotriacetate (sequestering 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 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 ½ 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. The results obtained were as follows :-

	COLOUR	λ MAX	D MAX	D MIN
A	Magenta	556	0.47	0.18
B	Yellow	452	0.71	0.46

These results show that the coatings yield dye images of sufficiently good quality for the polymer to be used in colour photographic material.

Example II

p-Toluene sulphonic acid (4 g) was dissolved in industrial alcohol (30 cm^3). 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 cm^3 flask to which were added 1 g of Monomer A (the magenta monomer), 0.5 g 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 the solution for 10 minutes at room temperature. The flask was then heated at 70°C and maintained at that temperature.

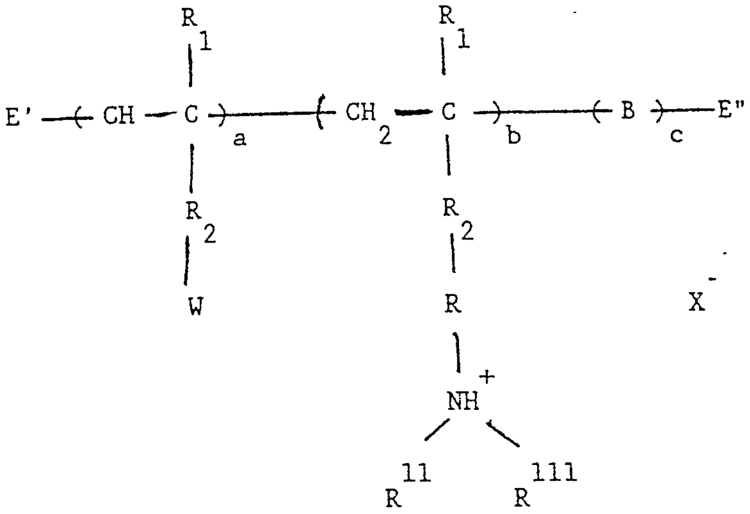
A free radical initiator solution was prepared which comprised 0.5 g azobis(isobutyronitrile) in 50 cm^3 of industrial alcohol. 4.8 cm^3 of this solution was added to the flask. After 2 hours a further 1.2 cm^3 of the initiator solution was added and this was repeated after a further 2 hours. After 7 hours reaction time the contents of the flask were added to ether (500 cm^3) 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 %). The powder was found to be completely water soluble.

0.1 g of this solid was then added to a similar emulsion as used in Example 1, and the emulsion was coated as 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 1.

Claims

1. A polymeric colour coupler of the general formula I :-



$$E'\!-\!\left(CH-\underset{\underset{W}{|}}{\underset{R_2}{|}}\overset{\overset{R_1}{|}}{C}\right)_a\!-\!\left(CH_2-\underset{\underset{\underset{R^{11}\;\;R^{111}}{\overset{+}{N}H}}{\underset{R}{|}}}{\underset{R_2}{|}}\overset{\overset{R_1}{|}}{C}\right)_b\!-\!\left(B\right)_c\!-\!E''\qquad X^-$$

wherein E′ and E″ represent the end groups of the polymer chain, R$_1$ is methyl, hydrogen, chlorine or bromine, R$_2$ is a divalent organic radical, R^{11} and R^{111} are each lower alkyl groups having 1 to 6 carbon atoms, or together represent the atoms required to form a five or size-membered heterocyclic ring, R^1 is an alkylene chain or an interrupted alkylene chain, W is the residue of a colour coupler which can react with an oxidised colour developer to yield a dye and B is the residue of an ethylenically unsaturated monomer which comprises no colour coupling residue nor a water solubilising group, a is from 10 to 60% by weight of the polymer, b is from 40 to 90% by weight of the polymer and c is from 0 to 20% by weight of the polymer, at least 10% by weight of the polymer being derived from the monomer which comprises the colour coupler residue and X is an anion.

2. A polymer according to claim 1 wherein R$_1$ is hydrogen or methyl.

3. A polymer according to claim 1 wherein R$_2$ the divalent organic radical is the residue of urethane, a urea, a carbonate, an ester, an ether, a ketone or an amide.

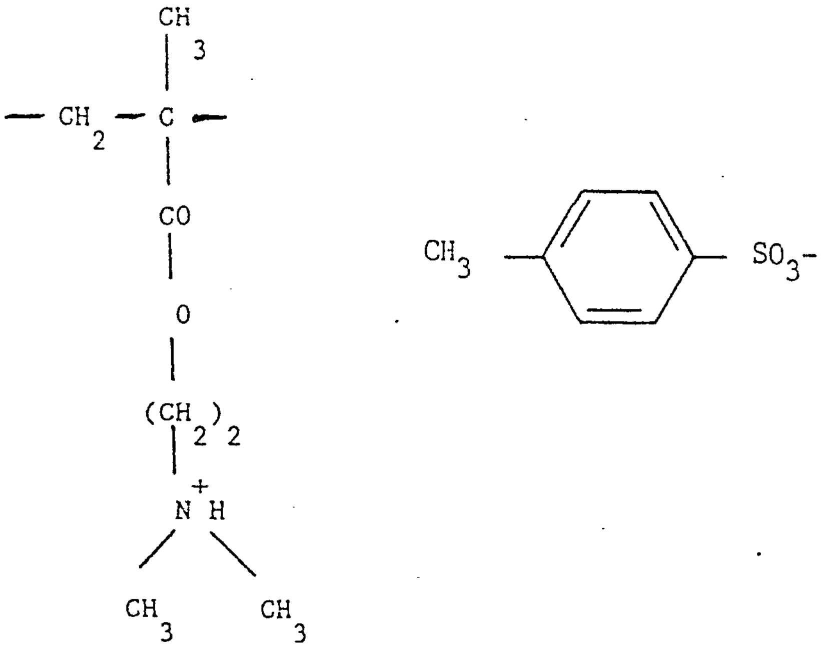
4. A polymer according to claim 3 wherein R_2 is the linkage - C - (O) - NH -.

5. A polymer according to claim 1 where in the quaternary ammonium residue in the polymer colour coupler formulated in claim 1 R_1 is methyl or hydrogen and R_2 is -CO - O -, R^1 is an alkylene group and R^{11} and R^{111} are each methyl groups.

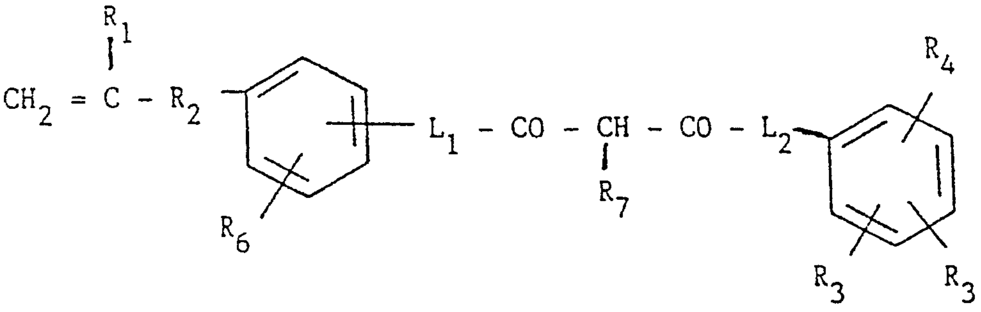
6. A polymer according to claim 5 wherein R^1 is $-CH_2\,CH_2\,CH_2$ -or-$CH_2\,CH_2\,CH_2\,CH_2$ -.

7. A polymer according to claim 5 wherein X is para-toluene sulphonate.

8. A polymer according to claim 1 wherein the quaternary ammonium residue in the polymeric colour coupler formulated in claim 1 has the formula :-

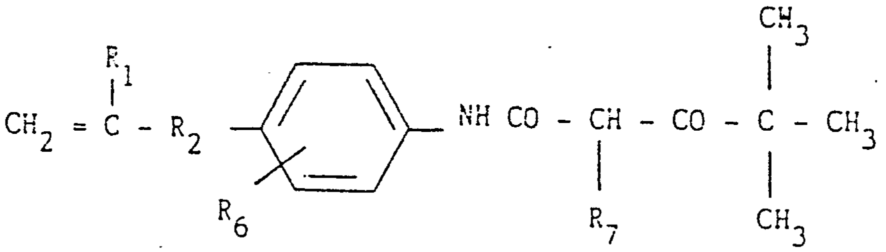


9. A polymer according to claim 1 which comprises the residue of a yellow dye forming monomeric colour coupler of the general formula :-



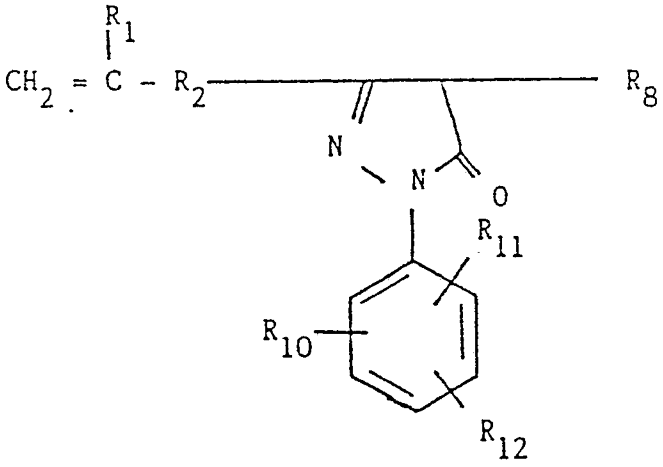
wherein each of R_3, R_4, R_5 and R_6 are hydrogen, halogen, alkoxy, sulphoxy or sulphonamido, R_1 and R_2 are as defined in claim 1, R_7 is hydrogen or a leaving group and L_1 and L_2 are direct linkages or -NH-.

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



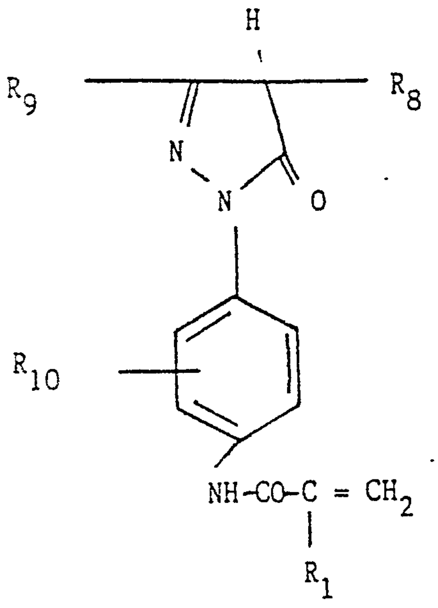
wherein R_1 and R_2 and R_6 and R_7 are as defined in claim 9.

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



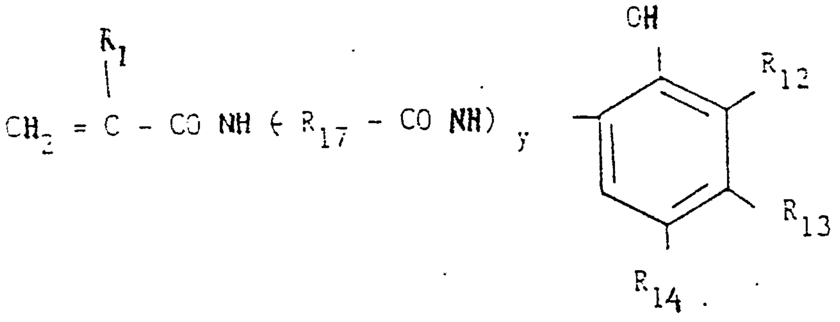
where R_1 and R_2 are as defined in claim 1, R_8 is hydrogen or a leaving group and R_{10}, R_{11} and R_{12} are each hydrogen, halogen or alkoxy.

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

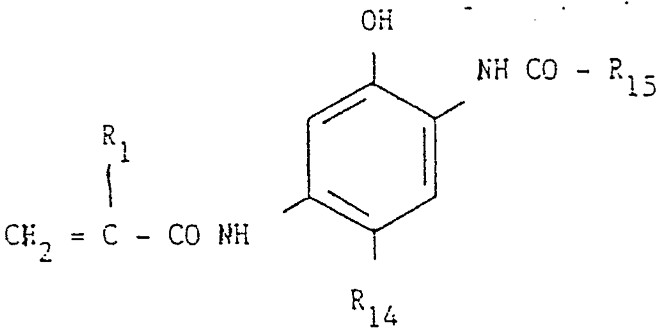


wherein R_1, R_8 and R_{10} are as defined in claim 11 and R_9 is alkyl, dialkylamino, optionally substituted aryl and optionally substituted acylamino.

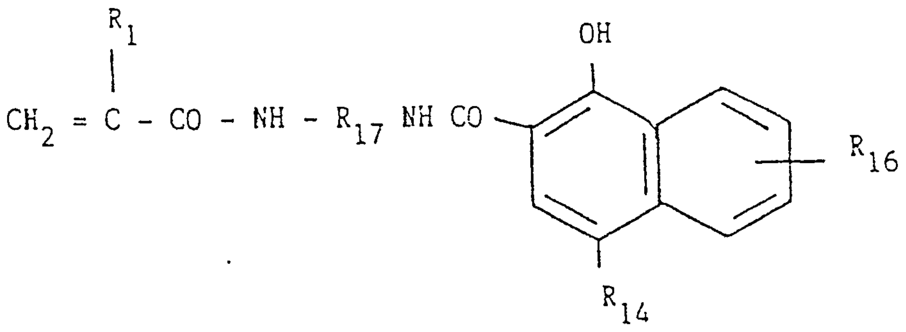
13. A polymer according to claim 1 which comprises the residue of a cyan dye forming monomeric colour coupler which is a phenol coupler of the general formula :-



or is a phenol coupler of the general formula :-



or is a naphthol coupler of the general formula



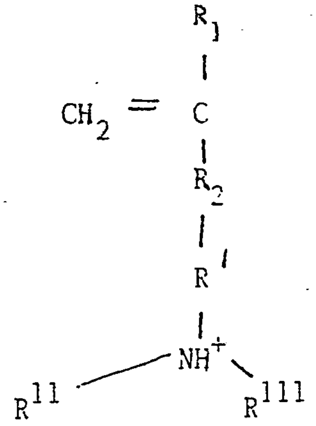
where in the above three formula R_1 and R_{12} are as defined, R_{14} is hydrogen or a leaving group such as a halogen atom or a substituted alkoxy group, R_{13} is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, R_{15} is a linking group and y is 0 or 1, and R_{16} is an alkoxy, amino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

14. A polymer according to claim 1 wherein the polymer comprises units derived from simple, non-colour coupling, photographically inert comonomers.

15. A polymer according to claim 14 wherein the photographically inert comonomer is methyl acrylate, ethyl acrylate, butyl acrylate, ethyl hexyl acrylate, vinyl acetate; hydroxyethyl methacrylate, hydroxypropylmethacrylate; methacrylic acid, acrylic acid, itoconic 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; sulphoethyl methacrylate, vinyl sulphonic acid and salts thereof, acrylonitrile and vinylidene chloride.

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

17. A process for the production of a polymer of formula I which comprises dissolving in a water-miscible organic solvent a monomeric colour coupler, a monomer which comprises a quaternary ammonium group of the formula :-



wherein R_1, R_2, R^1, R^{11} and R^{111} are as defined in claim 1 and optionally another monomer in the ratio as defined in claim 1, heating the solution and adding a solution of free radical polymerisation initiating agent and precipitating the polymer by addition of a water immiscible organic sovlent.

18. A method of preparing colour photographic material which comprises forming a polymeric colour coupler as claimed in claim 1, mixing this polymer with an aqueous gelatino silver halide emulsion and coating the emulsion on a photographic base.

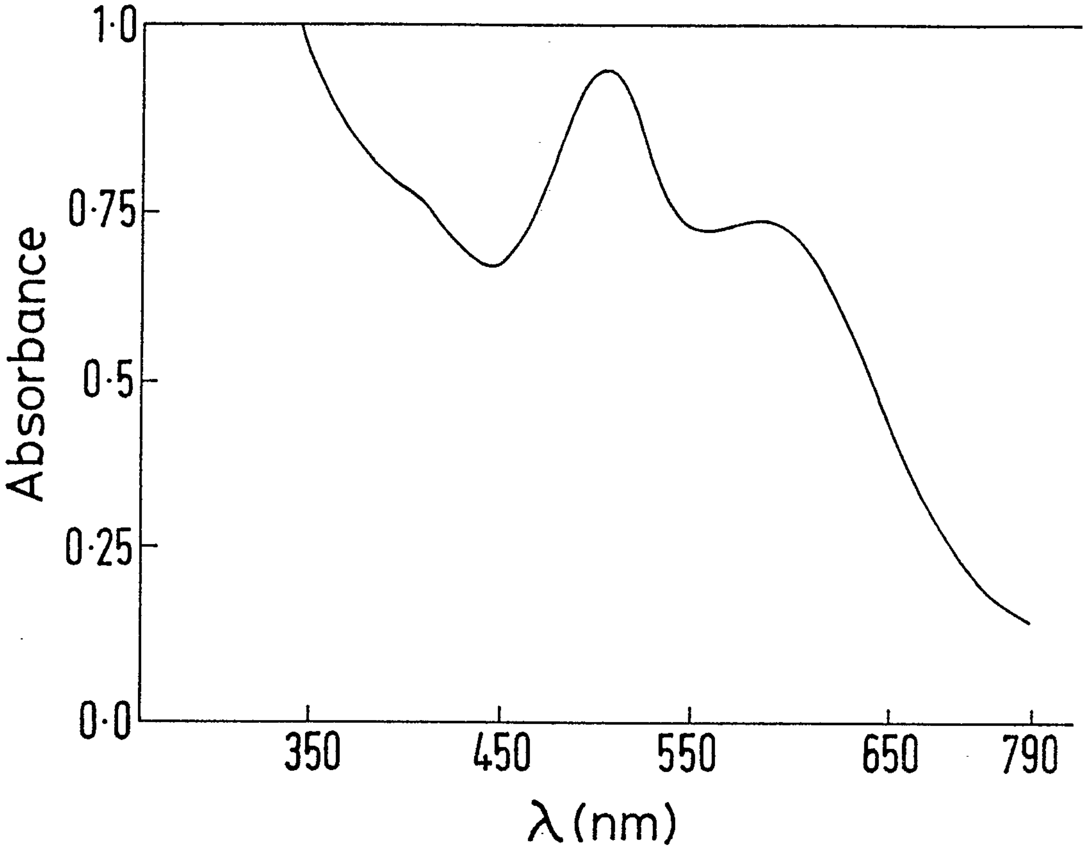


FIG.1