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(54) **Silver halide color photographic material.**

(57) A color photographic materials that contain a rapid-acting hardener and water-soluble polymer couplers containing carboxyl groups or amino groups. The silver halide color photographic material of the present invention is superior in fastness to diffusion of the employed couplers, in color reproduction and in color-forming property. Further, according to the invention, there are attained a rapid hardening-reaction of gelatin and less posthardening of the film not to soften by swelling even in the rapid and higher-temperature procesing over normal temperature to afford a photograph having a excellent preservability.

SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL

BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates to color photographic materials that contain a rapid-acting hardener and water-soluble polymer couplers containing carboxyl groups or amino groups.

(2) Description of the Prior Art

After a silver halide photographic material is exposed to light, when it is color-developed, the oxidized primary amine developing agent reacts with dye-forming couplers to form a color image. Generally, in this technique, color reproduction is effected by a substractive color process in which to reproduce blue, green and red, complementary color images of yellow, magenta, and cyan are formed.

As yellow dye image-forming agents, for example, acylacetanilide or benzylmethane-type couplers are used; as magenta dye image-forming agents, for example, pyrazolone, pyrazolotriazole, pyrazolobenzimidazole, cayanoacetophenone or indazolone-type couplers are used; and as cyan dye forming agents, for example, phenol or naphthol-type couplers are used.

In multi-layer color photographic materials, to lessen color mixing, which improves the color reproduction, it is necessary to secure the couplers in their respective separate layers, thereby rendering them fast to diffusion. To render couplers fast to diffusion, many techniques have been used.

One method introduces a long-chained aliphatic group into the molecule of couplers to prevent diffusion. The couplers used in this technique are immiscible with aqueous gelatin solutions. Therefore, it is necessary that for the coating the couplers are either dissolved in an alkali and added to an aqueous gelatin solution, or they are dissolved in a high-boiling solvent and emulsified and dispersed into an aqueous gelatin solution.

In such a technique, however, the coupler is liable to crystallize out in the emulsion layer. On the other hand, when a high-boiling solvent is used, since the solvent softens the emulsion layer, it has been required to use a large amount of gelatin, which disadvantageously deteriorates the sharpness of the dye image.

Other techniques for rendering couplers fast to diffusion are to polymerize them.

For example, polymer couplers that are prepared by joining reactive couplers to synthesized polymers (e.g., acrylic acid homopolymers, and p-aminostyrene homopolymers) or natural high-molecular compounds (e.g. gelatin) are described in U.S. Patent Nos. 2,698,797, 2,852,381, 2,852,383, and 2,870,712 and Japanese Patent Publication Nos. 16932/1960 and 3661/1969, and polymer couplers that are prepared by copolymerizing couplers synthesized in the form of ethylenically unsaturated monomers with other polymerizable monomers are disclosed in British Patent Nos. 880,206, 955,197, 967,503, 967,504, 995,363, and 1,104,658. The above hydrophilic polymer couplers, however, are insufficiently fast to diffusion, and they are liable to allow colors to mix. Further, in the worst cases, the couplers disadvantageously flow out during the development processing. To overcome this, hydrophilic polymer couplers having phenolic hydroxyl groups or active methylene groups were suggested, as described in U.S. Patent Nos. 4,207,109, 4,215,195, and 4,421,915 and Japanese Patent Application (OPI) No. 27139/1983 and 28744/1983. However, polymers of this type are still inadequately fast to diffusion, and the dye images obtained are low in density.

Other techniques using polymer couplers include dispersing, into an aqueous gelatin solution, lipophilic polymer couplers obtained by emulsion polymerization or solution polymerization of coupler monomers, if necessary, together with other copolymerizable components. Emulsion polymerization is described in U.S. Patent Nos. 3,370,952 and 4,080,211. Solution polymerization is described in U.S. Patent No. 3,451,820.

A considerable improvement in sharpness has been obtained using these lipophilic polymer couplers. Difficulties exist, however, in that the color-forming property is not yet satisfactory and the amount of gelatin used cannot be decreased significantly, and still further improvement in sharpness is desired.

On the other hand, in color photographic materials, in the processing temperature at which a color image is formed is atmospheric temperature (20 to 25°C) or higher, and currently the processing temperature is 30°C or higher, in general.

However, in high-temperature rapid processing, a hydrophilic colloid, for example gelatin in which silver halides, color couplers, and other additives are dispersed, becomes softened and swollen. As a result, the emulsion layers are likely to be damaged or to exfoliate from the base. Therefore, the emulsion layers must be hardened when processed at high temperatures. This hardening can be accomplished by introducing the emulsion layers first into a hardening bath during the development processing, or by adding a preliminary hardener such as formaldehyde, dialdehyde, and mucochloric acid into the silver halide emulsions during preparation.

It is important in the hardening of photographic layers that the photographic layers reach their maximum hardness as quickly as possible after drying, so as not to change the premeability to the developing solution.

Recently it has become important to use, instead of hardeners that act over a long period of time, those that act quickly. Through a high speed hardening reaction, it is possible to obviate changes in photographic materials during storage and avoid the continuous lowering of permeability to the developing solutions.

The term "a rapid-acting hardener" in this specification and claims means a compound capable of causing gelatin to crosslink within a short time period, if possible during the coating and drying. A maximum crosslink can be attained within 24 hours.

Quite interesting rapid-acting hardeners are carbodiimides, such compounds as found in U.S. Patent Nos. 2,938,892 and 3,098,693, a report by E.Schmidt, F.Hitzler, and E.Lahde in Berichte 71,1933 (1938), and in a report by G.Amiard and R.Heymes in Bul. Soc. Chim. France 1360 (1956); dihydroquinone compounds, described in German Patent Application (OLS) No. 2,322,317; carbamoylpyridinium compounds, described in German Patent Application (OLS) Nos. 2,225,230, 2,317,677, and 2,439,551; and carbamoyloxypyridinium compounds, described in German Patent Application (OLS) No. 2,408,814.

One characteristic common to all of these rapid-acting hardeners is that they activate a carboxyl group in gelatin. This action can be illustrated by the known reaction between carbodiimides and a carboxylic acid. In this reaction an N-acylurea or an acid anhydride is used as an active group. For a protein having carboxyl groups and amino groups, the reaction proceeds further and the activated carboxyl group forms a peptide linkage with the amino group. These compounds are, therefore, known as peptide reagents. (See Chemical Review 67, (1967), pages 107 to 152)

In some cases, however, even if the above rapid-acting hardeners are used, conventional silver halide color photographic materials are not necessarily increased in film strength. Further, silver halide color photographic materials in which all performances such as color-forming property, film strength, and nondiffusibility are satisfactory are not yet available.

BRIEF SUMMARY OF THE INVENTION

Therefore, the first object of the invention is to provide a silver halide color photographic material that is excellent in fastness of the contained couplers to diffusion, good in color reproduction, and which produces dye images of high density.

The second object of the invention is to provide a silver halide color photographic material that is rapid in the hardening reaction of the gelatin and wherein less posthardening of the film occurs.

The third object of the invention is to provide a silver halide color photographic material wherein the film strength is high and the sharpness of an image is remarkably improved by making the film thinner.

Other and further objects, features, and advantages of the invention will appear more fully from the following description.

DETAILED DESCRIPTION OF THE INVENTION

These objects can be attained by providing a silver halide color photographic material characterized in that the silver halide color photographic material contains a hardener that acts by activating a carboxyl group and water-soluble polymer couplers having at least one or more types of repeating units represented by the following formula (I):

Formula (I) $-\!\left(A \right)\!-$

wherein A represents a vinyl polymer unit having a color coupler residue capable of coupling with the oxidized product of an aromatic primary amine developing agent, and at least one or more types of repeating units represented by the following formula (II):

Formula (II) $-\!\left(B \right)\!-$

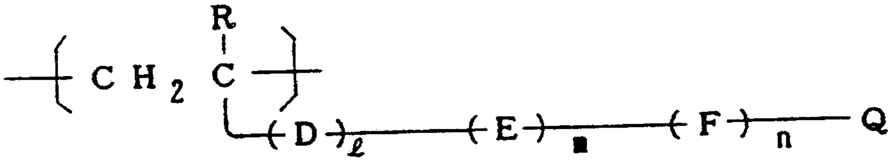
wherein B represents a vinyl monomer unit having at least one group -COOM, in which M represents a hydrogen atom or an alkali metal, or having at least one amino group.

In the present invention, a vinyl monomer unit represented by formula (II) may have both -COOM and an amino group in the unit.

That is, in the present invention, the water-soluble polymer couplers contained in the silver halide photographic material are formed from at least one carboxyl-group-containing monomer or at least one amino-group-containing monomer as a monomer unit, and a hardener that activates an carboxyl group in gelatin, has a function of reacting with gelatin to form a crosslinkage, so that said polymer couplers may be prevented from diffusing in a constitutional layer or between constitutional layers. Thus the disadvantages hitherto involved can be obviated.

Preferable examples of monomer units represented by formula (I) capable of coupling with the oxidized product of an aromatic primary amine developing agent to form a dye are those represented by formula (III):

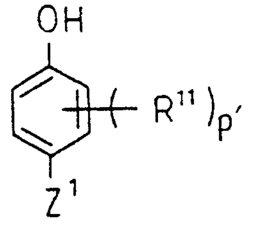
Formula (III)



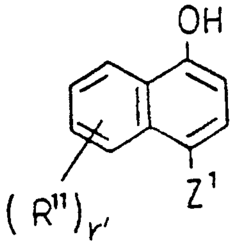
$$-\!\left(CH_2 - \overset{R}{\underset{|}{C}} \right)\!- \qquad \text{C}-\left(D \right)_{\ell}-\left(E \right)_{m}-\left(F \right)_{n}-Q$$

wherein R represents a hydrogen atom, a chlorine atom, or an alkyl group having 1 to 4 carbon atoms; D represents -CO-, -CONR′-, or a substituted or unsubstituted phenyl group; E represents a substituted or unsubstituted alkylene group, phenylene group, or aralkylene group; F represents -CONR′-, NR′CONR′-, -NR′COO-, NR′-CO-, -OCONR′-, -NR′-, -COO-, -OCO-, -CO-, -O-, -SO^2-, NR′SO^2, or -SO^{2}NR′-, in which R′ represents a hydrogen atom or a substituted or unsubstituted alkyl group or aryl group, and if R′ is present two or more in number in the same molecule, they may be the same or different. As substitutents in D, E, and R′ can be mentioned an alkyl group (e.g., methyl and ethyl), an alkoxy group (e.g., methoxy group and ethoxy group), an aryloxy group (e.g., phenyloxy), an alkoxycarbonyl group (e.g., methoxycarbonyl), an acylamino group (e.g., acetylamino), a carbamoyl group, an alkylcarbamoyl group (e.g., methylcarbamoyl, and ethylcarbamoyl), a dialkylcarbamoyl group (e.g., dimethylcarbamoyl), an arylcarbamoyl group (e.g., phenylcarbamoyl), an alkylsulfonyl group (e.g., methylsulfonyl), an arylsulfonyl group (e.g., phenylsulfonyl), an alkylsulfonamido group (e.g., methanesulfonamido), an arylsulfonamido group (e.g., phenylsulfonamido), a sulfamoyl group, an alkylsulfamoyl group (e.g., ethylsulfamoyl), a dialkylsulfamoyl group (e.g., dimethylsulfamoyl), an alkylthio group (e.g., methylthio), an arylthio group (e.g., phenylthio), a cyano group, a nitro group, and a halogen atom (e.g., fluorine, chlorine, and bromine). If the substituents are present two or more in number, they may be the same or different. ℓ, m, and n are 0 or 1, provided that ℓ, m, and n are not 0 at the same time, and Q represents cyan, magenta, or yellow dye forming coupler residue capable of coupling with the oxidized product of an aromatic primary amine developing agent to form a dye.

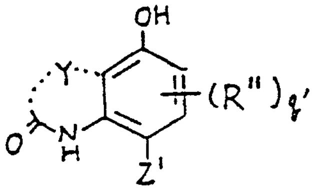
Of the color coupler residues represented by Q, as cyan forming coupler residues, preferable compounds are respresented by phenol type (IV) or (V), or naphthol type (VI) or (VII) (a hydrogen atom other than one positioned at the coupling position or the 1-positioned OH group will slit off to join with F of formula (III)).



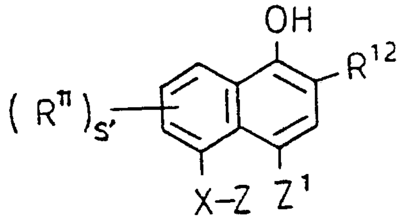
..... (IV)



...... (V)



..... (V')



..... (VI)

wherein R^{11} represents a group capable of replacing on a phenol ring or a naphthol ring such as a halogen atom, a hydroxy group, an amino group, a sulfo group, a cyano group, an aliphatic group, an aromatic group, a heterocyclic group, a carbonamide group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an acyloxy group, an acyl group, an aliphatic oxy group, an aliphatic sulfonyl group, an aromatic oxy group, an aromatic thio group, an aromatic sulfonyl group, a sulfamoylamino group, a nitro group, and an imido group, with R^{11} having 0 to 3 carbon atoms,

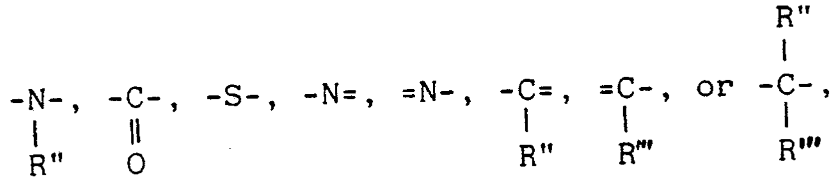
R^{12} represents $-CONR^{13}R^{14}$, $-NHCOR^{13}$, $-NHCOOR^{15}$, $-NHSO^2R^{15}$, $-NHCONR^{13}R^{14}$, or $-NHSO^2R^{13}R^{14}$, in which R^{13} or R^{14} represents a hydrogen atom, an aliphatic group having 1 to 30 carbon atoms (e.g., methyl, ethyl, butyl, methoxyethyl, n-decyl, n-dodecyl, n-hexadecyl, trifluoromethyl, heptafluoropropyl, dodecyloxypropyl, 2,4-di-tertamylphenoxypropyl, and 2,4-di-tert-amylphenoxybutyl), an aromatic group having 6 to 30 carbon atoms (e.g., phenyl, tolyl, 2-tetradecyloxyphenyl, pentafluorophenyl, and 2-chloro-5-dodecyloxycarbonylphenyl), or a heterocyclic group having 2 to 30 carbon atoms (e.g., 2-pyridyl, 4-pyridyl, 2-furyl, anmd 2-thienyl), R^{15} represents an aliphatic group having 1 to 30 carbon atoms (e.g., methyl, ethyl, butyl, dodecyl, and hexadecyl), an aromatic group having 6 to 30 carbon atoms (e.g., phenyl, tosyl, 4-chlorophenyl, and naphthyl), or a heterocyclic group (e.g., 4-pyridyl, quinolyl, and 2-furyl), and R^{13} and R^{14} may bond together to form a heterocyclic ring (e.g., morpholine, piperidine, and pyrrolidine), p' is a integer of 0 to 3, q' is a integer of 0 to 2, r' and s' are each integers of 0 to 5.

X represents an oxygen atom, a sulfur atom, or $R^{16}N<$, in which R^{16} represents a hydrogen atom or a monovalent group such as an aliphatic group having 1 to 30 carbon atoms (e.g., methyl, ethyl, butyl, methoxyethyl, and benzyl), an aromatic group having 6 to 30 carbon atoms (e.g., phenyl, and tolyl), a heterocyclic group having 2 to 30 carbon atoms (e.g., 2-pyridyl, and 2-pyrimidyl), a carbonamido group having 1 to 30 carbon atoms (e.g., formamido, acetamido, N-methylacetamido, and benzamido), sulfonamido group having 1 to 30 carbon atoms (e.g., methanesulfonamido, toluenesulfonamido, and 4-

chlorobenzenesulfonamido), an imido group having 4 to 30 carbon atoms, $-OR^{17}$, $-SR^{17}$-, $-COR^{17}$, $-CONR^{17}R^{18}$, $-COCOR^{17}$, $-COCONR^{17}R^{18}$, $-COOR^{19}$, $-COCOOR^{19}$, $-SO^2R^{19}$, $-SO^2OR^{19}$, $-SO^2NR^{17}R^{18}$, and $-NR^{17}R^{18}$, in which R^{17} and R^{18}, which may be the same or different, each represent a hydrogen atom, an aliphatic group having 1 to 30 carbon atoms (e.g., methyl, ethyl, butyl, dodecyl, methoxyethyl, ethyl, trifluoromethyl, and heptafluoro propyl), an aromatic group having 6 to 30 carbon atoms (e.g., phenyl, tolyl, 4-chlorophenyl, pentafluorophenyl, 4-cyanophenyl, and 4-hydroxyphenyl), or a heterocyclic group having 2 to 30 carbon atoms (e.g., 4-pyridyl, 3-pyridyl, and 2-furyl), and R^{17} and R^{18} may bond together to form a heterocyclic ring (e.g., a morpholino group, and a pyrrolidino group), and as examples of R^{19} can be mentioned substituents defined for R^{17} and R^{18}, excluding a hydrogen atom,

Z^1 represents a hydrogen atom, or a group that can split off by the coupling reaction with the oxidized product of an aromatic primary amine developing agent. As examples that can split off can be mentioned a halogen atom (e.g., fluorine, chlorine, bromine and iodine), an aliphatic oxy group having 1 to 30 carbon atoms (e.g., methoxy, ethoxy, 2-hydroxyethyoxy, carboxymethyloxy, 3-carboxypropyloxy, 2-methoxyethoxycarbamoylmethyloxy, 2-methansulfonylethoxy, 2-carboxymethylthioethoxy, 2-carboxymethylthioethoxy, and triazolylmethyloxy), an aromatic oxy group having 6 to 30 carbon atoms (e.g., phenoxy, 4-hydroxyphenoxy, 2-acetoamidophenoxy, 2,4-dibenzenesulfonamidophenoxy, and 4-phenylazophenoxy), a heterocyclic oxy group having 2 to 3 carbon atoms (e.g., 4-pyridyloxy and 1-phenyl-5-tetrazolyloxy), an aliphatic thio group having 1 to 30 carbon atoms (e.g., dodecylthio), an aromatic thio group having 6 to 30 carbon atoms (e.g., 4-dodecylphenylthio), a heterocyclic thio group having 2 to 30 carbon atoms (e.g., 4-pyridylthio and 1-phenyltetrazol-5-ylthio), an acyloxy group having 2 to 30 carbon atoms (e.g., acetoxy, benzoyloxy, and lauroyloxy), a carbonamido group having 1 to 30 carbon atoms (e.g., dichloroacetylamido, trifluorobenzamido), pentafluorobutaneamido, and pentafluorobenzamido), a sulfonamido group having 1 to 30 carbon atoms (e.g., methanesulfonamido, and toluenesulfonamido), an aromatic azo group having 6 to 30 carbon atoms (e.g., phenylazo, 4-chloroephenylazo, 4-methoxyphenylazo, and 4-pivaloylaminophenylazo), an aliphatic oxycarbonyloxy group having 1 to 30 carbon atoms (e.g., ethoxycarbonyloxy, and dodecyloxycarbonyloxy), an aromtic oxycarbonyloxy group having 6 to 30 carbon atoms (e.g., phenoxycarbonyloxy), a carbamoyloxy group having 1 to 30 carbon atoms (e.g., methylcarbamoyloxy, dodecylcarbamoyloxy, and phenylcarbamoyloxy), and a heterocyclic ring group having 1 to 30 carbon atoms and connected to the active position of the coupler through the nitroben atom (e.g., succinimido, phthalimido, hydantoinyl, pyrazolyl, and 2-benzotriazolyl), and

Y represents a group of atoms required to form a 5-, 6-or 7-membered ring together with the carbon atom to which Y is connected, and more specifically represents -O-,



$$-\underset{R''}{\underset{|}{N}}-,\quad -\underset{O}{\underset{\|}{C}}-,\quad -S-,\quad -N=,\quad =N-,\quad -\underset{R''}{\underset{|}{C}}=,\quad =\underset{R'''}{\underset{|}{C}}-,\quad \text{or}\quad -\overset{R''}{\overset{|}{\underset{R'''}{\underset{|}{C}}}}-,$$

which may be combined, and wherein R'' and R''' each represent a hydrogen atom, an alkyl group, an aryl group, a halogen atom, an alkyl group, an aryl group, a halogen atom, an alkyloxy group, an alkyloxycarbonyl group, an arylcarbonyl group, an alkylcarbamoyl group, an arylcarbamoyl group, or a cyano group.

Examples of substituents preferably used in the invention are given below.

Preferable substituents represented by R^{11} include a halogen atom (e.g., fluorine, chlorine and bromine), an aliphatic group (e.g., methyl, ethyl, and isopropyl), a carbonamido group (e.g., acetamido, and benzamido), and a sulfonamido group (e.g., methanesulfonamido, and toluenesulfonamido).

Preferable substituents represented by R^{12} include $-CONR^{13}R^{14}$, such as a carbamoyl group, an ethylcarbamoyl group, a morpholinocarbonyl group, a dodecylcarbamoyl group, a hexadecylcarbamoyl group, a decyloxypropyl group, a dodecyloxypropyl group, and a 2,4-di-tert-amylphenoxybutyl group.

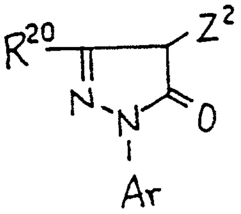
Preferable substituents represented by X include $R^{16}N<$, in which R^{16} more preferably represents $-COR^{17}$(e.g., formyl, acetyl, trifluoroacetyl, chloroacetyl, benzoyl, pentafluorobenzoyl, and p-chlorobenzoyl), $-COOR^{19}$(e.g., methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl, dodecyloxycarbonyl, methoxyethoxycarbonyl, and phenoxycarbonyl), $-SO^2R^{19}$(e.g., methanesulfonyl, ethanesulfonyl, butanesulfonyl, hexadecanesulfonyl, benzenesulfonyl, toluenesulfonyl, and p-chlorobenzenesulfonyl), $-CONR^{17}R^{18}$ (e.g., N,N-dimethylcarbamoyl, N,N-diethylcarbamoyl, N,N-dibutylcarbamoyl, morpholinocarbonyl, piperidinocarbonyl, 4-cyanophenylcarbamoyl, 3,4-dichlorophenylcarbamoyl, and 4-methanesulfonylphenylcarbamoyl), and $-SO^2NR^{17}R^{18}$(e.g., N,N-dimethylsulfamoyl, N,N-diethylsulfamoyl, and N,N-dipropylsulfamoyl). More preferably represented by R^{16} are groups represented by $-COR^{17}$, $-COOR^{19}$, and $-SO^2R^{19}$.

Preferable groups represented by Z^1 are a hydrogen atom, a halogen atom, an aliphatic oxy group, an aromatic oxy group, a heterocyclic thio group, and an aromatic azo group.

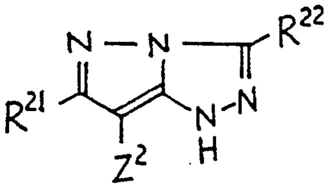
The couplers represented by general formulae (IV), (V), (V'), and (VI) may be combined themselves at the substituent R^{11}, R^{12}, X or Z^1 via a divalent or higher valent linking group to become a dimer or higher polymer. In that case, of course, the number of carbon atoms defined for the substituents above would not apply.

Magenta color-forming coupler residues are coupler residues represented by formula (VII), (VIII), (IX), (X), (XI), (XII), and (XIII), and they are connected to F of formula (III) at any part of Ar, Z^2, and R^{20} to R^{32}.

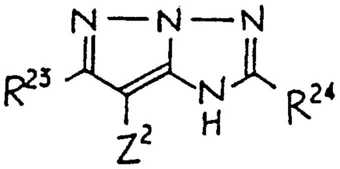
Formula (VII)



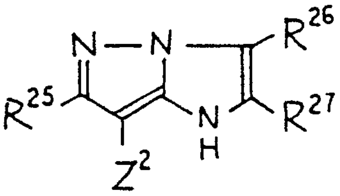
Formula (VIII)



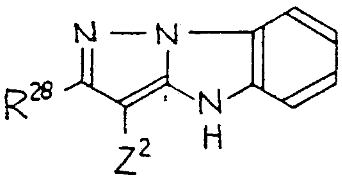
Formula (IX)



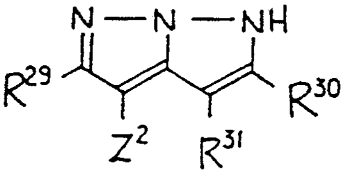
Formula (X)



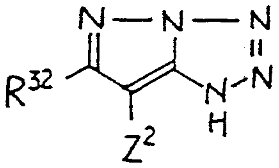
Formula (XI)



Formula (XII)



Formula (XIII)



wherein Ar respresents a known substituent at the first position of a 2-pyrazoline-5-on coupler, for example an unsubstituted or substituted alkyl group (e.g., haloalkyl such as fluoroalkyl, cyanoalkyl, and benzylalkyl); an unsubstituted or substituted aryl group [examples of the substituent are an alkyl group (e.g., methyl and ethyl), alkoxy group (e.g., methoxy and ethoxy), aryloxy group (e.g., phenyloxy), alkoxycarbonyl group (e.g., methoxycarbonyl), acylamino group (e.g., acethylamino), carbamoyl group, alkylcarbamoyl group (e.g., methylcarbamoyl and ethylcarbamoyl), dialkylcarbamoyl group (e.g., dimethylcarbamoyl), arylcarbamoyl group (e.g., phenylcarbamoyl), alkylsulfonyl group (e.g., methylsulfonyl), arylsulfonyl group (e.g., phenylsulfonyl), alkylsulfonamido group (e.g., .methanesulfonamido), arylsulfonamido group (e.g., phenylsulfonamido), sulfamoyl group, alkylsulfamoyl group(e.g., ethylsulfamoyl), dialkylsulfamoyl group (e.g., dimethylsulfamoyl), alkylthio group (e.g., methylthio) arylthio group (e.g., phenylthio), cyano group, nitro group, and halogen atom (e.g., fluorine, chlorine, and bromine): When the substituents are two or more, they may be the same or different, and particularly preferred examples of substituents are a halogen atom, alkyl group, alkoxy group, an alkoxycarbonyl group, and cyano group]; or a heterocyclic group (e.g., triazole, thiazole, benzthiazole, furan, pyridine, quinaldine, benzoxazole, pyrimidine, oxazole, and imidazole).

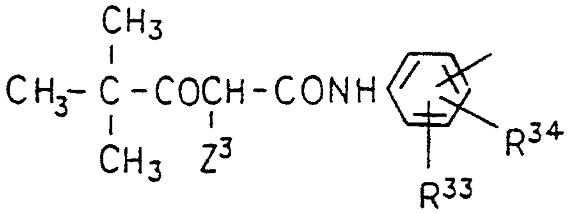
R^{20} represents an unsubstitued or substituted anilino group, an unsubstituted or substituted acylamino group (e.g., alkylcarbonamido, phenylcarbonamido, alkoxycarbonamido, and phenyloxycarbonamido), or an unsubstituted or substituted ureido group (e.g., alkylureido and phenylureido): Example substituents of these substituted groups are a halogen atom (e.g., fluorine, chlorine, and bromine), straight-chain or branched-chain alkyl group (e.g., methyl, t-butyl, octyl, and tetradecyl), alkoxy group (e.g., methoxy, ethoxy, 2-ethylhexyloxy, and tetradecyloxy), acylamino group (e.g., acetamido, benzamido, butaneamido, octaneamido, tetradecaneamido, α-(2,4-di-tert-amylphenoxy)acetoamido, α-(2,4-di-tert-amylphenoxy)-butylamido, α-(3-pentadecylphenoxy)hexaneamido, α-(4-hydroxy-3-tert-butylphenoxy)tetradecaneamido, 2-oxo-pyrrolidine-1-yl, 2-oxo-5-tetradecylpyrrolidine-1-yl, and N-methyl-tetradecaneamido), sulfonamido group (e.g., methanesulfonamido, benzenesulfonamido, ethylsulfonamido, p-toluenesulfonamido, octanesulfonamido, p-dodecylbenzenesulfonamido, and N-methyl-tetradecanesulfonamido), sulfamoyl group (e.g., sulfamoyl, N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dimethylsulfamoyl, N,N-dihexylsulfamoyl, N-hexadecylsulfamoyl, N-[3-(dodecyl)propyl]sulfamoyl, N-[4-(2,4-di-tert-amylphenoxy)butyl]sulfamoyl, and N-methyl-N-tetradecylsulfamoyl), carbamoyl group (e.g., N-methylcarbamoyl, N-butylcarbamoyl, N-octadeclcarbamoyl, N-[4-(2,4-di-tert-amylphenoxy)butyl]carbamoyl, and N-methyl-N-tetradecylcarbamoyl), diacylamino group (N-succinimido, N-phthalimido, 2,5-dioxo-1-hydantoinyl, and 3-(N-acetyl-N-dodecylamino)-succinimido), alkoxycarbonyl group (e.g., methoxycarbonyl, tetradecyloxycarbonyl, and benzyloxycarbonyl), alkoxysulfonyl group (e.g., methoxysulfonyl, butoxysulfonyl, octyloxysulfonyl, and tetradecyloxysulfonyl), aryloxysulfonyl group (e.g., phenoxysulfonyl, p-methylphenoxysulfonyl, and 2,4-di-tert-amylphenoxysulfonyl), alkanesulfonyl group (e.g., methanesulfonyl, ethanesulfonyl, octanesulfonyl, 2-ethylhexylsulfonyl, and hexadecanesulfonyl), arylsulfonyl group (e.g., benzenesulfonyl and 4-nonylbenzenesulfonyl), alkylthio group (e.g., methylthio, ethylthio, hexylthio, benzylthio, tetradecylthio, and 2-(2,4-di-tert-amylphenoxy)ethylthio), arylthio group (e.g., phenylthio and p-trylthio), alkyl-oxycarbonylamino group (e.g., methoxycarbonylamino, ethyloxycarbonylamino, benzyloxycarbonyl, and hexadecyloxycarbonylamino), alkylureido group (e.g., N-methylureido, N,N-dimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, and N,N-dioctadecylureido), acylgroup (e.g., acetyl, benzoyl, octadecanoyl, and p-dodecaneamidobenzoyl), nitro group, carboxyl group, sulfo group, hydroxyl group, or trichloromethyl group.

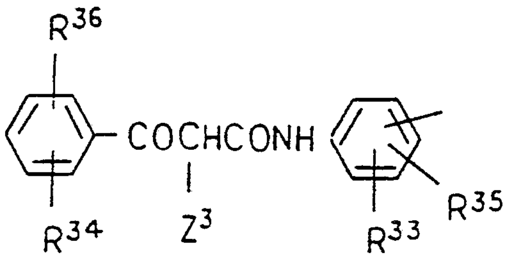
Of the above-mentioned substituents, the number of carbon atoms of a substituent defined as an alkyl group is 1 to 36, and that defined as an aryl group is 6 to 38.

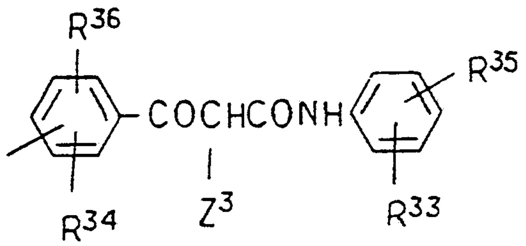
R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}, R^{28}, R^{29}, R^{30}, R^{31}, and R^{32} each represent a hydrogen atom, hydroxyl group, unsubstituted or substituted alkyl group (wherein the number of carbon atoms is preferably 1 to 20, e.g., methyl, propyl, t-butyl, trifluoromethyl, and tridecyl), unsubstituted or substituted aryl group (wherein the number of carbon atoms is preferably 6 to 20, e.g., phenyl, 4-t-butylphenyl 2,4-di-t-amylphenyl, and 4-methylphenyl), unsubstituted or substituted heterocyclic group (e.g., 2-furyl, 2-thienyl, 2-pirimidinyl, and 2-benzothiazolyl), alkylamino group (wherein the number of carbon atoms is preferably 1 to 20, e.g., methylamino, diethylamino, and t-butylamino), acylamino group (wherein the number of carbon atoms is preferably 2 to 20, e.g., acetylamino, propylamino, and benzamino), anilino group (e.g., phenylanilino and 2-chloroanilino), alkoxycarbonyl group (wherein the number of carbon atoms is preferably 2 to 20, e.g., methoxycarbonyl, butoxycarbonyl, and 2-ethylhexyloxycarbonyl), alkylcarbonyl group (wherein the number of carbon atoms is preferably 2 to 20, e.g., acetylcarbonyl, butylcarbonyl, and cyclohexylcarbonyl), arylcarbonyl group (wherein the number of carbon atoms is preferably 7 to 20, e.g., benzoyl and 4-t-butylbenzoyl), alkylthio group (wherein the number of carbon atoms is preferably 1 to 20, e.g., methylthio, octylthio, and 2-phenoxyethylthio), arylthio group (wherein the number of carbon atoms is preferably 6 to 20, e.g., phenylthio and 2-butoxy-5-t-octylphenylthio), carbamoyl group (wherein the number of carbon atoms is preferably 1 to 20, e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl, and N-methyl-N-butylcarbamoyl), sulfamoyl group (wherein the number of carbon atoms is preferably 20 or below, e.g., N-ethylsulfamoyl, N,N-di-ethylsulfamoyl, and N,N-dipropylsulfamoyl), or sulfonamido group (wherein the number of carbon atoms is preferably 1 to 20, e.g., methanesulfonamido, benzenesulfonamido, and p-toluensulfonamido).

Z^2 represents a hydrogen atom or a group which can split-off upon a coupling-reaction with the oxidation product of an aromatic primary amine developing agent. Examples of such coupling split-off groups include a halogen atom (e.g., chlorine atom and bromine atom), a coupling split-off group connected through the oxygen atom (e.g., acetoxy, propanoyloxy, benzoyloxy, ethoxyoxazoyloxy, pyruvinyloxy, cinnamoyloxy, pheoxy, 4-cyanophenoxyl, 4-titaniumsulfonamidophenoxy, α-naphtoxy, 4-cyanoxyl, 4-methansulfonamido-phenoxy, 3-pentadecylphenoxy, benzyloxycarbonyloxy, ethoxy, 2-cyanoethoxy, benzyloxy, 2-phenethyloxy, 2-phenoxy-ethoxy, 5-phenyltetrazoyloxy, and 2-benzothiazolyloxy), a coupling split-off group connected through the nitrogen atom (e.g., the groups described in Japanese Patent Application (OPI) No. 189538/1982 or benzenesulfonamido, N-ethyltoluenesulfonamido, heptafluorobutaneamido, 2,3,4,5,6-pentafluorobenzamido, octanesulfonamido, p-cyanophenylureido, N,N-diethylsulfamoylamino, 1-piperidyl, 5,5-dimethyl-2,4-dioxo-3-oxazolydinyl, 1-benzyl-5-ethoxy-3-hydantoinyl, 2-oxo-1,2-dihydro-1-pyrizonyl, imidazolyl, pyrazolyl, 3,5-diethyl-1,2,4-triazole-1-yl, 5-or 6-bromobenzotriazole-1-yl, 5-methyl-1,2,3,4-triazole-1-yl, and benzimidazolyl), and a coupling split-off group connected through the sulfur atom (e.g., phenylthio, 2-carboxyphenylthio, 2-methoxy-5-octylphenylthio, 4-methanesulfonylphenylthio, 4-octanesulfonamidophenylthio, benzylthio, 2-cyanoethylthio, 5-phenyl-2,3,4,5-tetrazoylthio, and 2-benzothiazolyl). Preferred examples of coupling split-off groups include a halogen atom, phenoxy group, and a coupling split-off group connected through the nitrogen atom. Particularly preferred examples include a halogen atom, phenoxy group, pyrazolyl group, imidazolyl group, and triazolyl group.

As a residue of yellow color-forming couplers, an acylacetoanilido type is preferable, and a pivaloylacetoanilido type (XIV), or a bezoylacetoanilido type (XV) or (XVI) is even more preferable.


(XIV)


(XV)

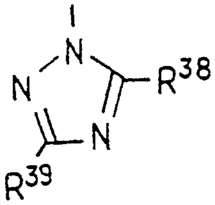

(XVI)

wherein R^{33}, R^{34}, R^{35} and R^{36}, which may be the same or different, each represent a hydrogen atom or a known substituent of the residue of yellow-color-forming coupler (e.g., alkyl, alkenyl, alkoxy, alkoxycarbonyl, halogen atom, alkoxycarbamoyl, aliphatic amino, alkylsulfamoyl, alkylsulfonamido, alkylureido, alkyl-substituted succinimido, aryloxy, aryloxycarbonyl, arylcarbamoyl, arylamido, arylsulfamoyl, arylsulfonamido, arylureido, carboxyl, sulfo, nitro, cyano, and thiocyano).

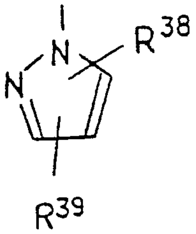
Z^3 represents a hydrogen atom or a group represented by the following formulas (XVII), (XVIII), (XIX), or (XX).

$-OR^{37}$ (XVII)

wherein R^{37} represents an aryl group or heterocyclic group which may be substituted.

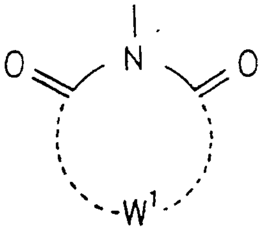


(XVIII)



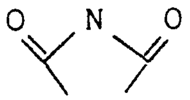
(XIX)

wherein R^{38} and R^{39}, which may be the same or different, each represent a hydrogen atom, halogen atom ester group of calboxylate, amino group, alkyl group, alkylthio group, alkoxy group, alkylsulfonyl group, alkylsulfinyl group, carboxylic group, sulfon group, unsubstituted or substituted phenyl or heterocyclic group.



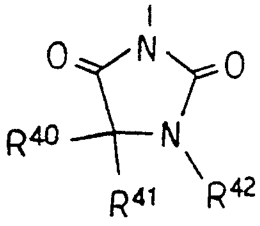
(XX)

wherein W^1 represents a non-metal atom necessary to form a 4-or 5-membered ring with

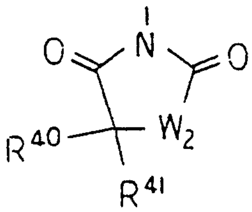


in the formula.

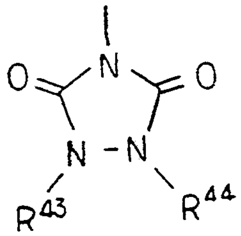
Preferred examples of compounds represented by formula (XX) include those represented by the following formulas (XXI) - (XXIII):



(XXI)



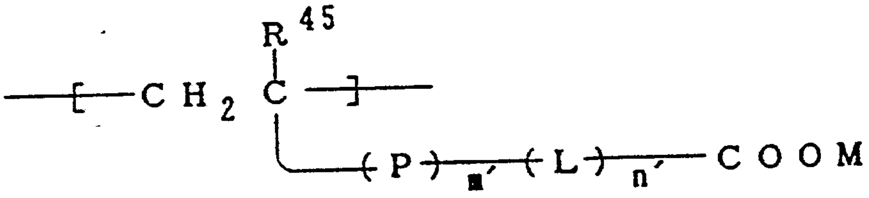
(XXII)



(XXIII)

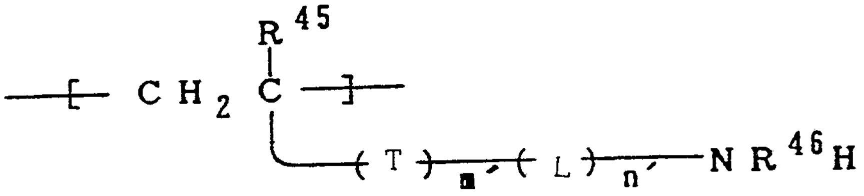
wherein R^{40} and R^{41} each represent a hydrogen atom, alkyl group, aryl group, alkoxy group, aryloxy group, or hydroxyl group; R^{42}, R^{43}, and R^{44} each represent a hydrogen atom, alkyl group, aryl group, alalkyl group, or acyl group; and W^2 represents an oxygen atom or sulfur atom.

Preferred examples of the monomer unit containing a carboxyl group or an amino group represented by formula (II) include compounds represented by the following formula (XXIVa) or (XXIVb):



$$-\left[CH_2-\underset{\underset{\displaystyle (P)_{m'}-(L)_{n'}-COOM}{|}}{\overset{\overset{\displaystyle R^{45}}{|}}{C}}\right]-$$

(XXIVa)



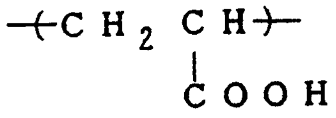
$$-\left[CH_2-\underset{\underset{\displaystyle (T)_{m'}-(L)_{n'}-NR^{46}H}{|}}{\overset{\overset{\displaystyle R^{45}}{|}}{C}}\right]-$$

(XXIVb)

wherein R^{45} represents a hydrogen atom, lower alkyl group having 1 to 4 carbon atoms, or chlorine atom; P represents -COO-, $-CONHR^{46'}-$, or a substituted or unsubstituted phenylene group; T represents -COO-, -CONH-, or a substituted or unsubstituted phenylene group; L represents a substituted or unsubstituted alkylene, a phenylene or an alalkylene group; M represents a hydrogen atom,alkali metal or ammonium; m' and n' each represent 0 or 1; R^{46} and $R^{46'}$ each represent a hydrogen atom, or a substituted or unsubstituted alkyl or aryl group. The substituents contained in P, T, L, R^{46} and $R^{46'}$, which may be the same or different, if they are present two or more in number, include an alkyl group (e.g., methyl and ethyl), alkoxy group (e.g., methoxy and ethoxy), aryloxy group (e.g., phenyloxy), alkoxycarbonyl group (e.g., methoxycarbonyl), acylamino group (e.g., acetylamino), carbamoyl group, alkylcarbamoyl group (e.g., methylcarbamoyl and ethylcarbamoyl), dialkyl-carbamoyl group (e.g., dimethylcarbamoyl), arylcarbamoyl group (e.g., phenylcarbamoyl), alkylsulfonyl group (e.g., methylsulfonyl), arylsulfonyl group (e.g., phenylsulfonyl), alkylsulfonamido group (e.g., methanesulfonamido), arylsulfonamido group (e.g., phenylsulfonamido), sulfamoyl group, alkylsulfamoyl group (e.g., ethylsulfamoyl), dialkylsulfamoyl group (e.g., dimethylsulfamoyl), alkylthio group (e.g., methylthio), arylthio group (e.g., phenylthio), cyano group, nitro group, and halogen atom (e.g., fluorine, chlorine, and bromine).

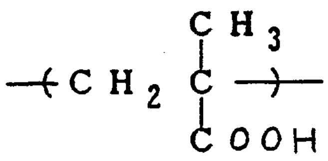
Specific examples of monomer units representing formula (XXIVa) are given below, but the invention is not limited to these.

IIa-1



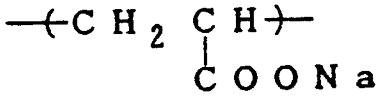
$$-\!\!\left(CH_2\,\underset{\displaystyle COOH}{\underset{|}{CH}}\right)\!\!-$$

IIa-2



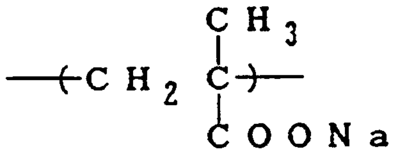
$$-\!\!\left(CH_2\,\underset{\displaystyle COOH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}\right)\!\!-$$

IIa-3



$$-\!\!\left(CH_2\,\underset{\displaystyle COONa}{\underset{|}{CH}}\right)\!\!-$$

IIa-4

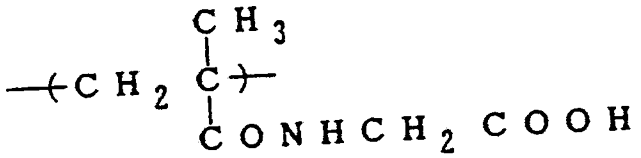


$$-\!\!\left(CH_2\,\underset{\displaystyle COONa}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}\right)\!\!-$$

IIa-5

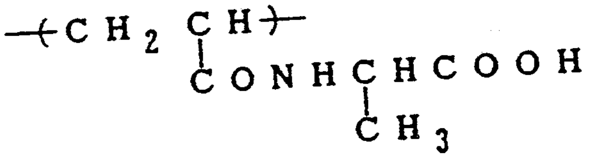
$$-\!\!\left(CH_2\,\underset{\displaystyle CONHCH_2COOH}{\underset{|}{CH}}\right)\!\!-$$

IIa-6



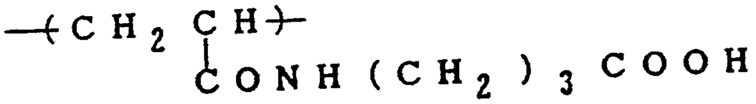
$$-\!\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CONHCH_2COOH}{C}}\right)\!\!-$$

IIa-7



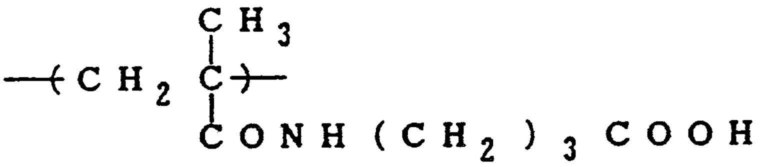
$$-\!\!\left(CH_2-\underset{\displaystyle CONH\underset{\displaystyle CH_3}{C}HCOOH}{CH}\right)\!\!-$$

IIa-8



$$-\!\!\left(CH_2-\underset{\displaystyle CONH(CH_2)_3COOH}{CH}\right)\!\!-$$

IIa-9



$$-\!\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CONH(CH_2)_3COOH}{C}}\right)\!\!-$$

The above-mentioned water-soluble polymer coupler to be used in the present invention may contain a non-color-forming ethylenically-unsaturated monomer unit which does not undergo a coupling reaction with the oxidation product of an aromatic primary amine developing agent other than those represented by formulas (I) and (II), and which does not contain -COOM or an amino group in the molecular. The amount of such monomer unit is contained in a range between 0 to 60%, in a weight ratio to the polymer coupler represented by formula (I) or (II).

As a non-color-forming ethylenically-unsaturated monomer unit which does not undergo coupling reaction with the oxidation product of an aromatic primary amine developing agent other than those represented by formulas (I) and (II), the following examples may be mentioned; acrylate esters, methacrylate esters, crotonate esters, vinyl esters, maleate diester, fumarate diesters, itaconate diesters, acrylamides, methacrylamides, vinyl ethers, and styrenes.

Examples of such monomers include acrylate esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, hexyl acrylate, 3-acroylpropanesulfonic acid, acetoacetoxyethyl acrylate, acetoxyethyl acrylate, phenyl acrylate, 2-methoxy acrylate, 2-ethoxy acrylate, and 2-(2-methoxyethoxy)ethyl acrylate; methacrylate esters such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, 2-hydroxyethyl methacrylate, and ethoxyethyl methacrylate; crotonate esters such as butyl crotonate and hexyl crotonate; vinyl esters such as vinyl acetate, vinyl propionate, vinyl butylate, vinylmethoxy acetate, and vinyl benzoate; maleate diesters such as diethyl maleate, dimethyl maleate, and dibutyl maleate; fumarate diesters such as diethyl fumarate, dimethyl fumarate, and dibutyl fumarate; itaconate diesters such as diethyl itaconate, dimethyl itaconate, and dibutyl itaconate; acrylamides such as acrylamide, methyl acrylamide, ethyl acrylamide, isopropyl acrylamide, n-butyl acrylamide, hydroxylmethyl acrylamide, diacetone acrylamide, acryloyl morpholine, and acrylamido-2-methylpropanesulfonate; methacrylamides such as methyl methacrylamide, ethyl methacrylamide, n-butyl methacryamide, tert-butyl mathacrylamide, 2-methoxy methacrylamide, dimethyl methacryamide, and diethyl methacrylamide; vinyl ethers such as methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, methoxyethyl vinyl ether, and dimethylaminoethyl vinyl ether; and styrenes such as styrene, methyl styrene, dimethyl styrene, trimethyl styrene, triethyl styrene, isopropyl styrene, butyl styrene, chloromethyl styrene, methoxy styrene, butoxy styrene, acetoxy styrene, chlorostyrene, dichlorostyrene, bromostyrene, 2-methyl styrene, vinyl benzoicmethyl ester, styrenesulfonic acid, and styrenesulfinic acid.

Examples of other monomers include allyl compounds (e.g., allyl acetates), vinyl ketones (e.g., methyl vinyl ketone), vinyl heterocyclic compounds (e.g., vinylpyridine), glycidyl esters (e.g., glycidyl acrylate), unsaturated nitriles (e.g., acrylonitrile), monalkyl itaconate (e.g., monometyl itaconate), monoalkyl maleate (monomethyl maleate), vinylsulfonic acid, acryloyloxyalkylsulfonate (e.g., acryloyloxypropanesulfonate), and acrylamidoalkylsulfonate (e.g., 2-acrylamido-2-methylpropanesulfonate). These acids may be the salts of alkali metal (e.g., Na, and K) or ammonium ion.

Of these monomers, preferred comonomers in view of hydrophilic, lipophilic or copolymerization property of the monomer, the color developing property of coupler formed, oil pKa′, and the tone of dye formed, include acroyloxyalkylsulfonate, methacryloy-loxyalkylsulfonate, acrylamidoalkylsulfonate, methacryl-amidoalkylsulfonate, and the alkali metal or ammonium salts of these acids.

Of these monomers, monomers that are highly hydrophilic are particularly preferable. Two or more of these monomers may be combined. Examples of combinations thereof include potassium styrenesulfinate/sodium acrylamide-2-methylpropanesulfonate, acetoacetoxyethyl methacrylate/sodium 3-acryloylpropanesulfonate, potassium styrenesulfinate/butyl acrylate/sodium styrenesulfonate, and potassium styrensulfonate/sodium acryloyloxypropane sulfonate.

Although it is desired that the proportion of the color-forming moiety corresponding to formula (I) in the polymer couplers of the present invention (in terms of the total of those corresponding to formula (I) and (II) and, ethylenically-unsaturated comonomer unit other than those of formula (I) and (II) if contained) is usually 5 to 80 wt. %, in view of the color reproduction, the color formation, and the stability, this proportion is preferably 20 to 70 wt. %. It is preferable that the proportion of the part (monomer unit) corresponding to formula (II) in the polymer couplers of the present invention is 95 to 20 wt.%, more preferably 2 to 30 wt.%. In this case, the molecular weight equivalent (the gram of a polymer containing 1 mol of a monomer coupler) is about 250 to 4000, but it is not limited to that.

The polymer coupler of the present invention is added to an amount of 0.005 to 0.5 mol, preferably 0.01 to 0.1 mol per mol of silver, into a silver halide emulsion layer in terms of the coupler monomer unit represented by formula (I).

It is preferable that the molecular weight of the polymer coupler of the present invention is 5×10^3 to 1×10^7. If the molecular weight is too low, the polymer moves easily, whereas if the molecular weight is too high, difficulty will sometimes arise in the coating process. More preferably the molecular weight is 1×10^4 to 2×10^6.

The synthesis of the water-soluble couplers of the present invention may be effected by using, as a polymerization initiator and a polymerization solvent, compounds described in Japanese Patent Application (OPI) Nos. 120252/1983, 145944/1983, 211756/1983, 224352/1983, 42543/1984, 17156/1984, 228252/1984, 35732/1985 and 46555/1985.

The water-soluble polymer couplers used in this invention can be synthesized by a solution polymerization method. As the solvent for polymerization, it is preferable such a solvent as having low coefficient value of chain transfer to a radical not reacting with a polymerization initiator. Examples of such solvent, which may be used by mixing two or more, include water, toluene, alcohols (e.g., methanol, ethanol, isopropyl alcohol, and t-butanol), tetrahydrofuran, dioxane, ethyl acetate, dimethylformamide, dimethylacetoamide, and dimethylsulfoxide.

It is necessary to set the polymerization temperature in association with the molecular weight of the polymer that will be produced, the type of the initiator, and so on, and although polymerization may be carried out in the range of up to 0°C or down to 100°C, generally it is carried out in the range of 30 to 100°C.

As the water-soluble polymerization initiator, for example, salts of persulfuric acid such as polassium persulfate, ammonium persulfate, sodium persulfate; water soluble azo compounds such as sodium 4,4′-azobis-4-cyanovalerate, and 2,2′-azobis(2-amidinopropane) hydrochloride; and hydrogen peroxide can be used. As the lipophilic polymerization initiator, it can be mentioned, for example, lipophilic azo compounds such as azobisisobutylonitrile, 2,2′-azobis-(2,4-dimethylvaleronitrile), 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile), dimethyl 2,2′-azobisisobutyrate, and 4,4′-azobis-4-cyanovalerate; and lipophilic peroxides such as benzoyl peroxide, lauryl peroxide, chlorobenzyl peroxide, diisopropyl peroxydicarbonate, and di-t-butyl peroxide. Of these, benzoyl peroxide, chlorobenzyl peroxide, and lauryl peroxide are preferable.

These polymerization initiators can be used in an amount of the range of 0.01 to 10 wt.%, preferably 0.1 to 5 wt.% to total amount of monomers.

The term "water-soluble" in this specification and claims means that the obtained polymer coupler will dissolve into water in an amount of 1.0 wt. % or more. In view of production it is preferable that the obtained polymer coupler dissolve into water in an amount of 10 wt. % or more.

It is possible that the polymer coupler can be added as an aqueous solution into a coating fluid, or that it can be dissolved in a solvent mixture of water and an organic solvent miscible with water, such as lower alcohols, THF, acetone, and ethyl acetate, and then added to a coating fluid.

Further, the polymer coupler can be dissolved in an aqueous alkali solution or an aqueous-alkali-containing organic solvent mixture and then added to a coating fluid. It is also possible to add a small quantity of a surface-active agent.

In any case, it is considered that the water-soluble polymer coupler of the present invention would not take the form of oil droplets or a latex in the coating fluid or in the coating film, but would interact with the hydrophilic binder, thereby each to some degree solubilizing the other.

Therefore, it is considered that the film strength exhibits excellent performance in comparison with oil-soluble (with latex type inclusive) polymer couplers.

Compound examples of the water-soluble polymer couplers of the present invention are shown below, but the invention is not limited to them.

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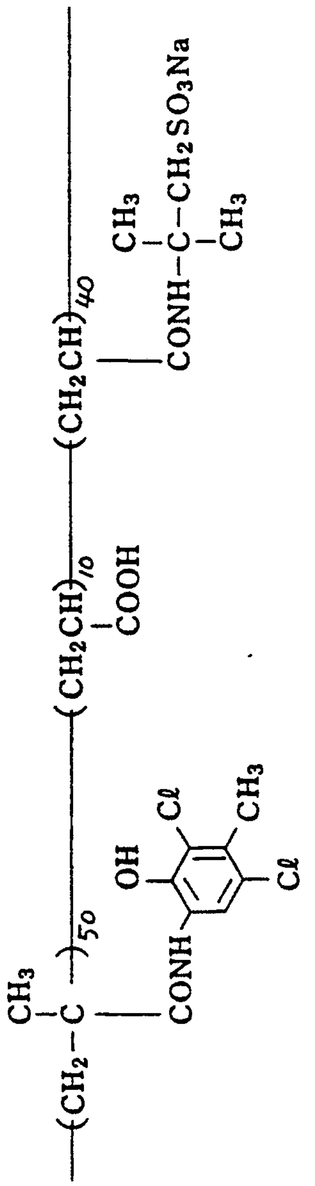

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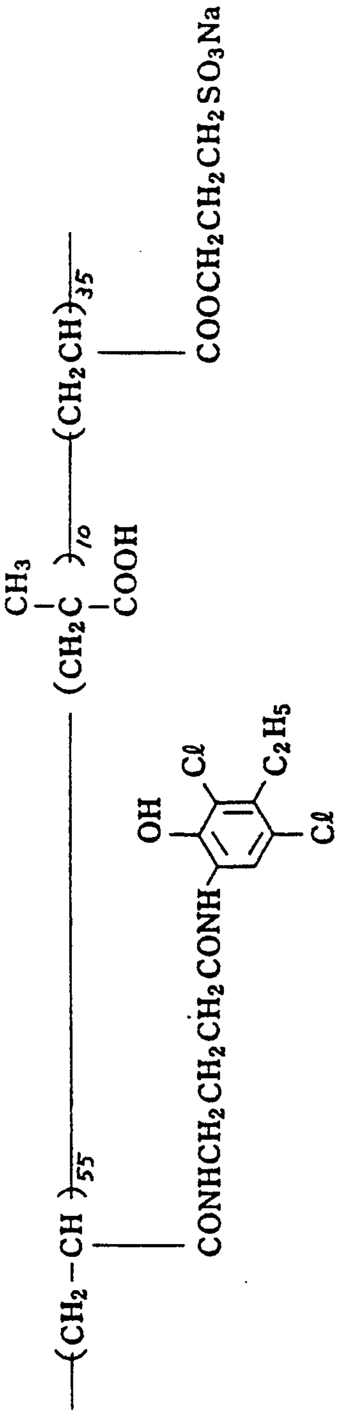

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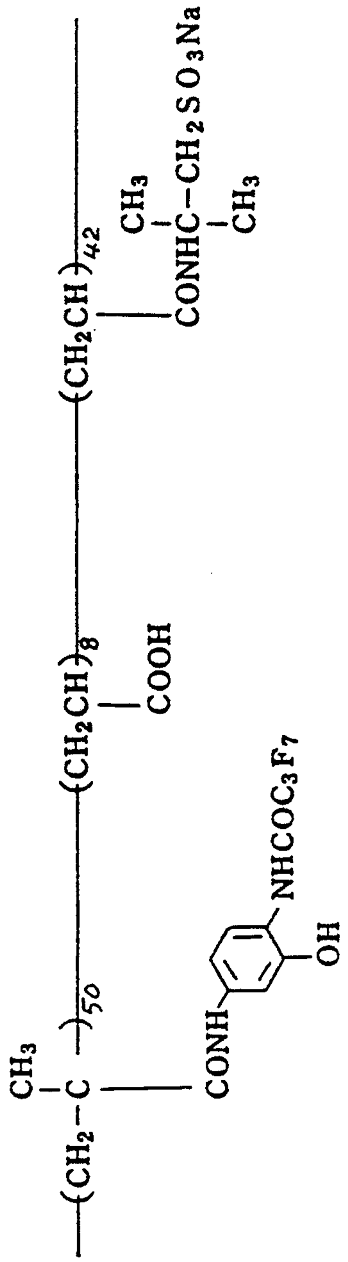

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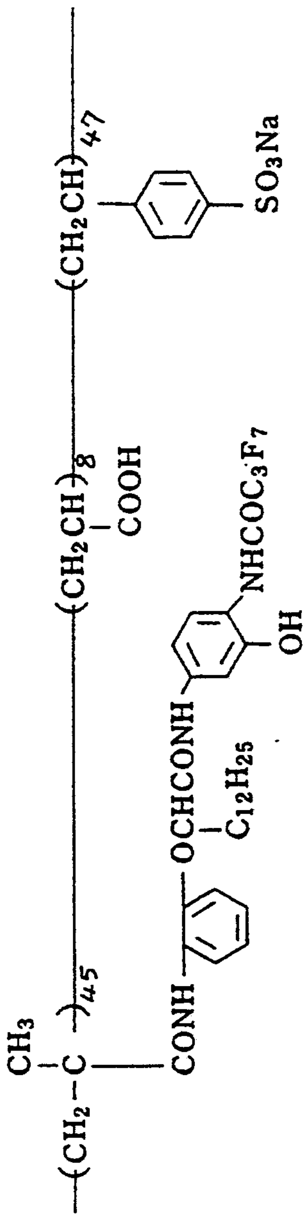

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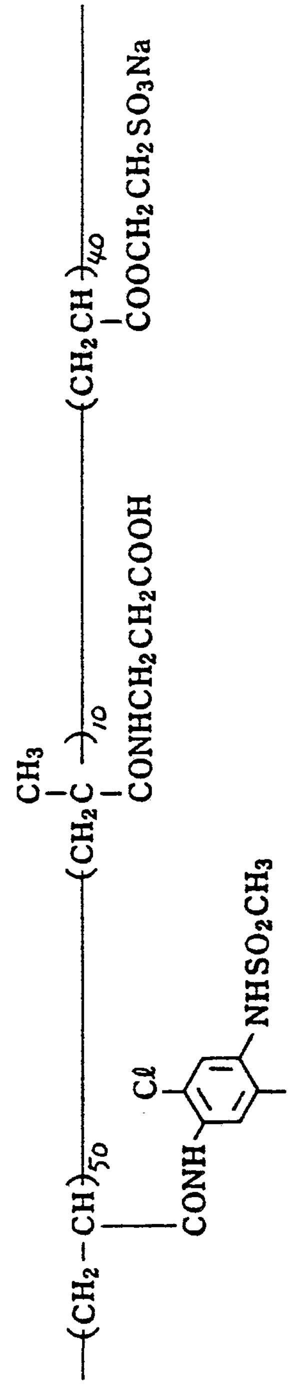

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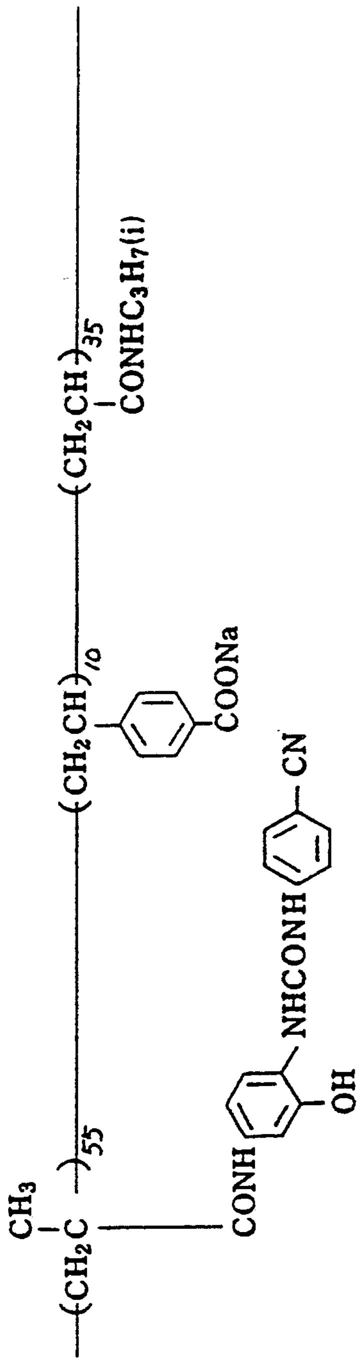

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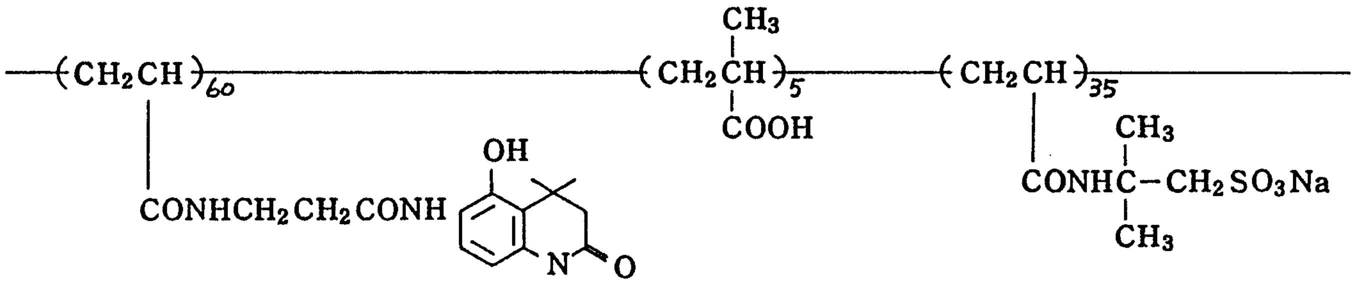

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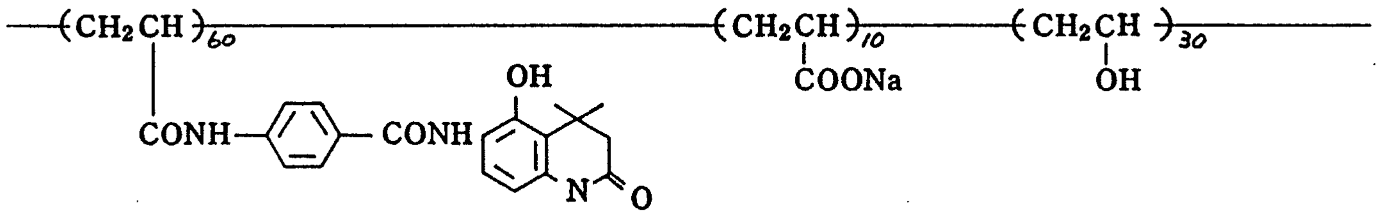

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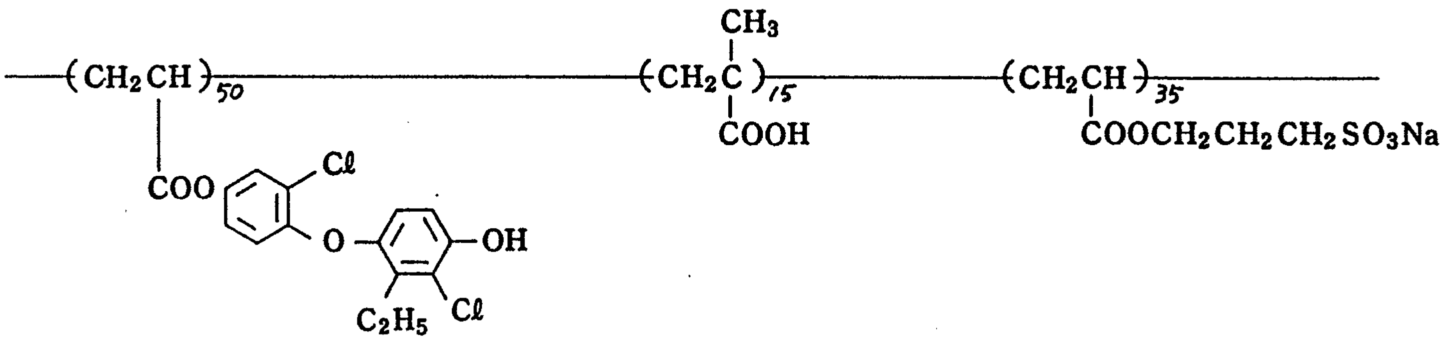

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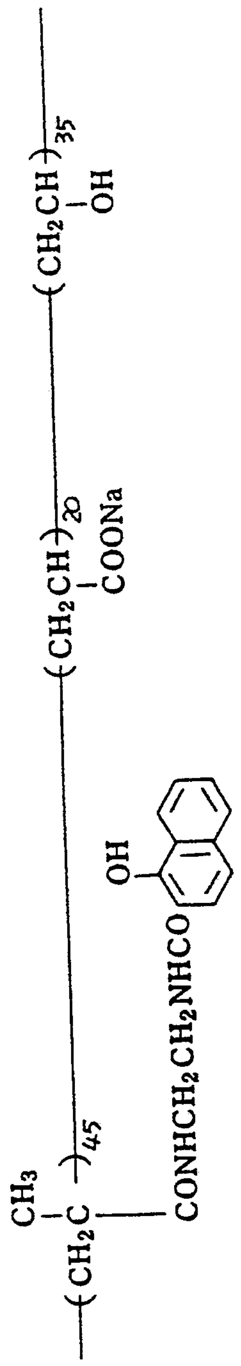

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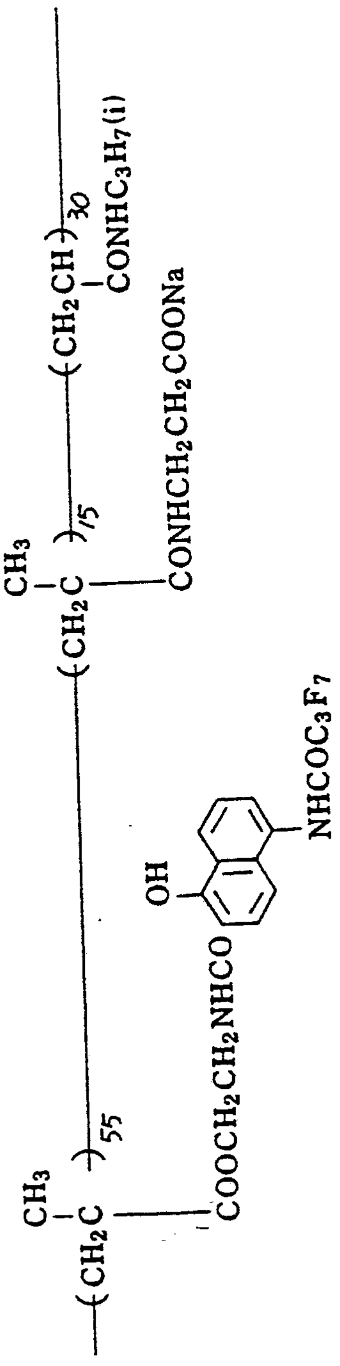

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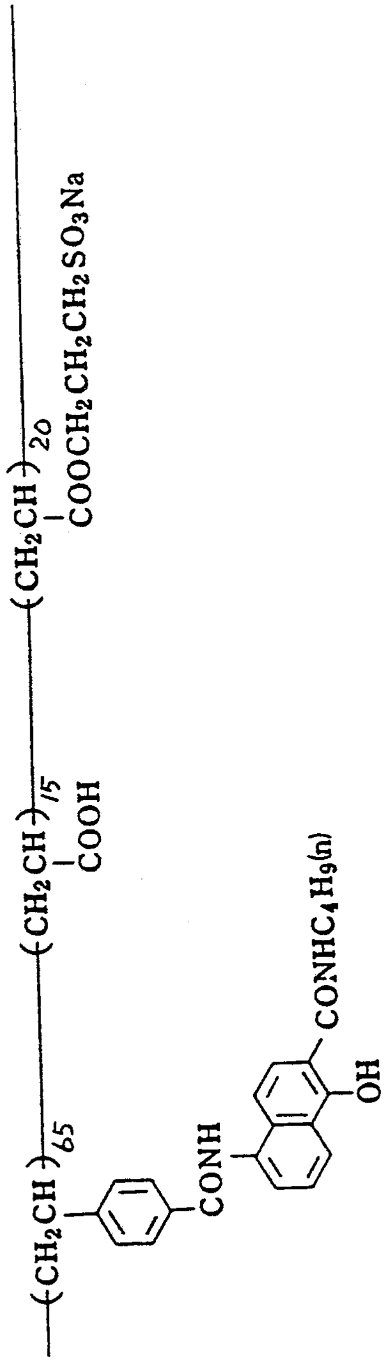

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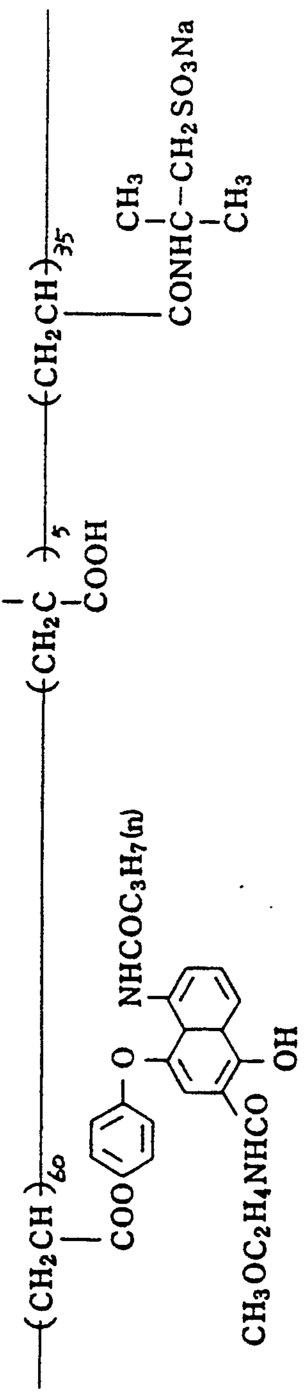

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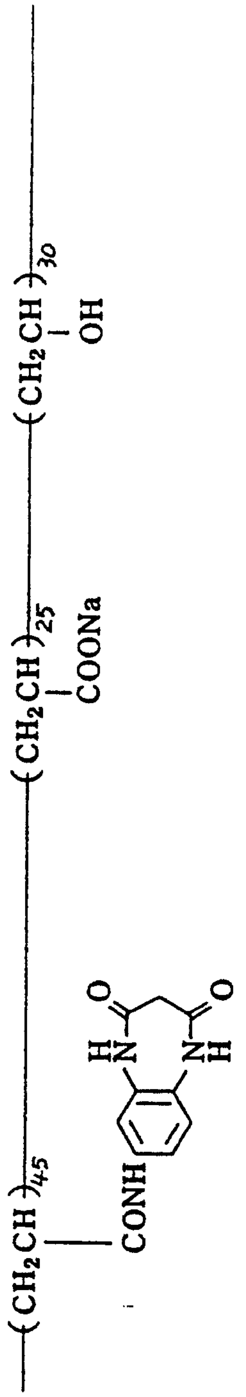

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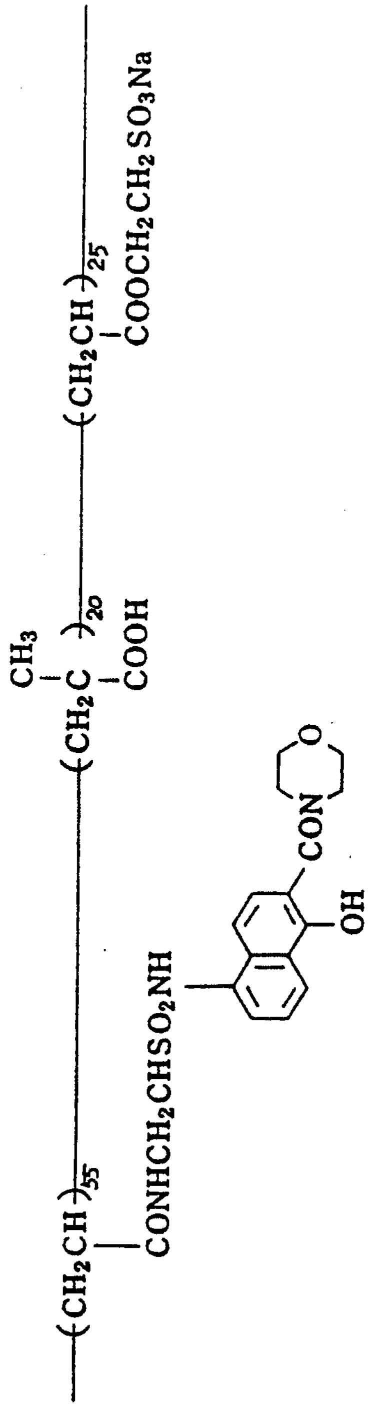

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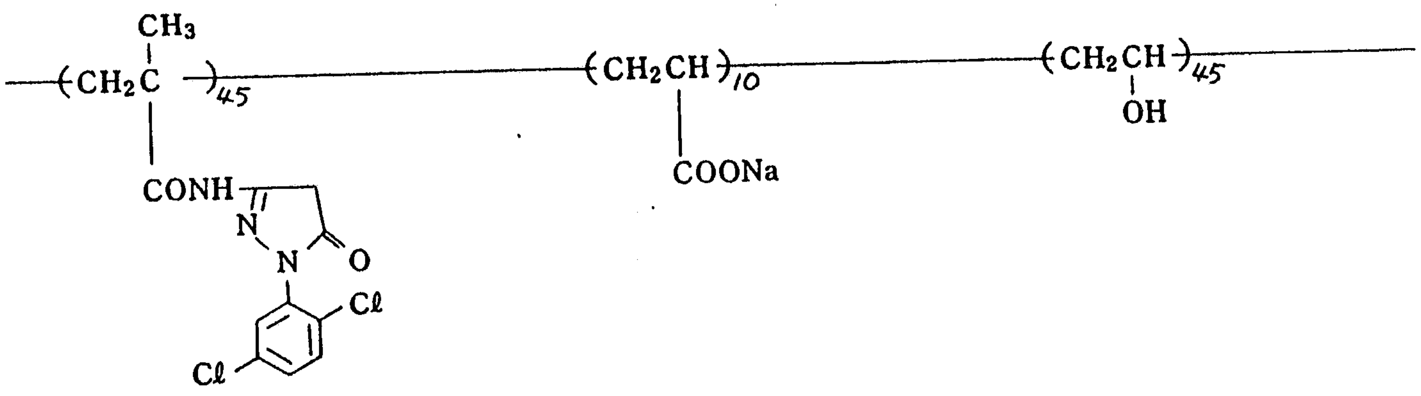

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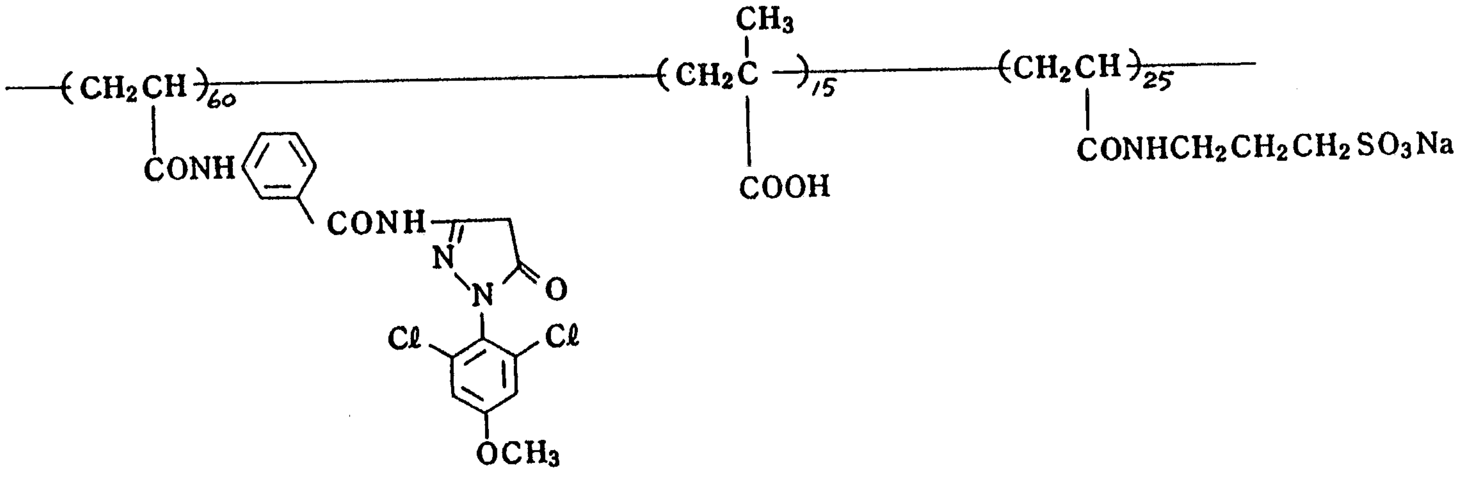

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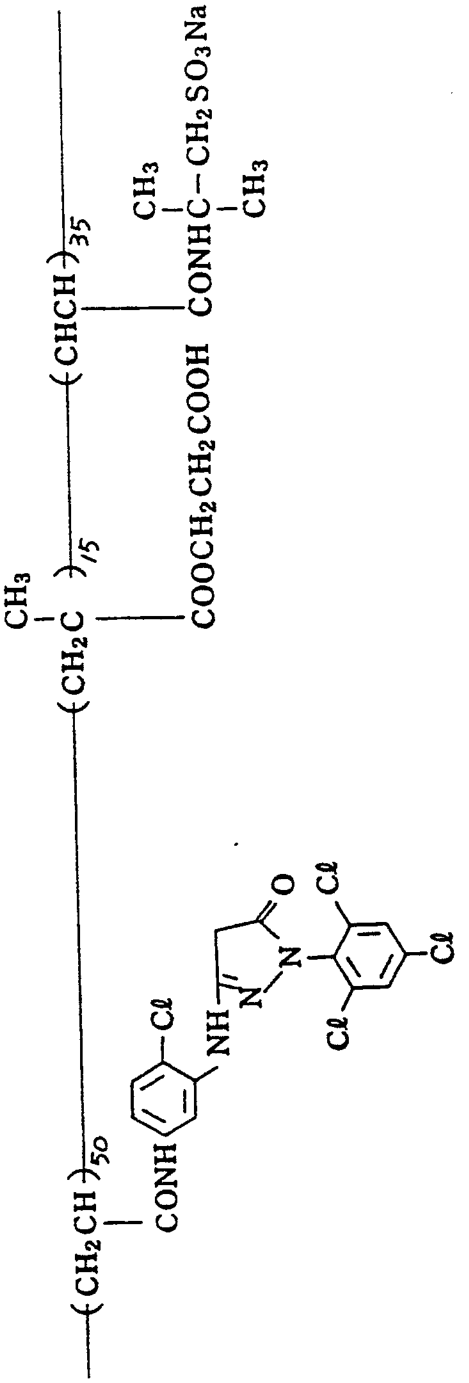

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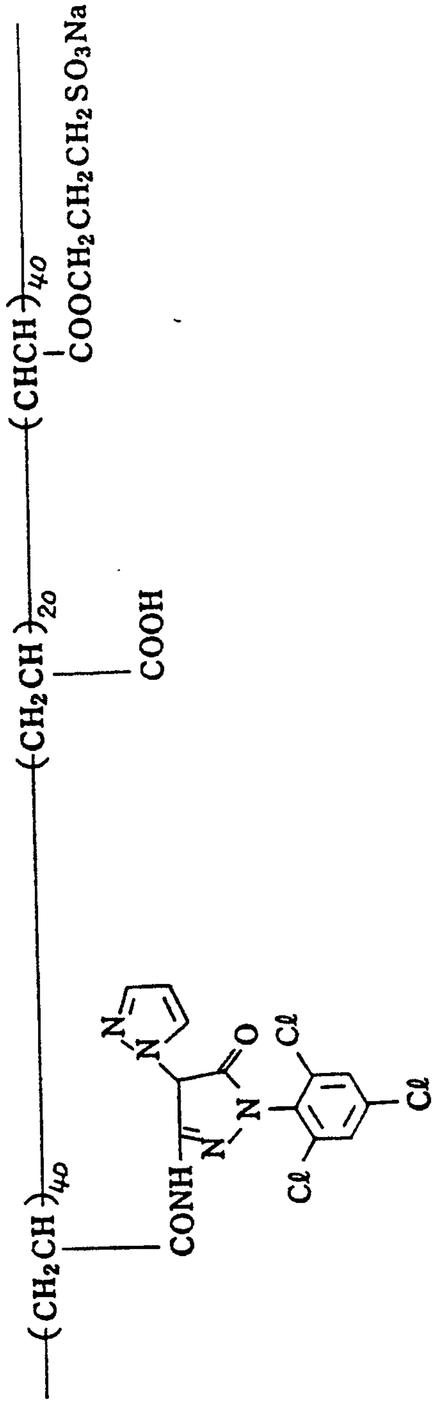

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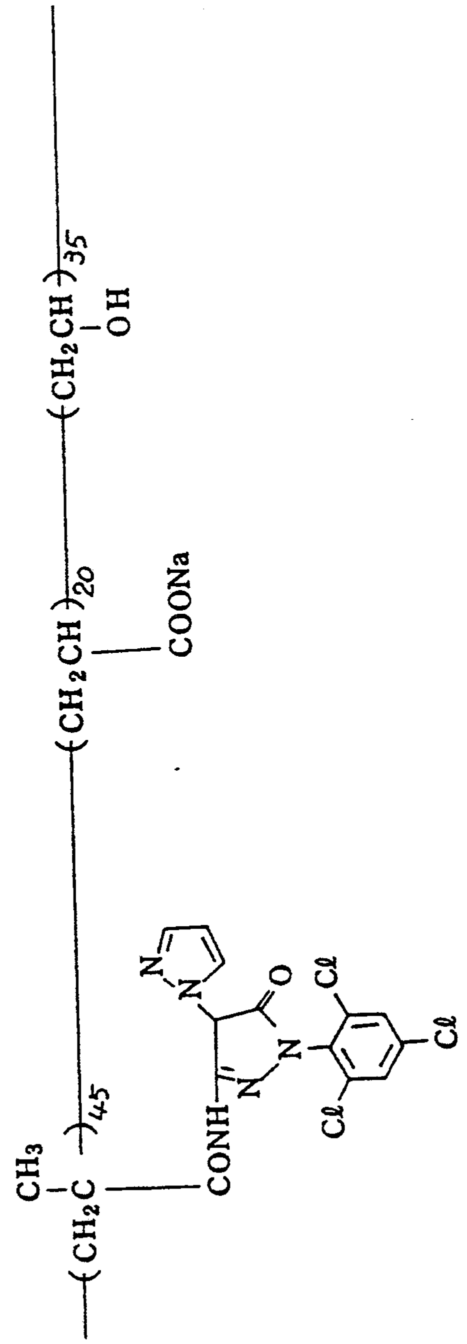

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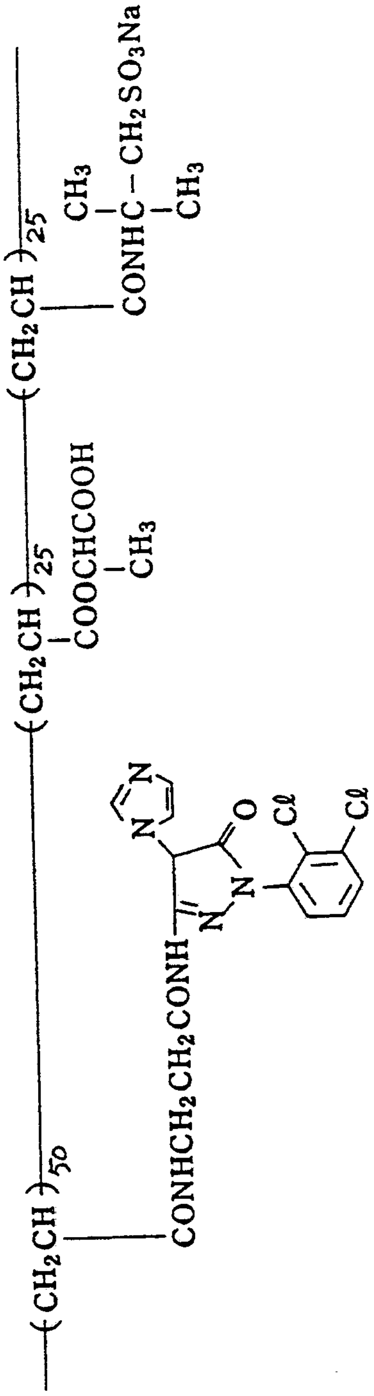

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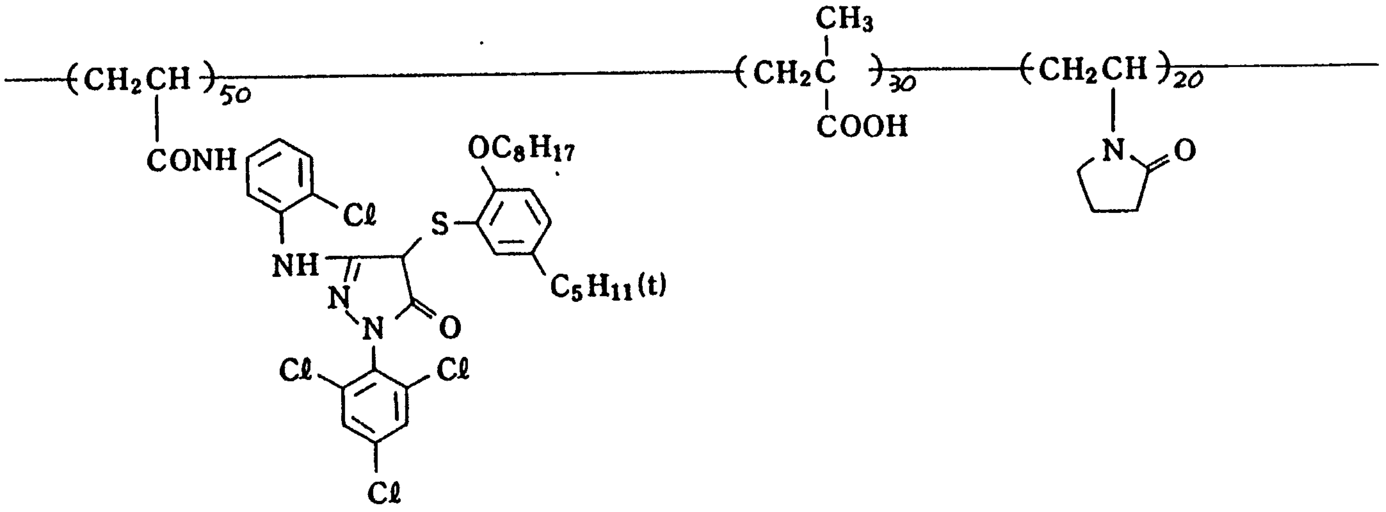

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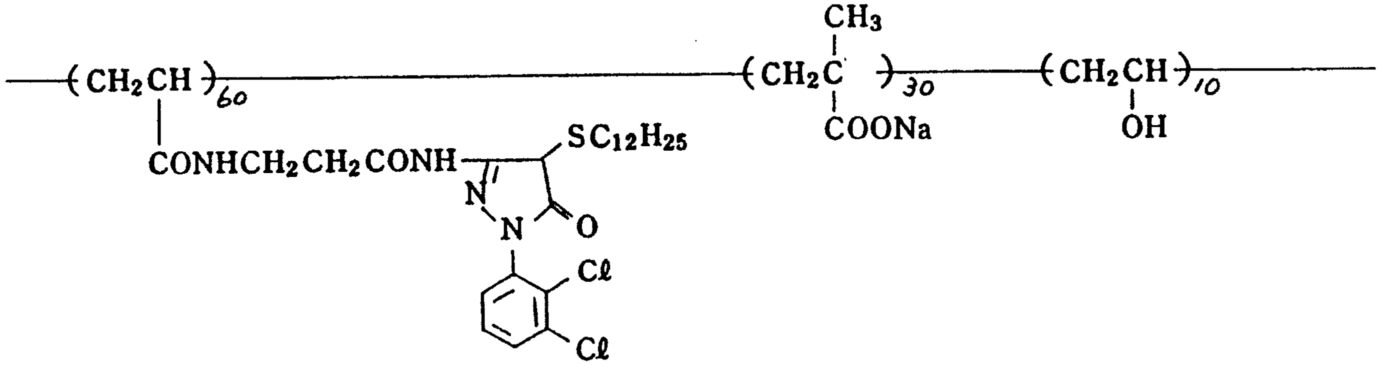

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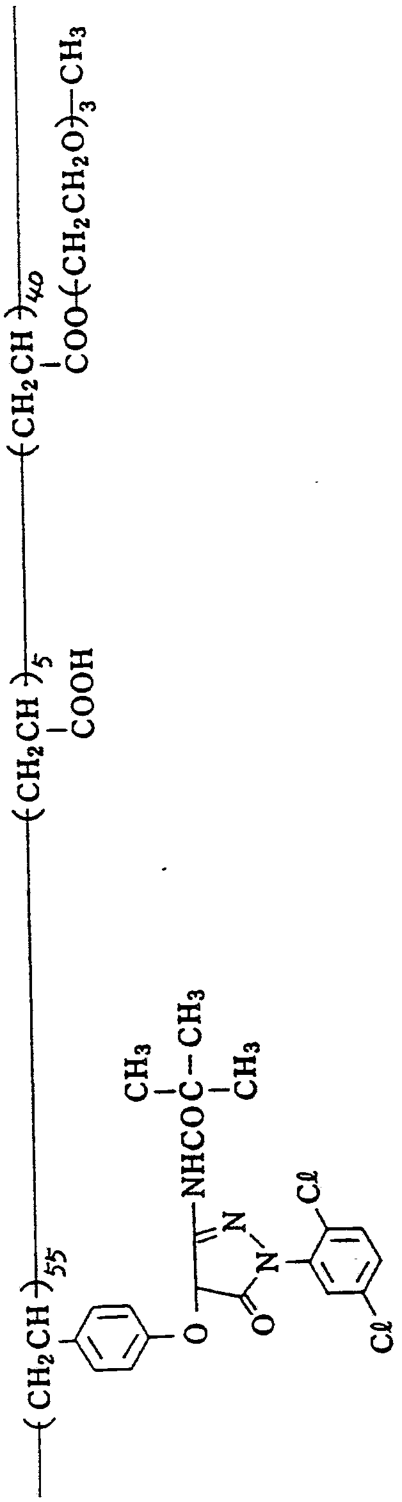

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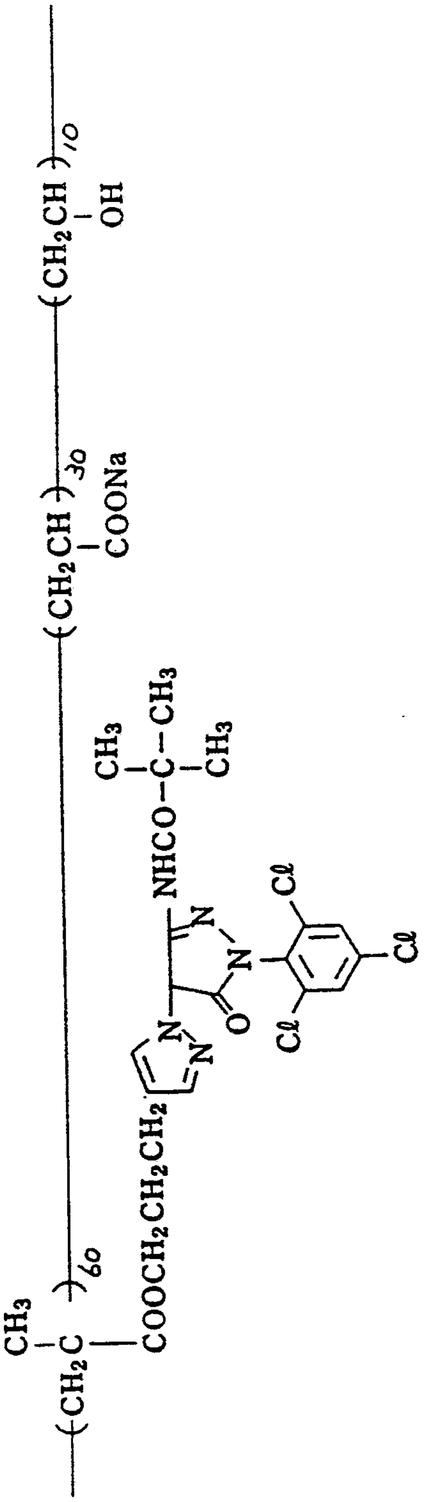

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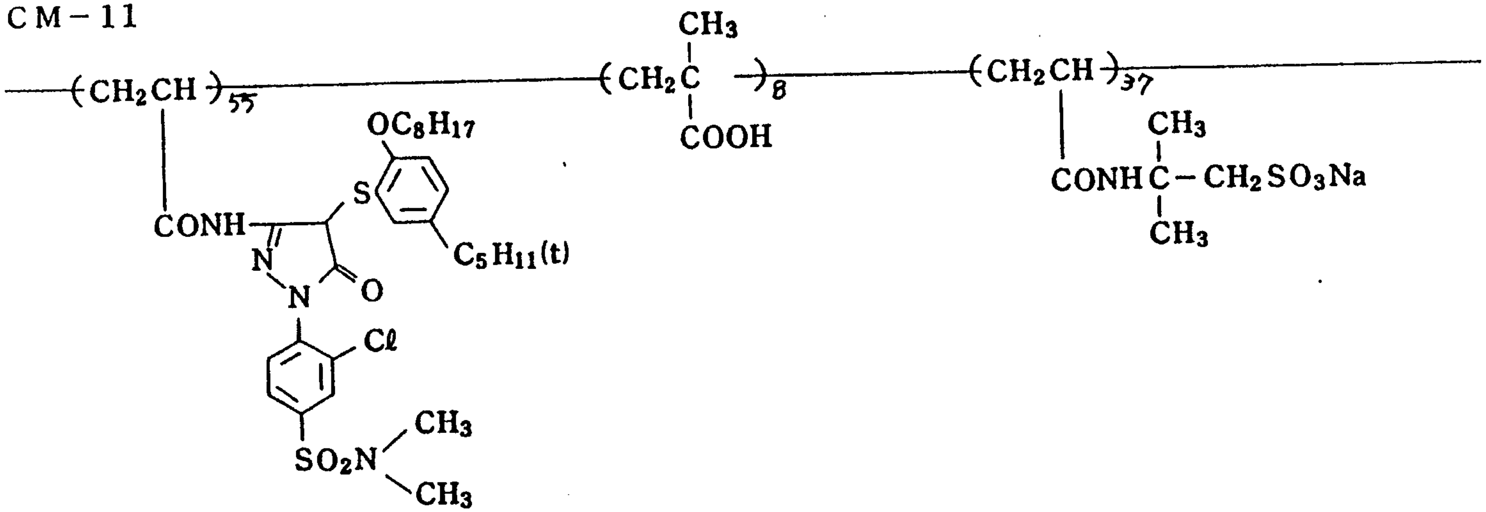

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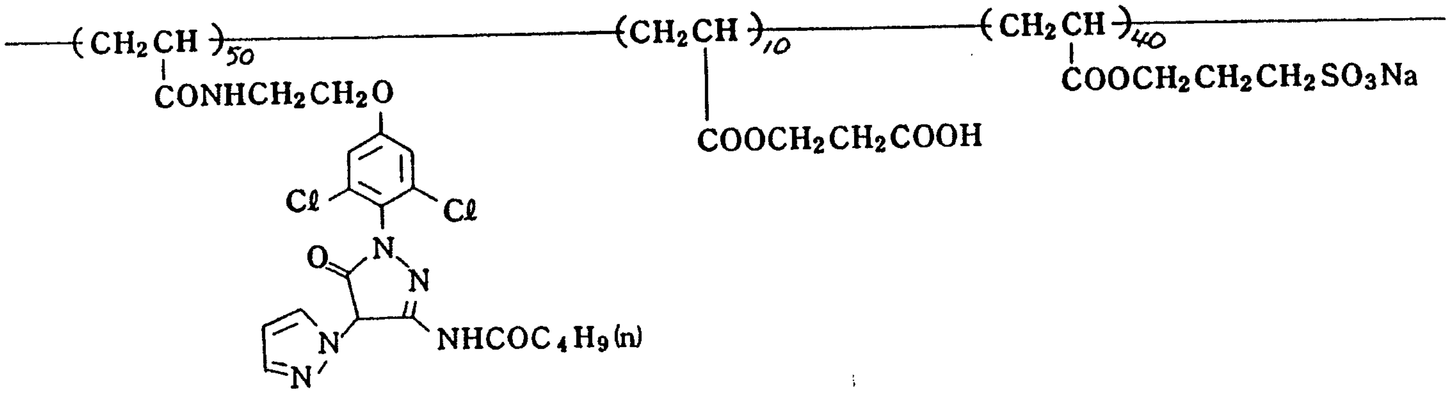

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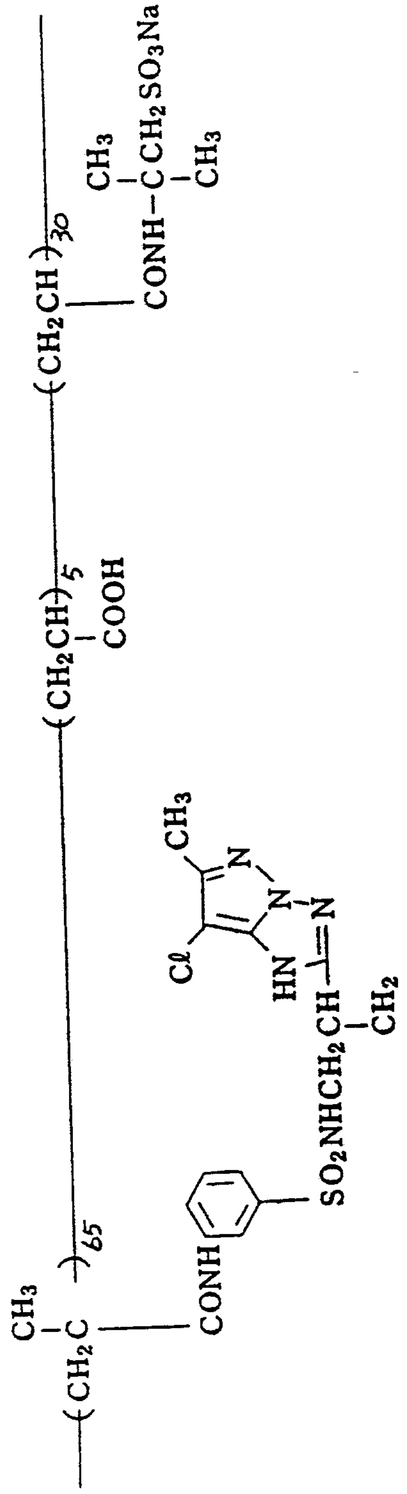

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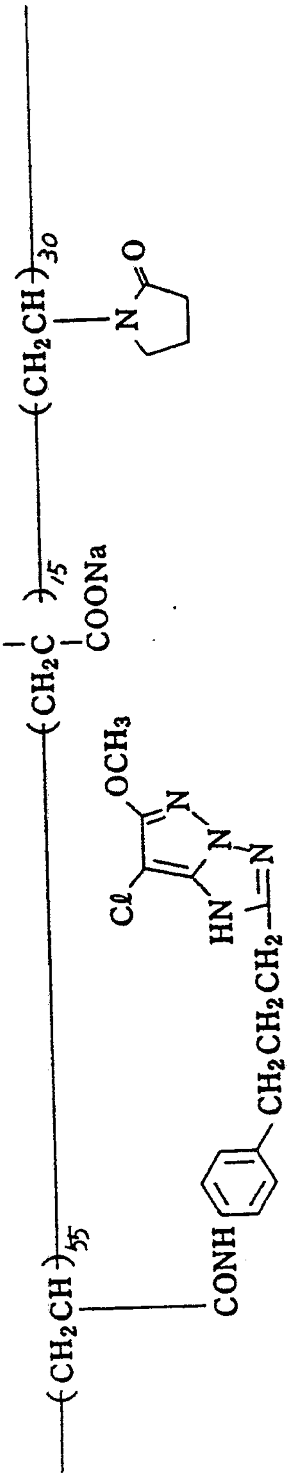

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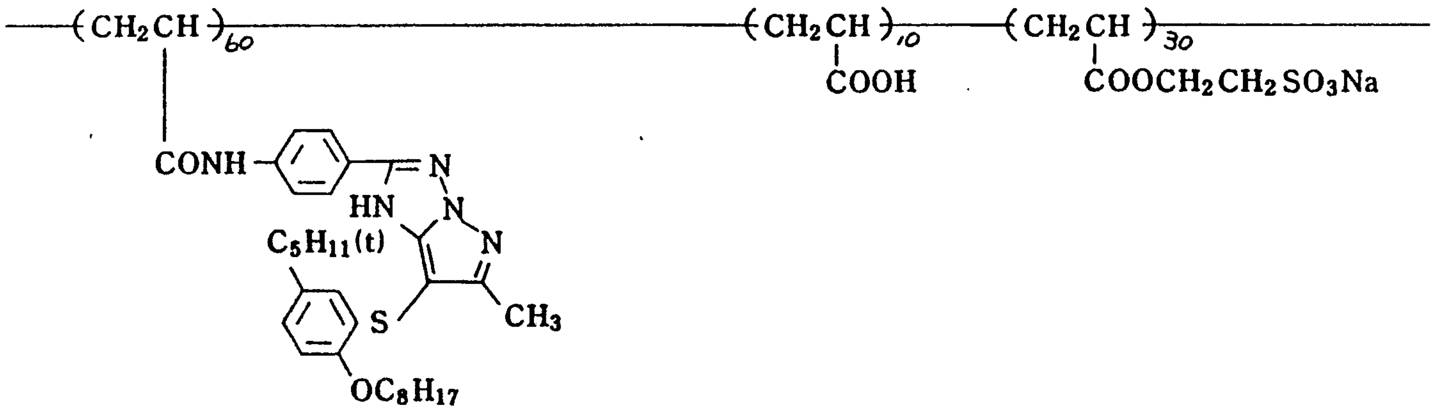

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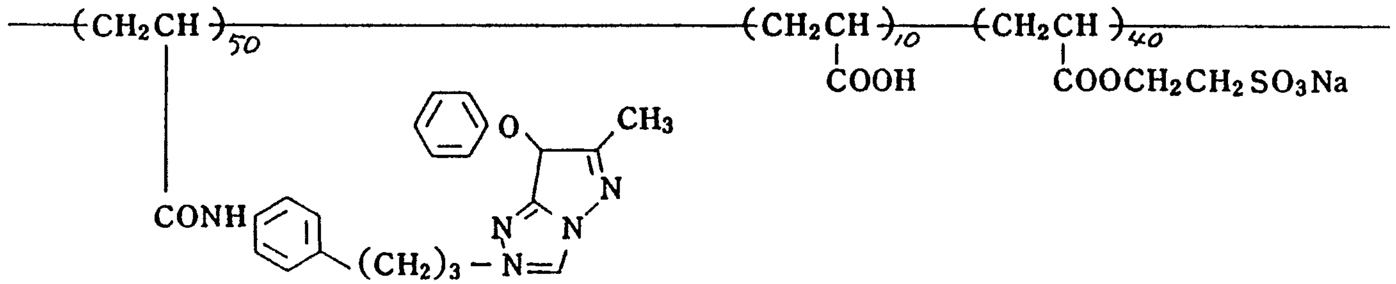

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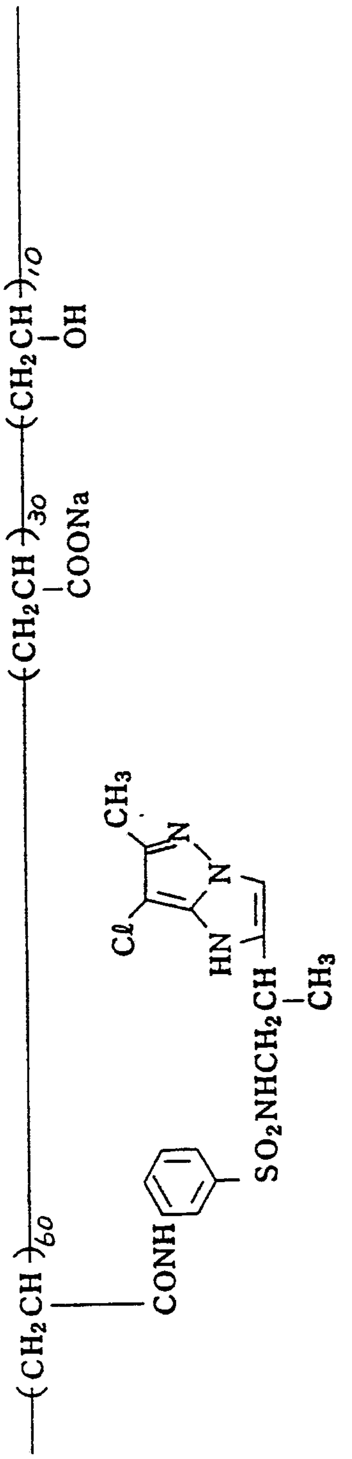

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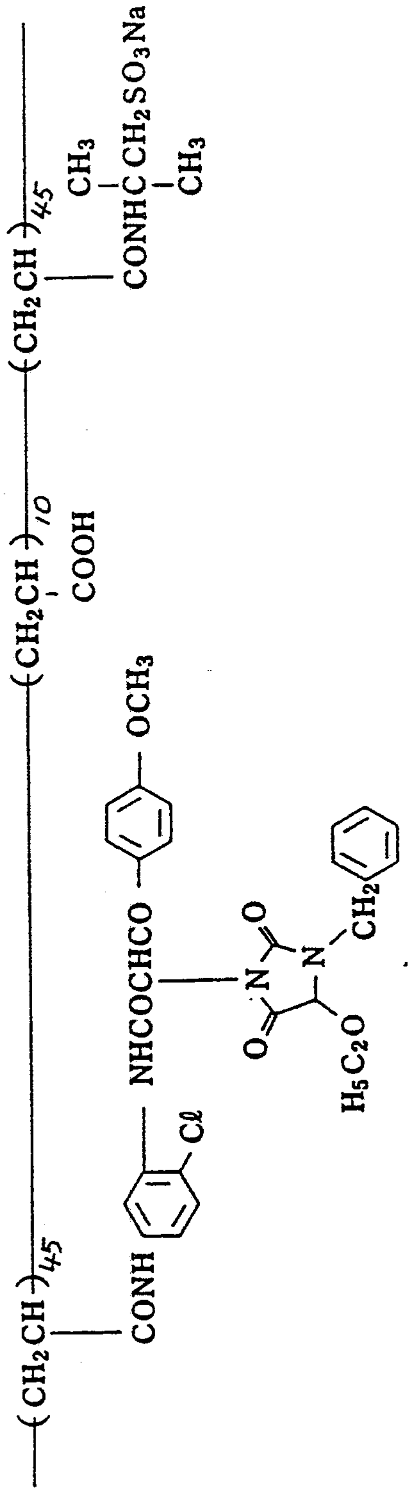

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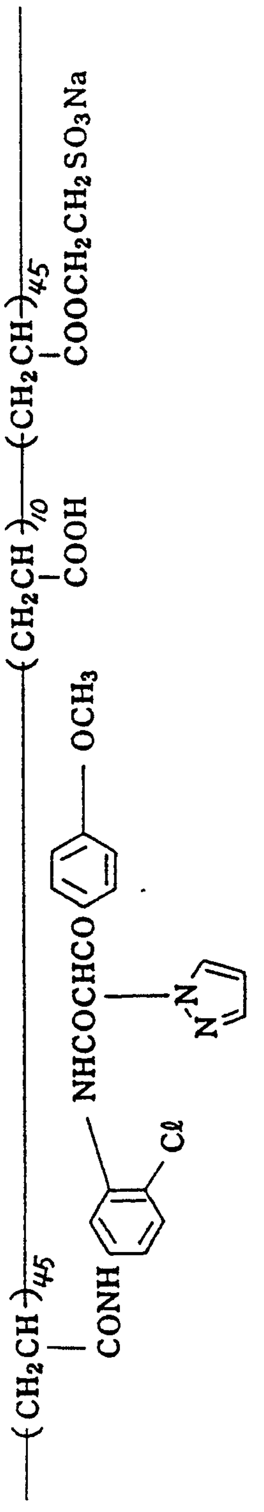

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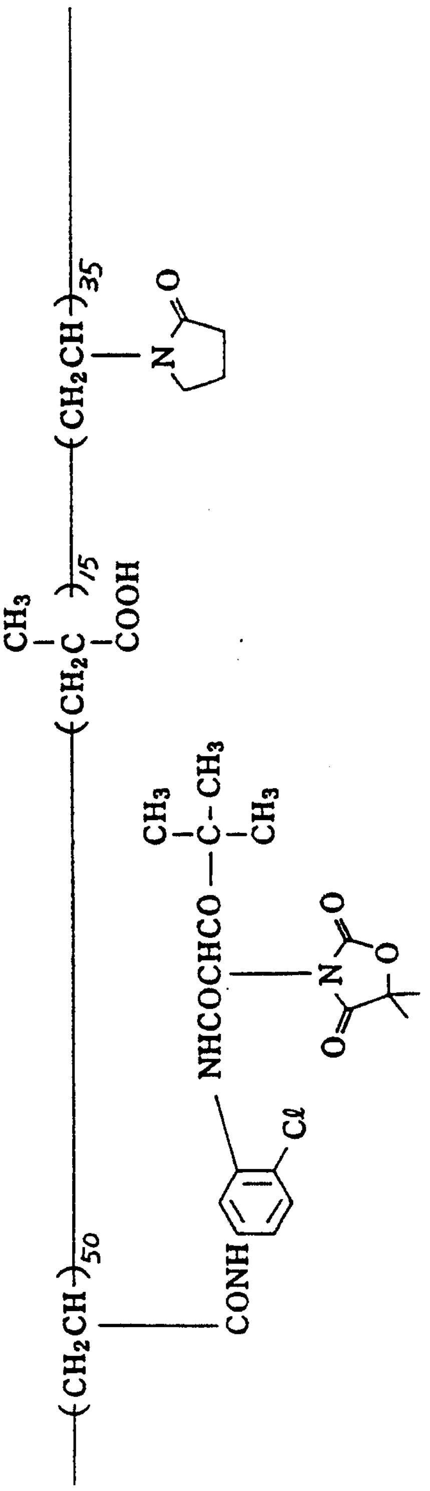

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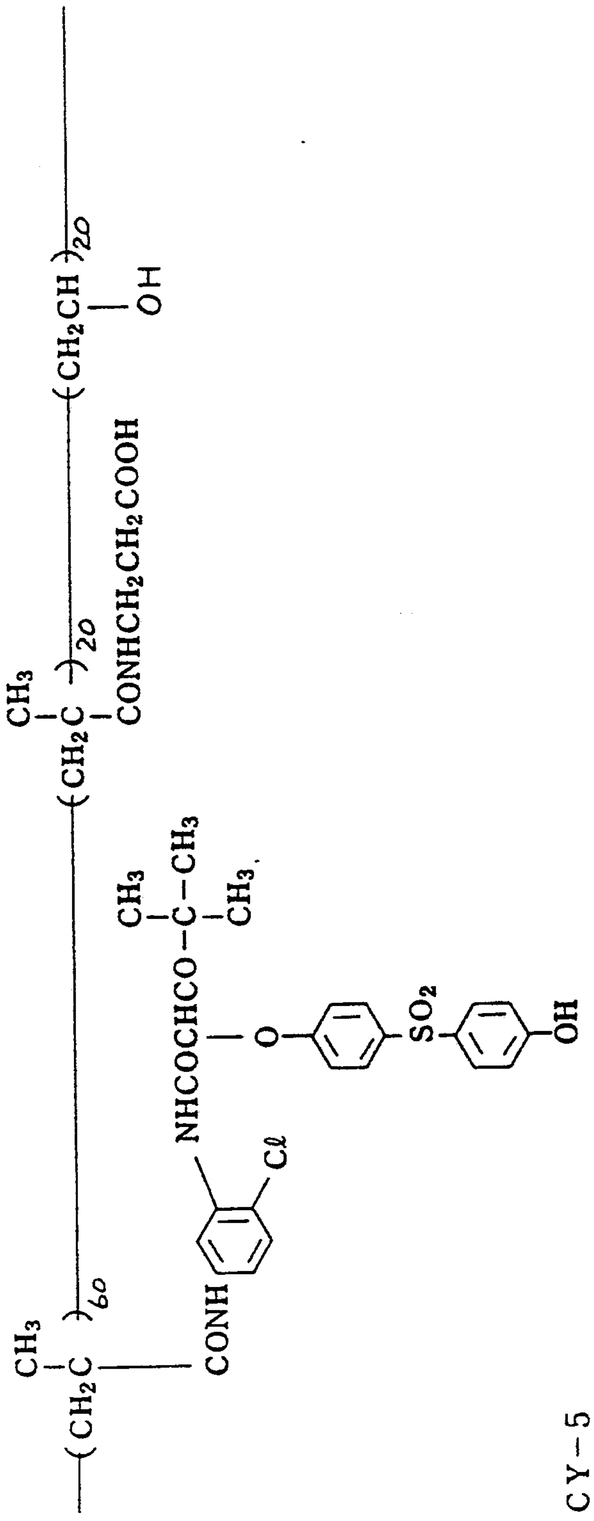

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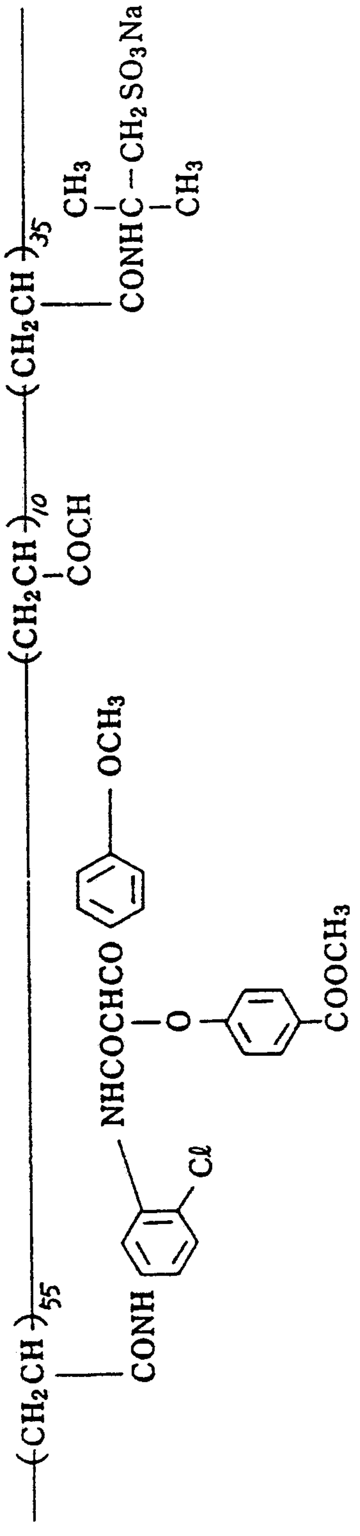

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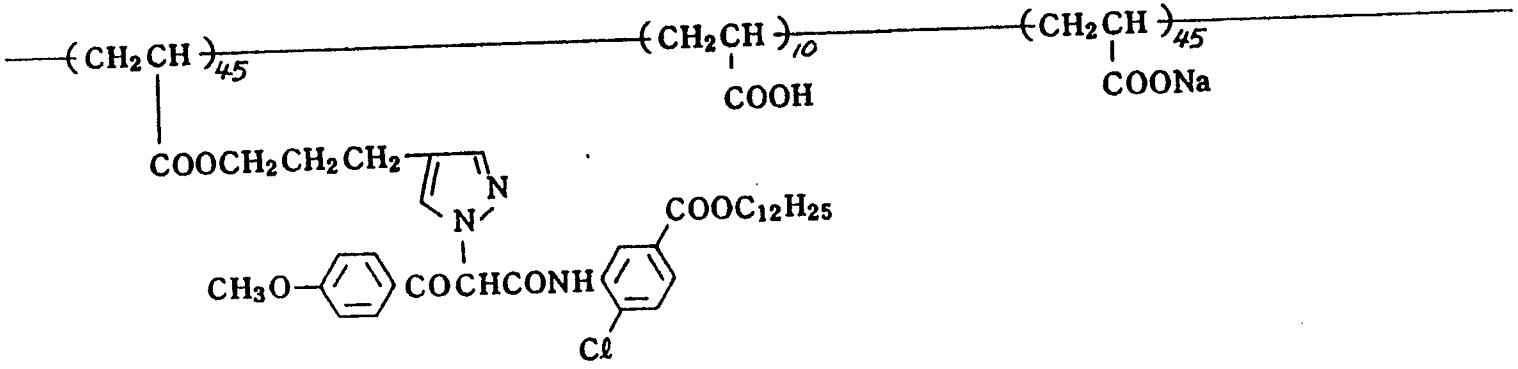

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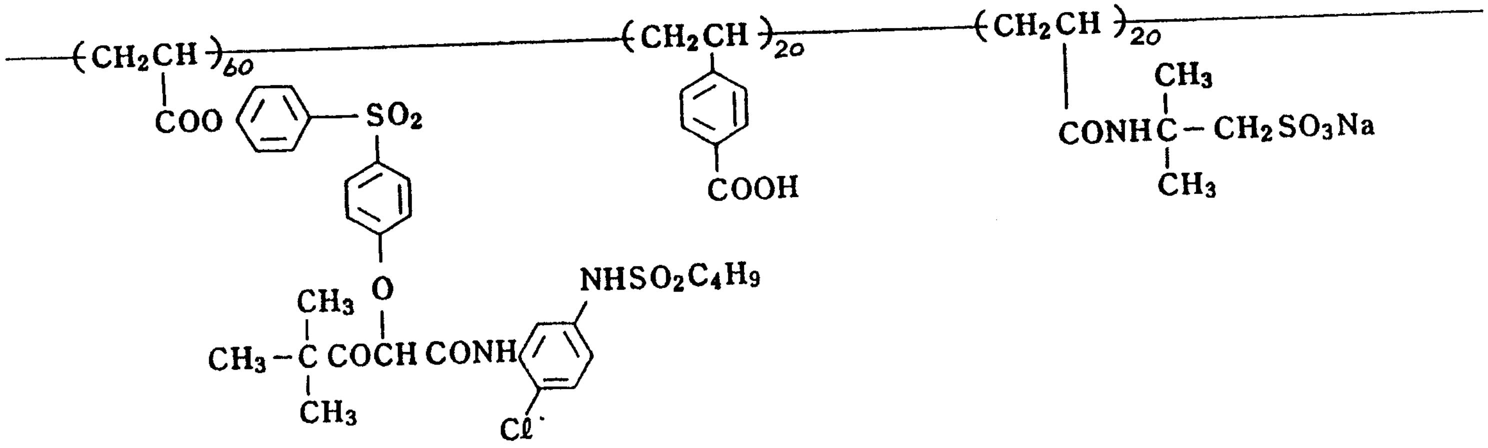

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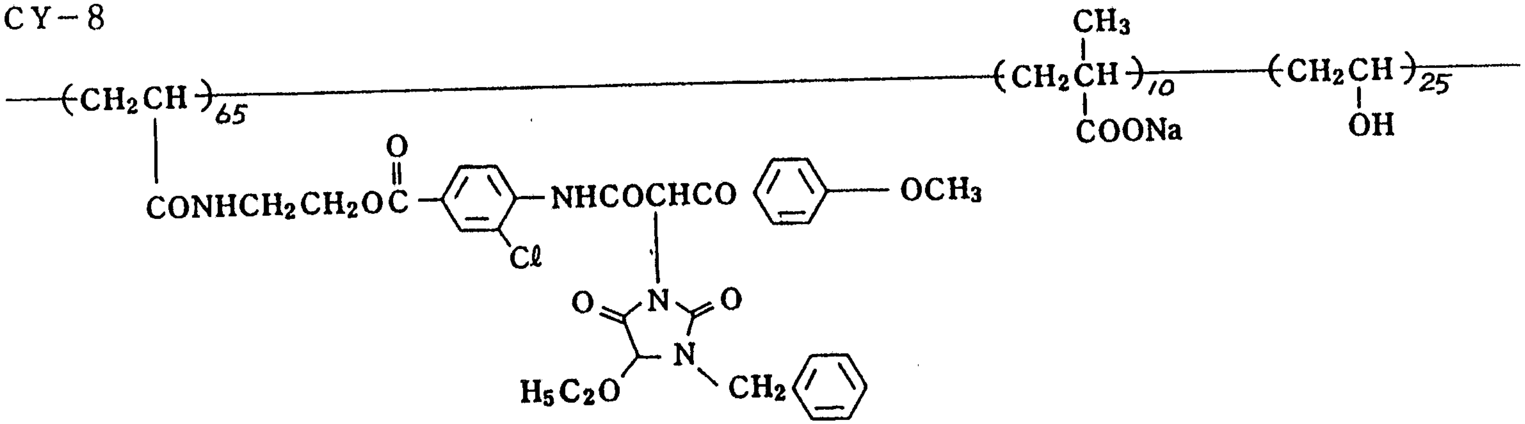

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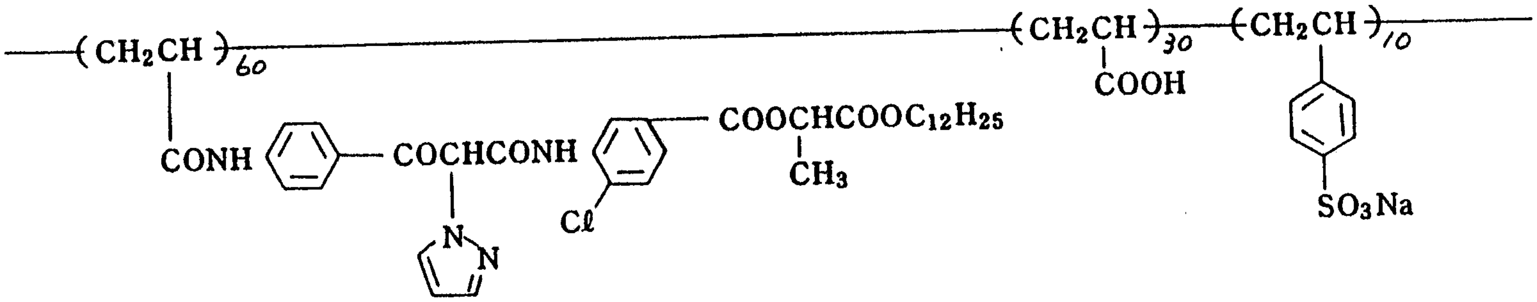

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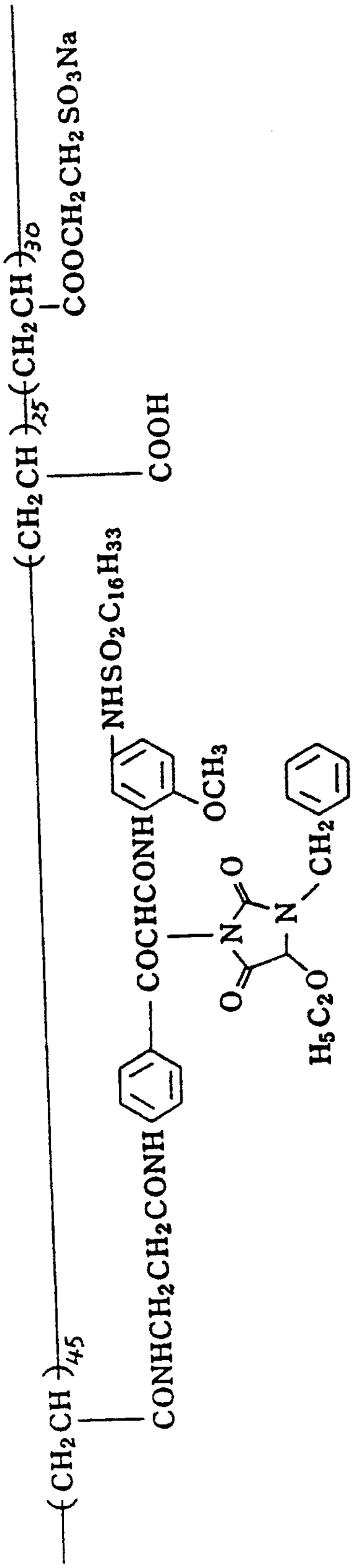

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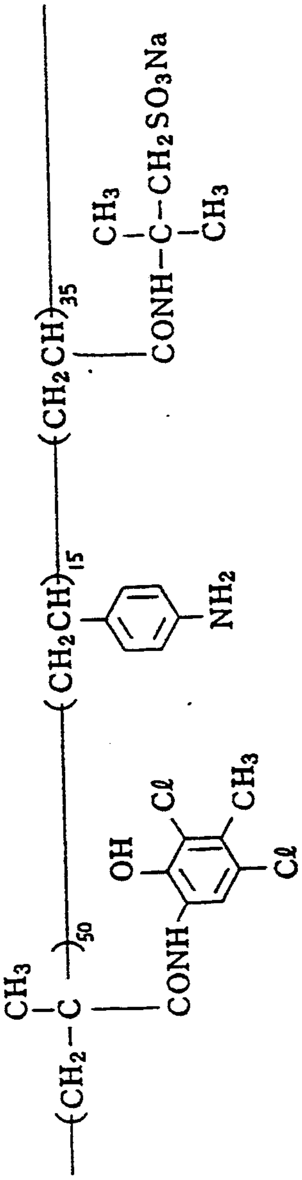

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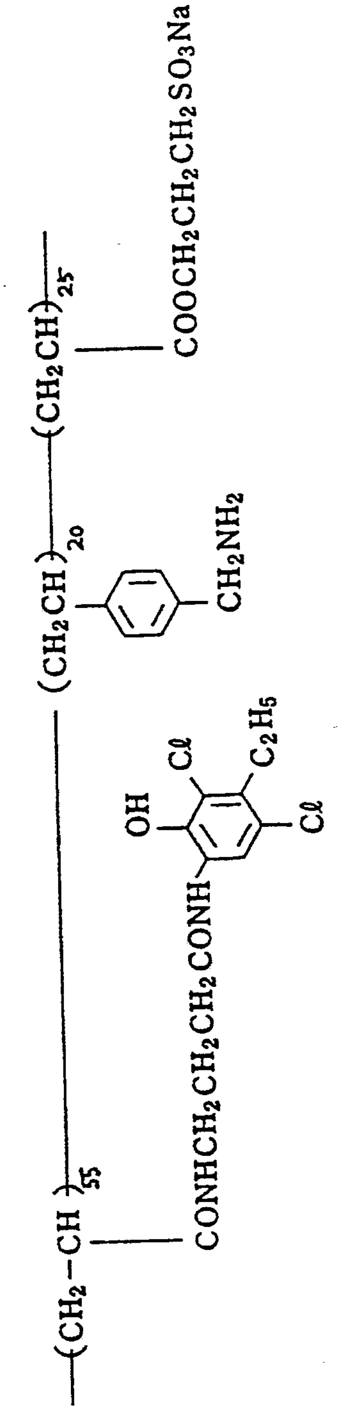

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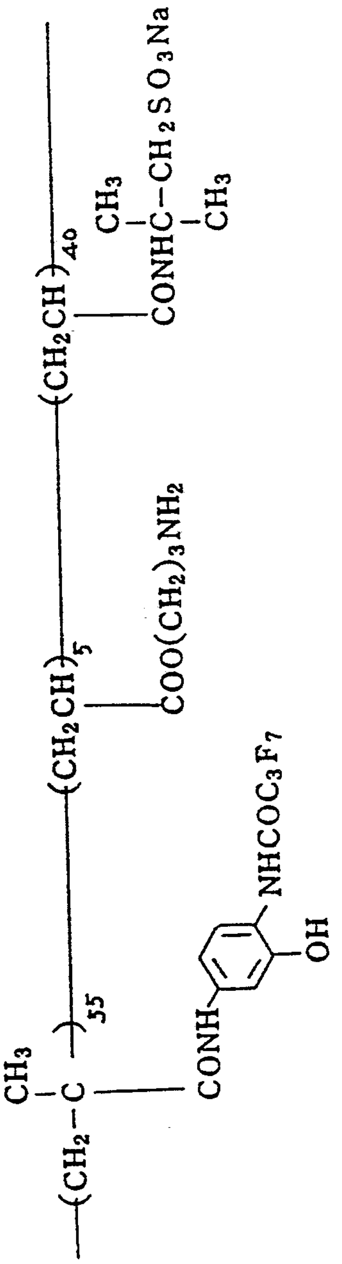

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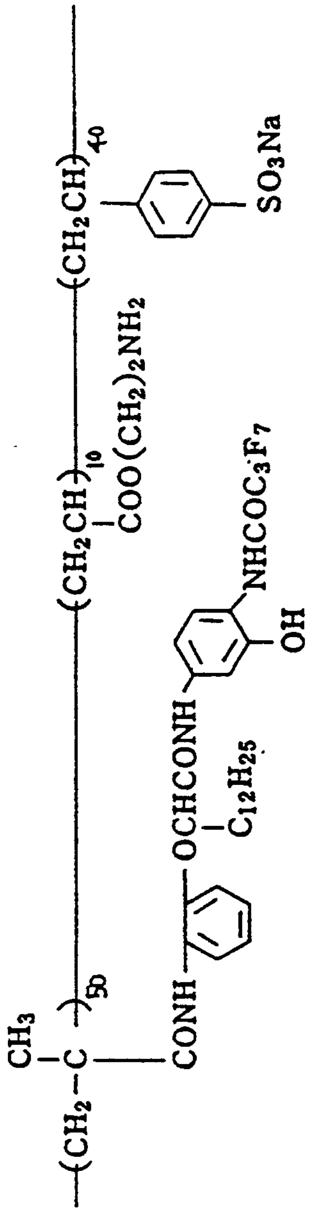

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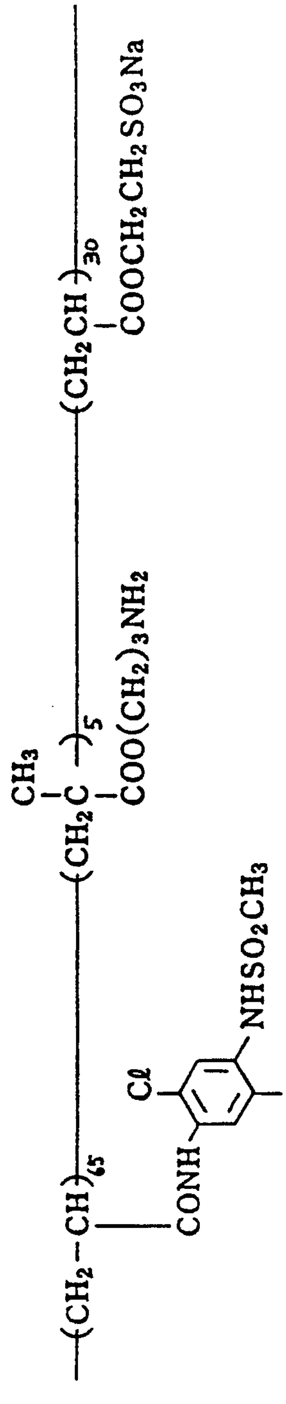

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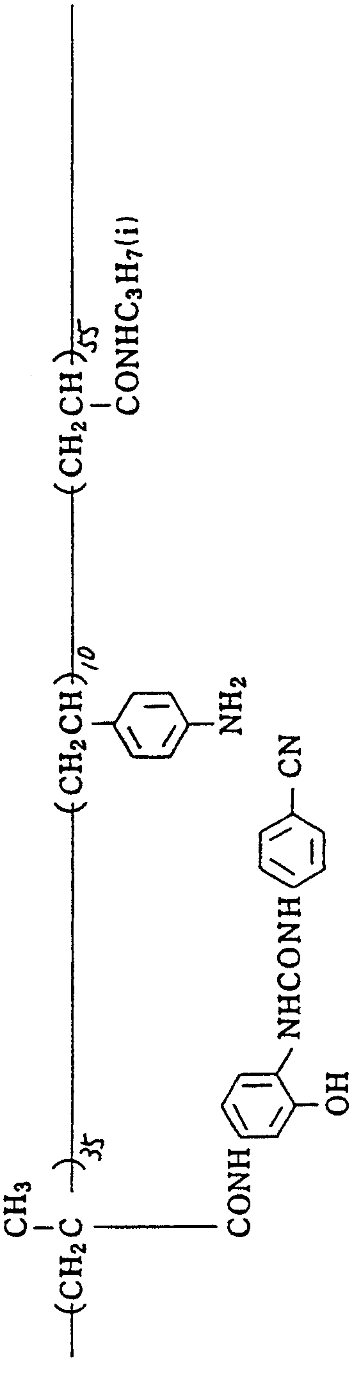

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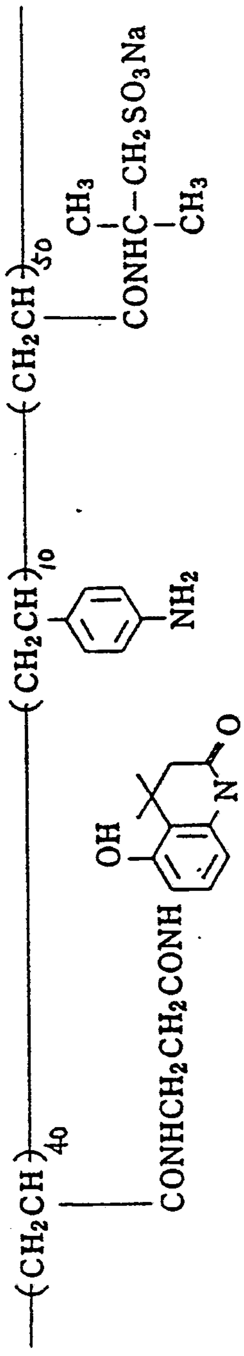

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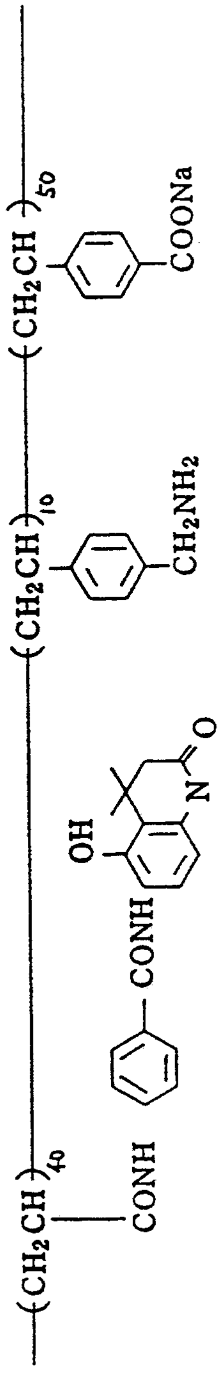

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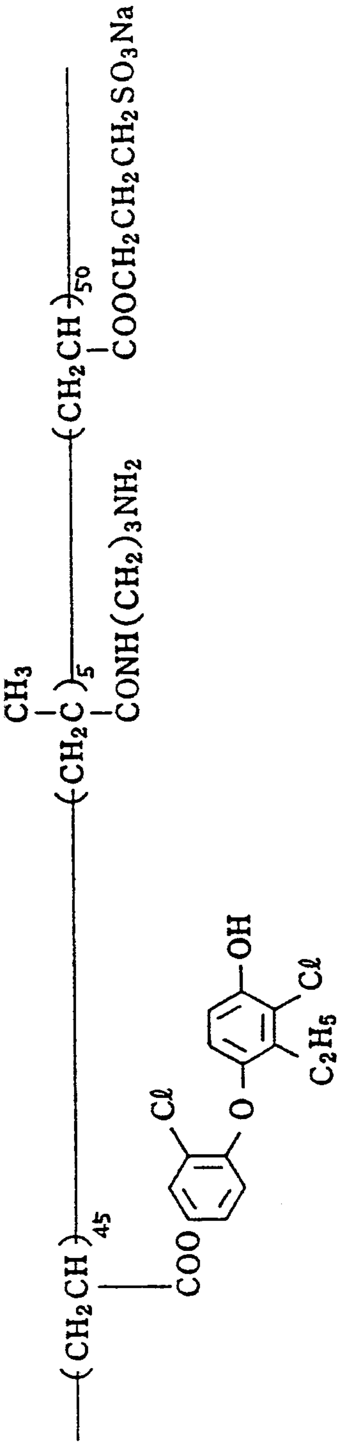

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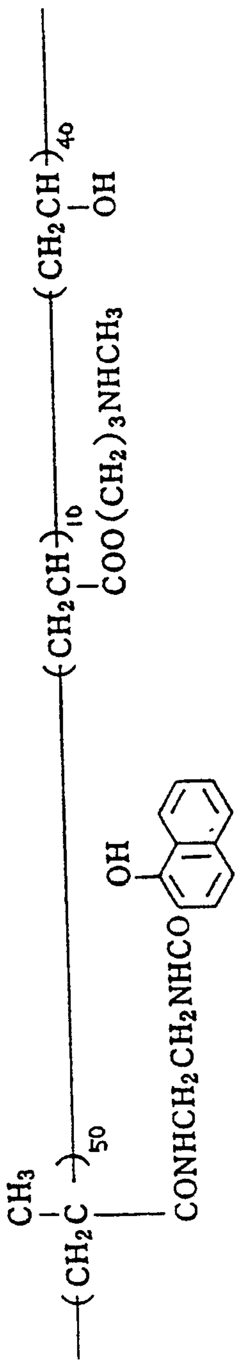

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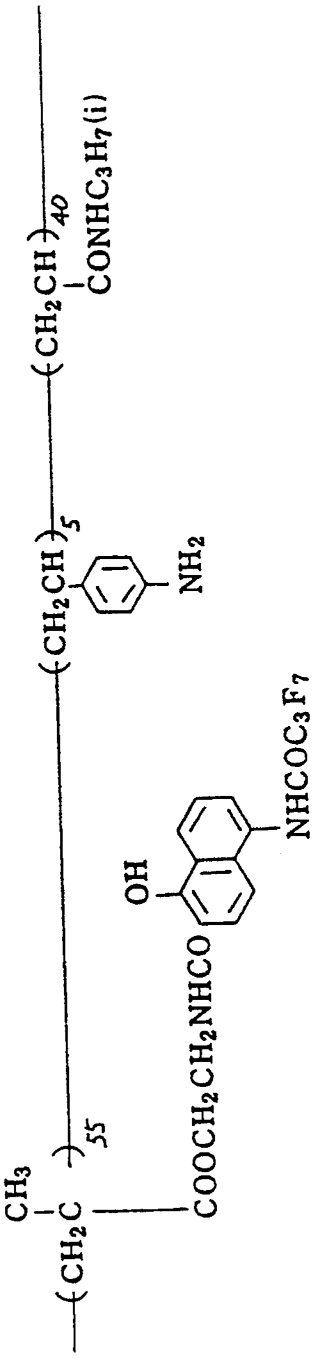

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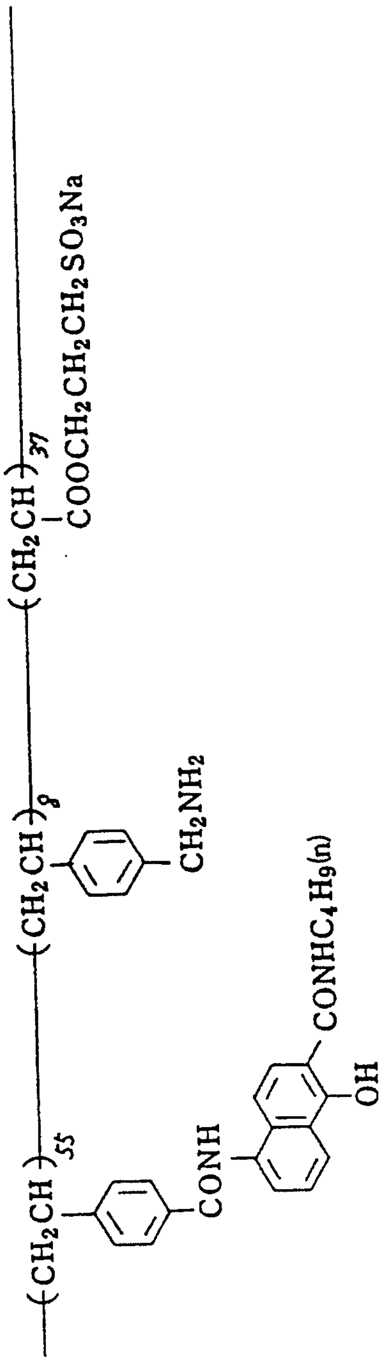

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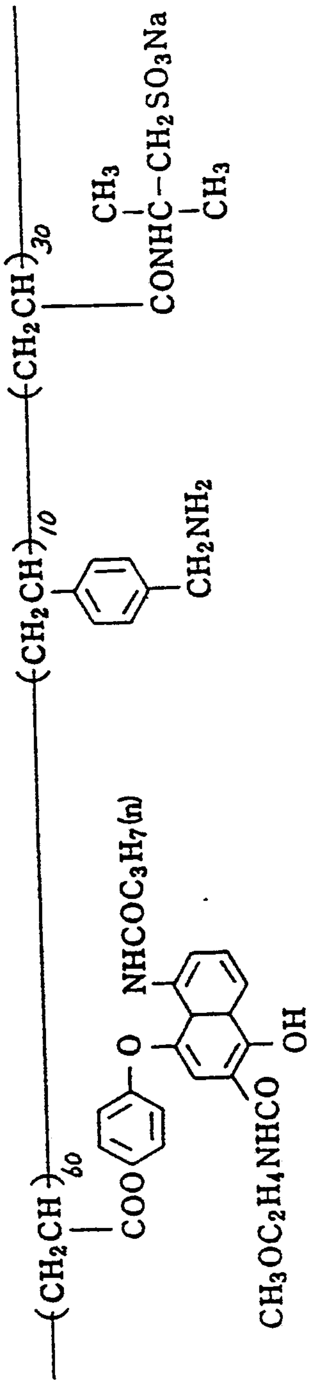

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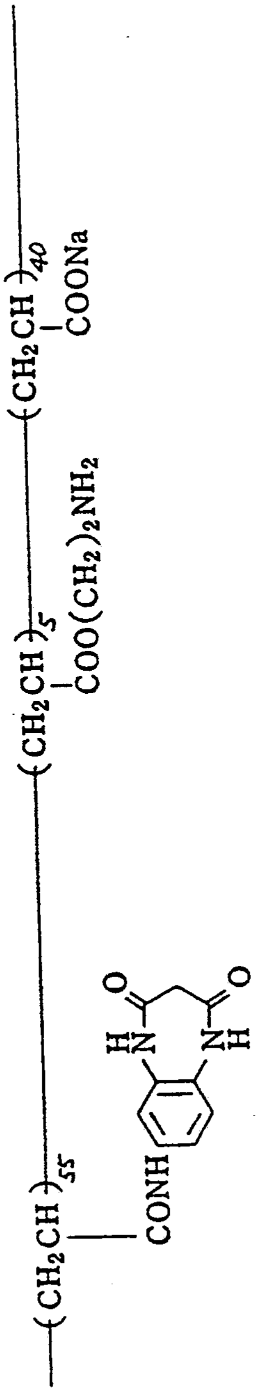

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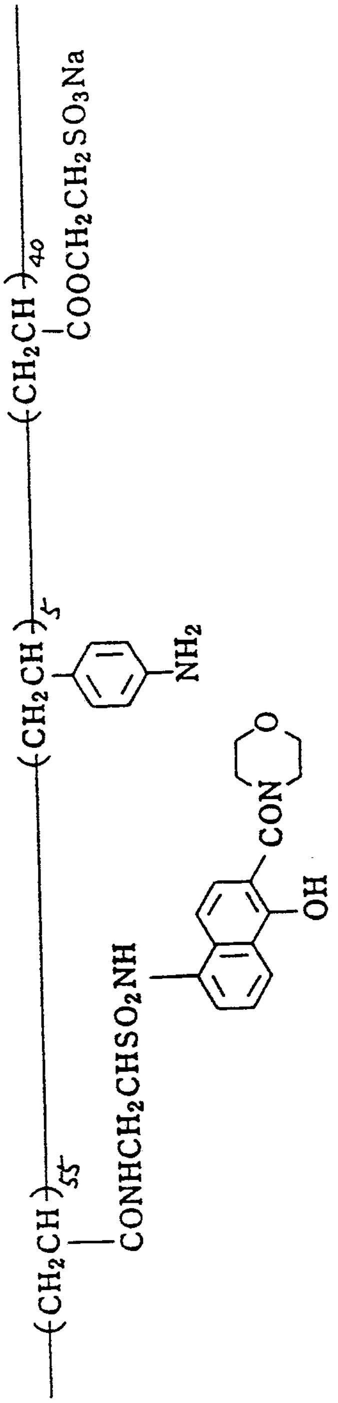

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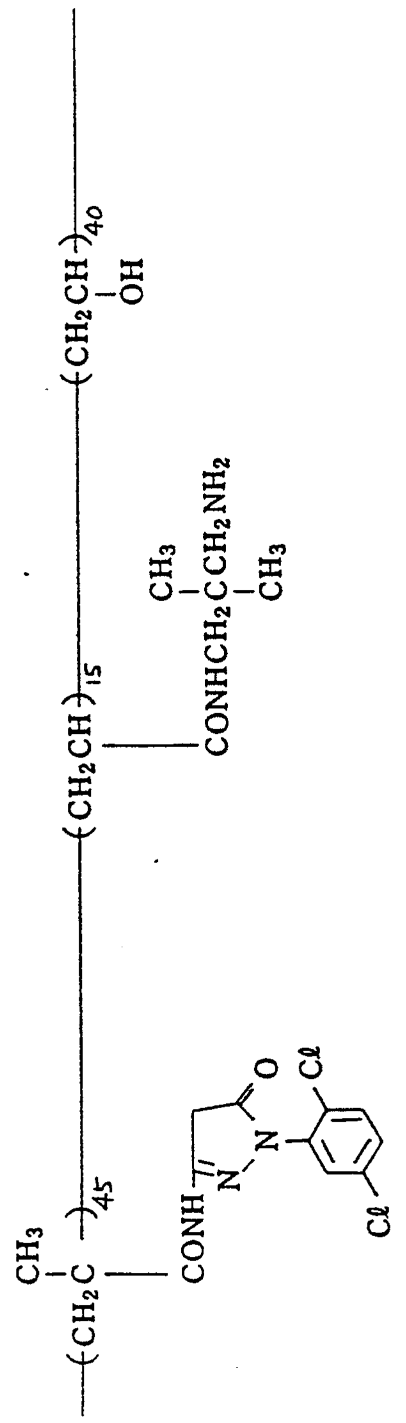

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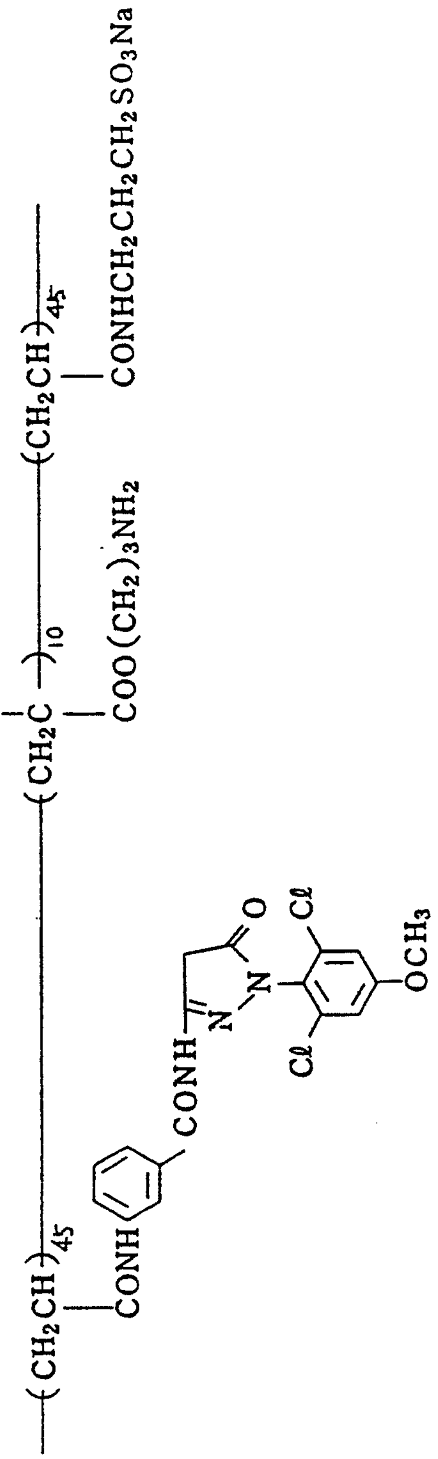

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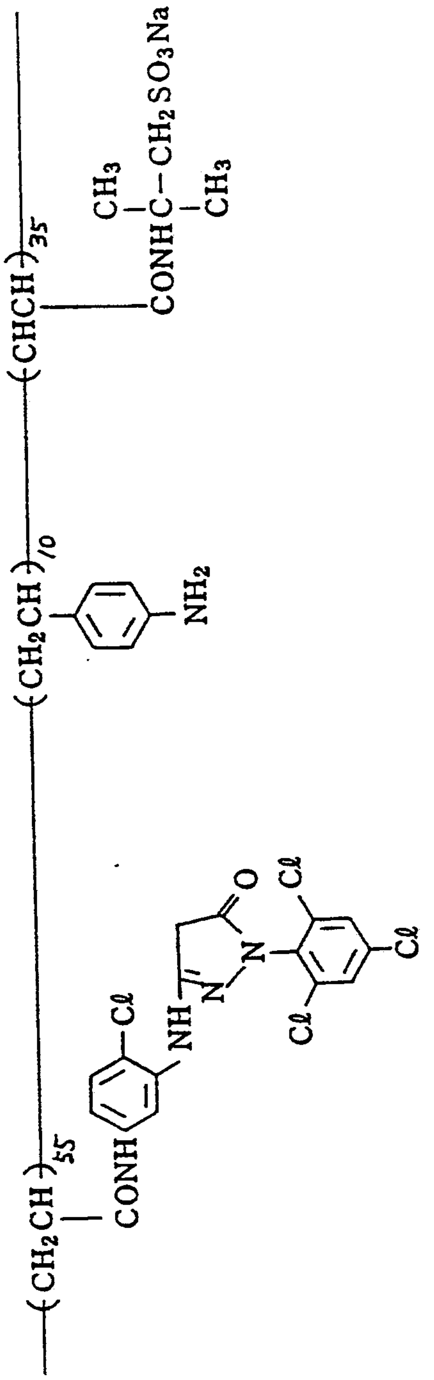

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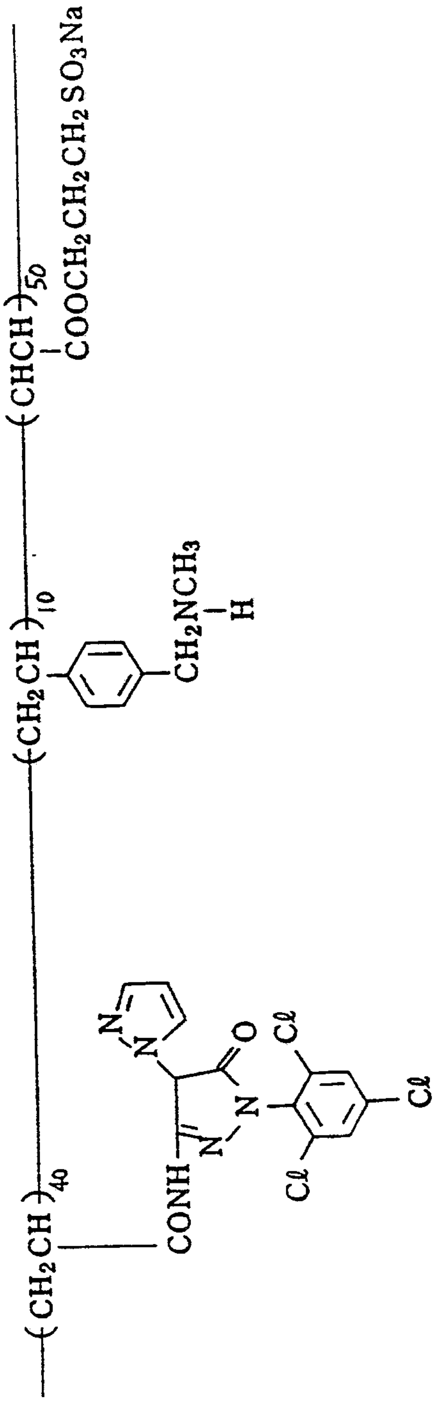

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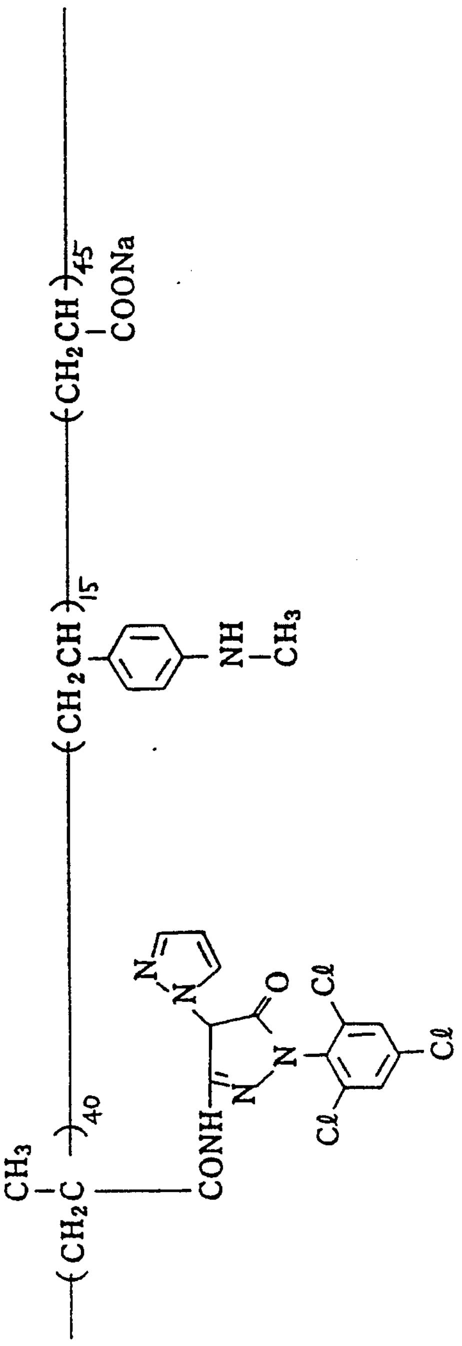

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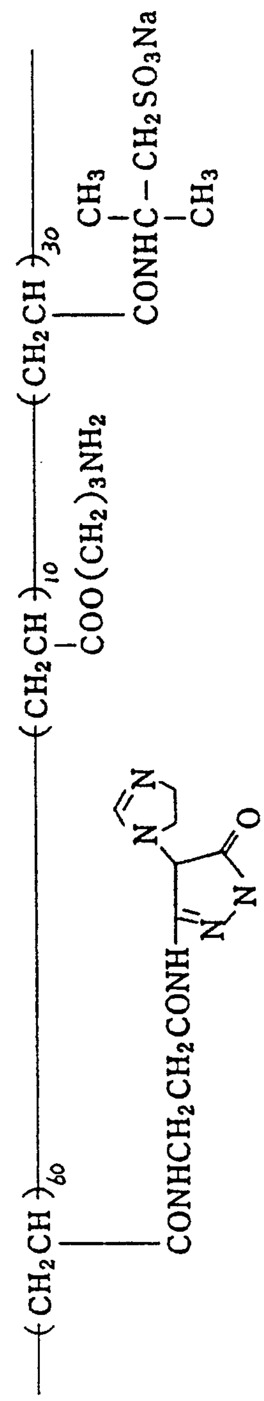

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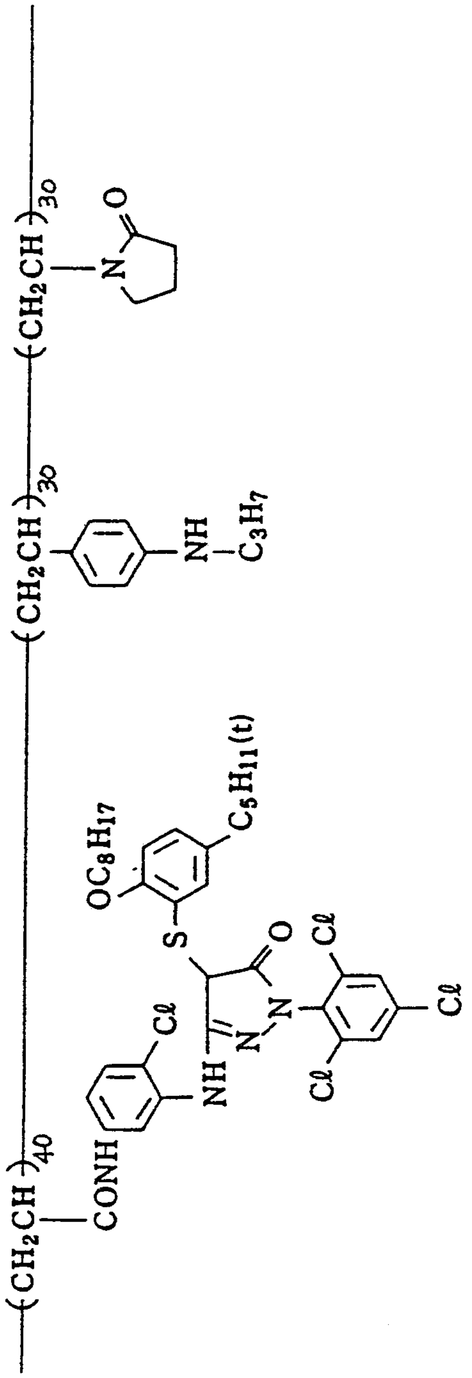

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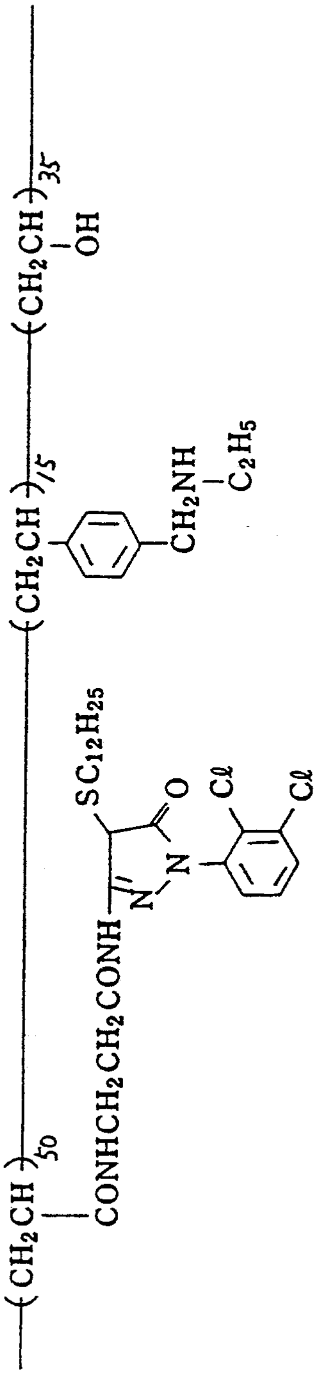
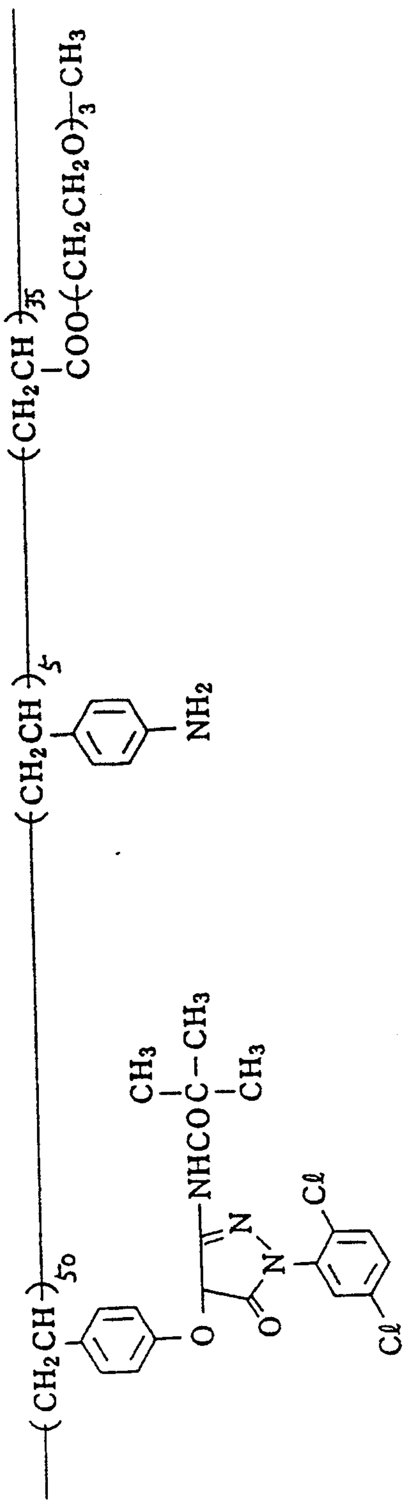


M－9



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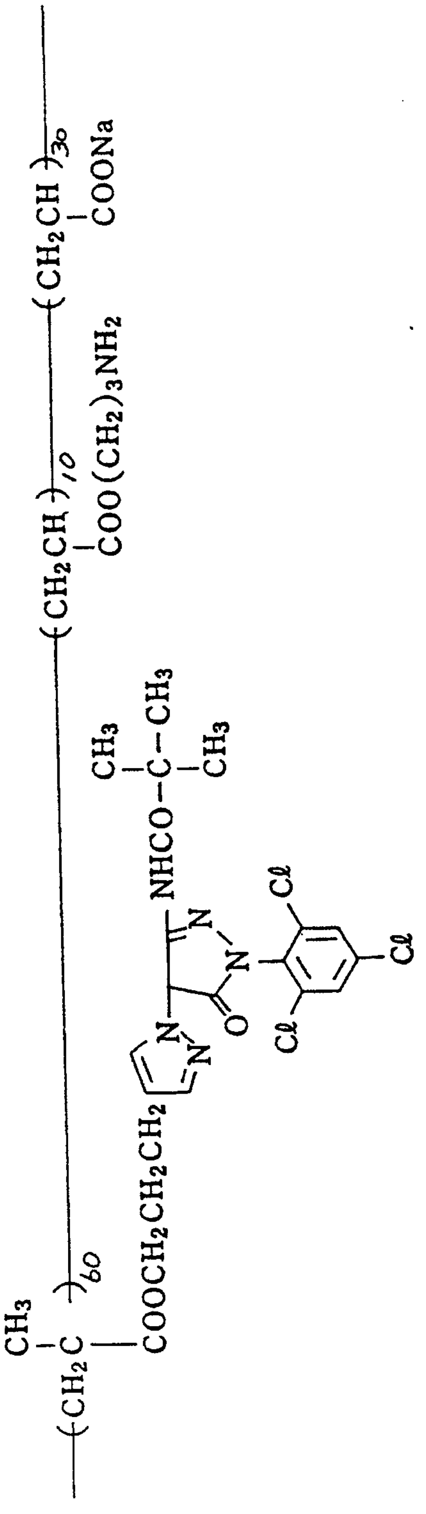

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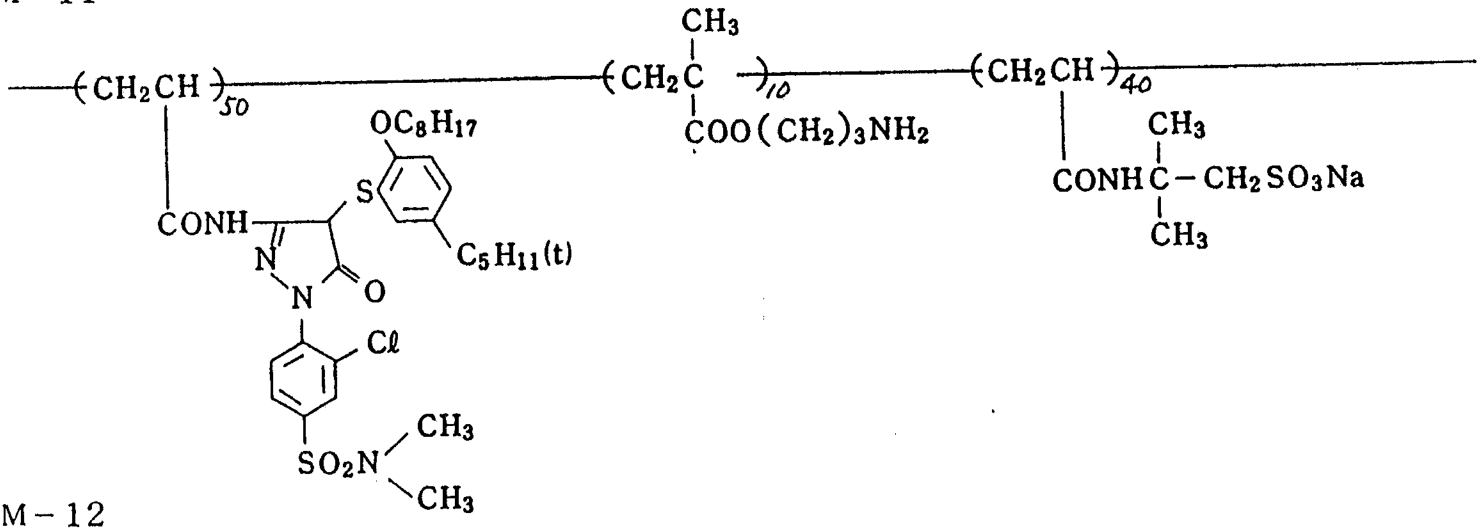

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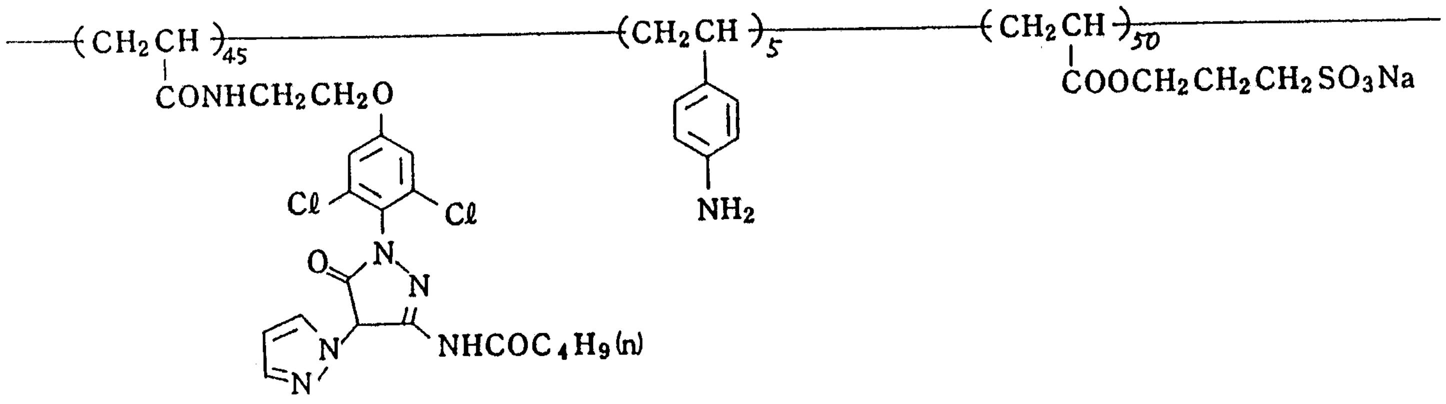
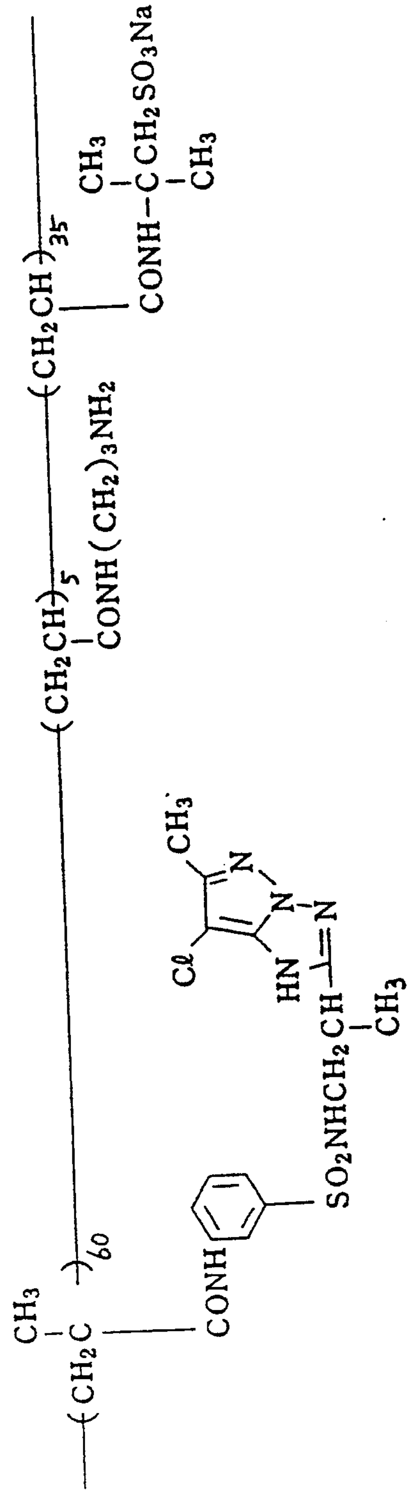


M-13



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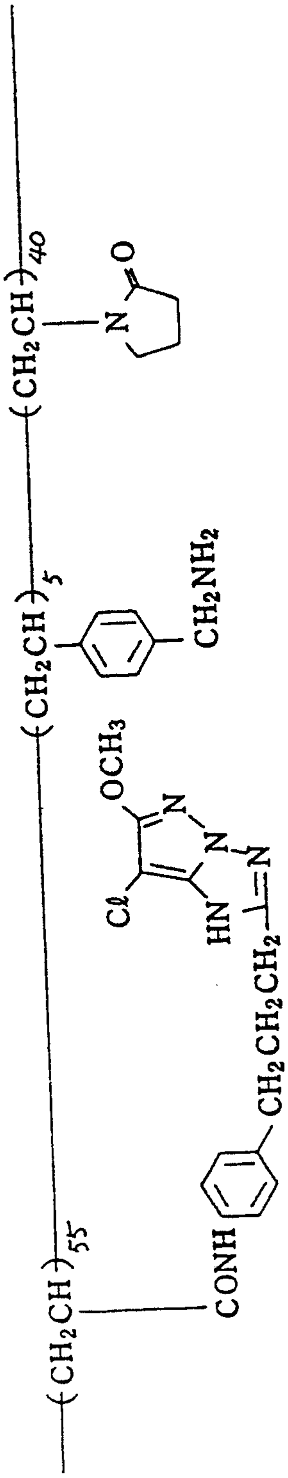
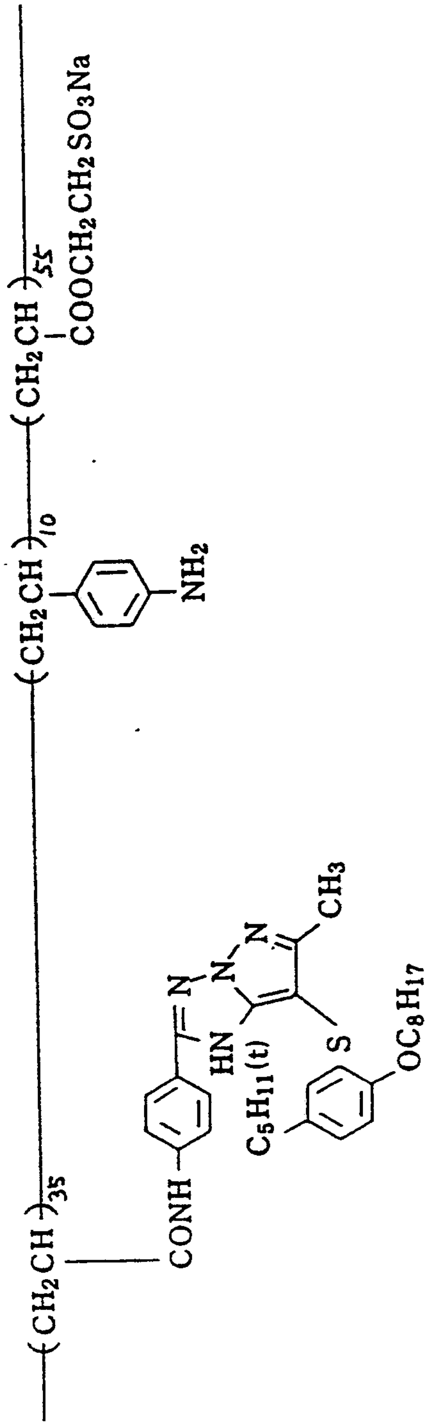


M - 15



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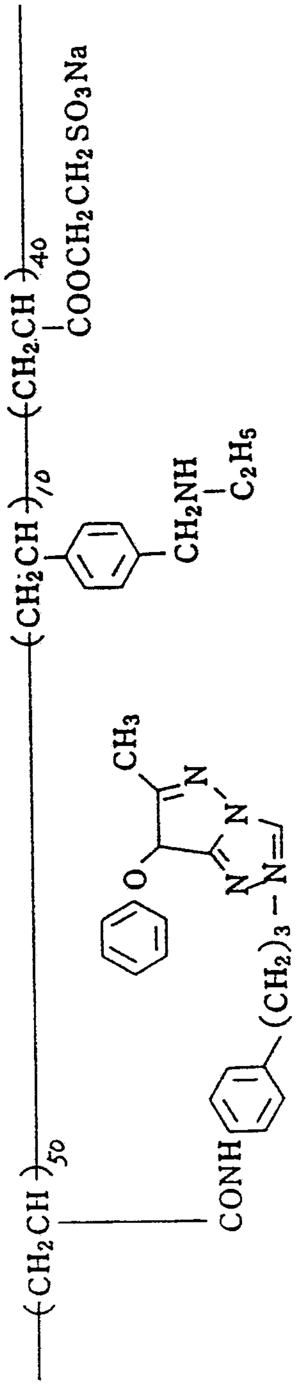
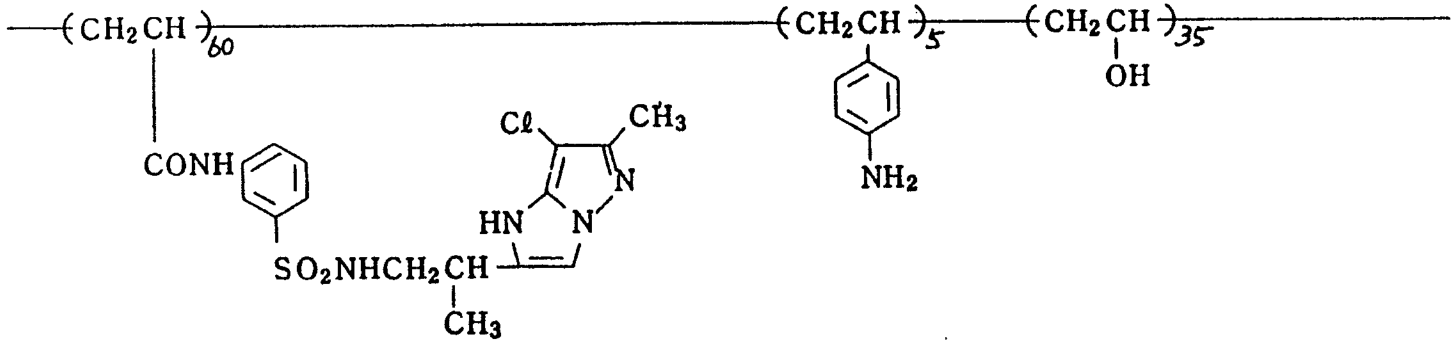
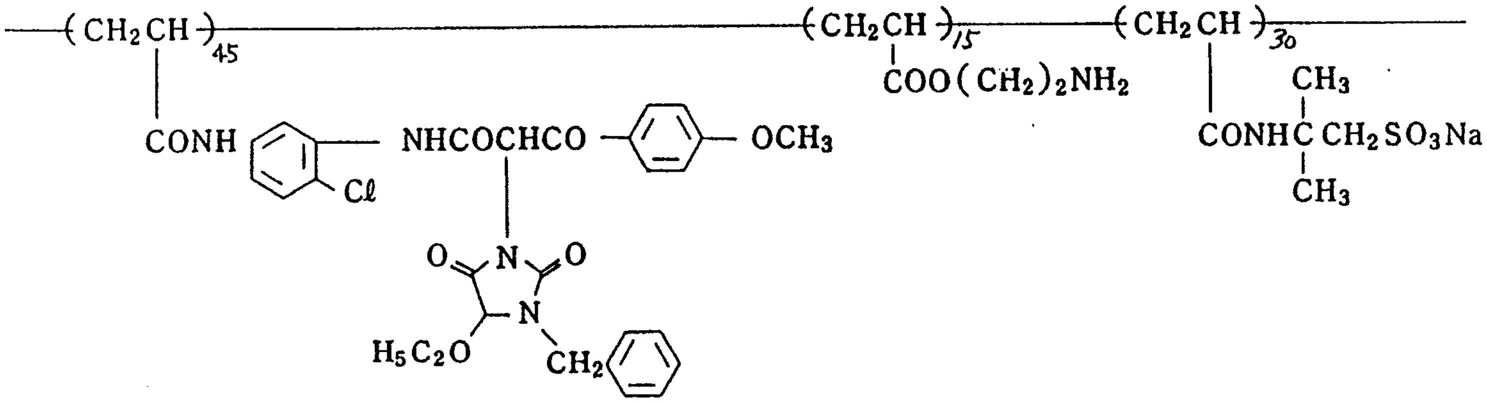


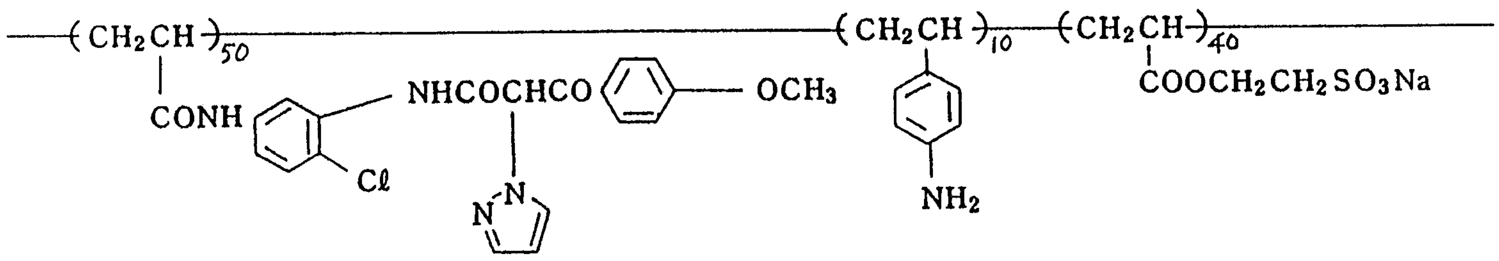
M-17



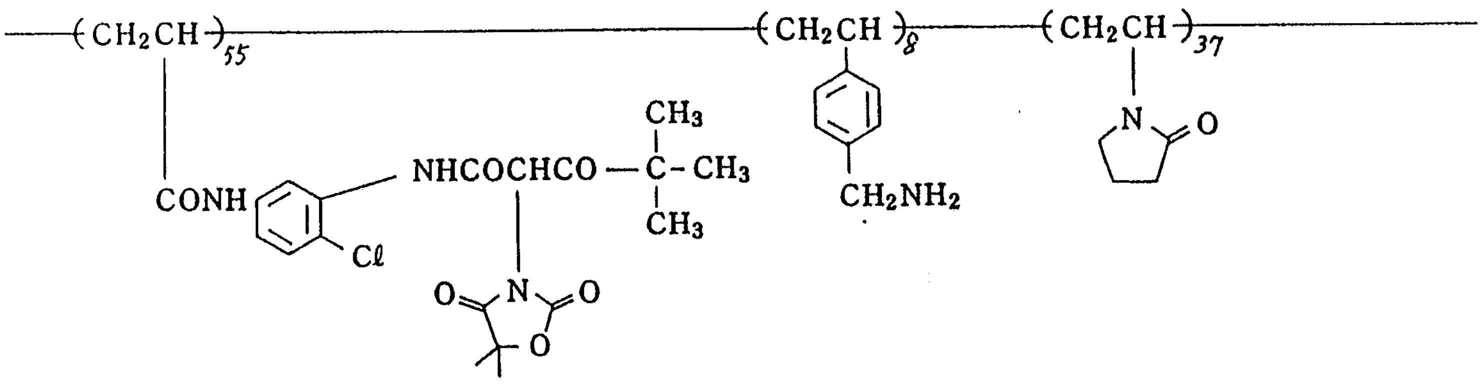
Y-1



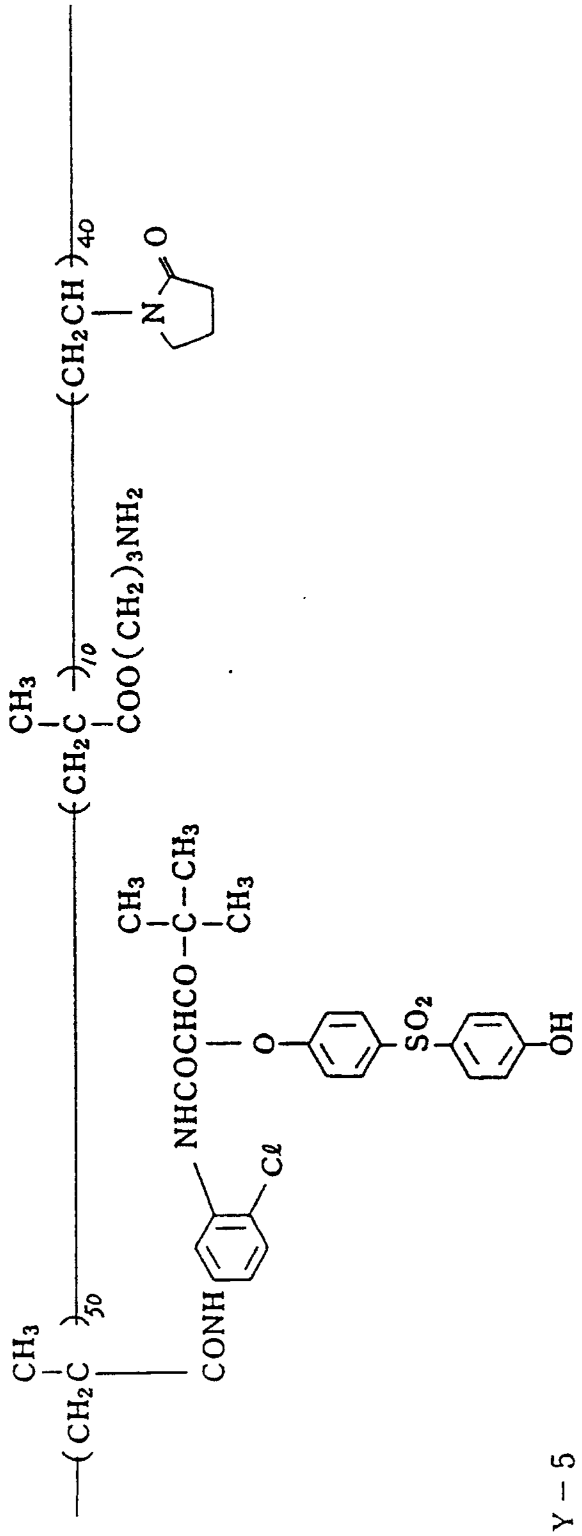
Y – 2



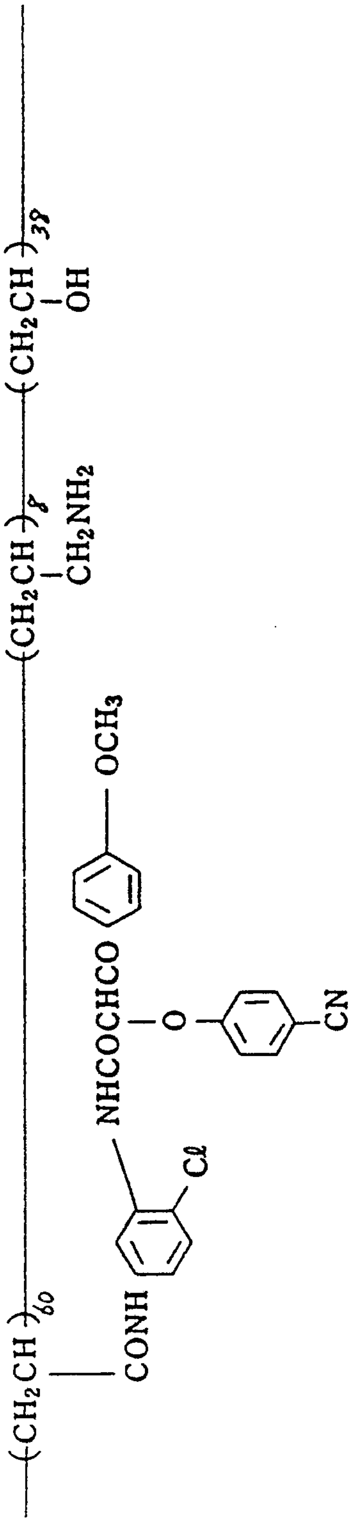
Y – 3



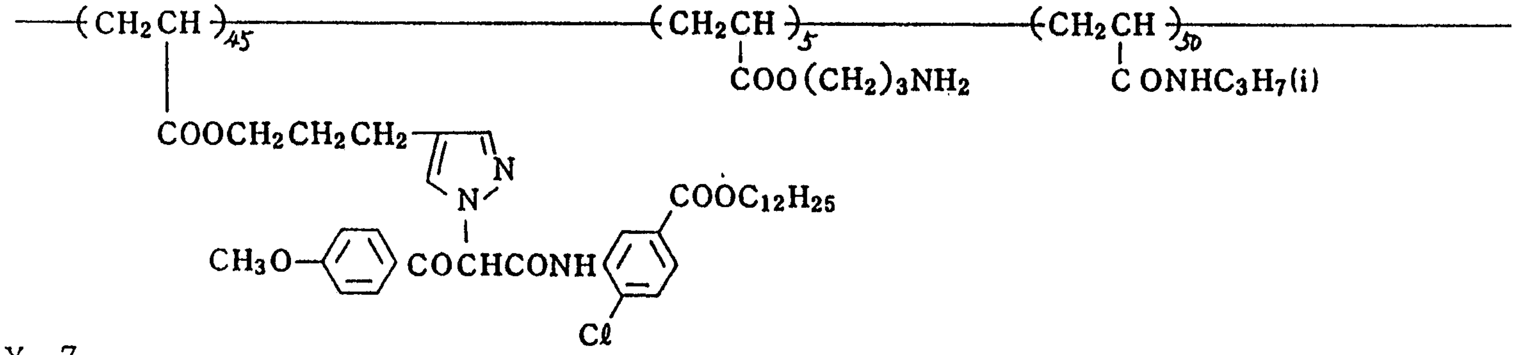
Y − 4



Y − 5



Y − 6



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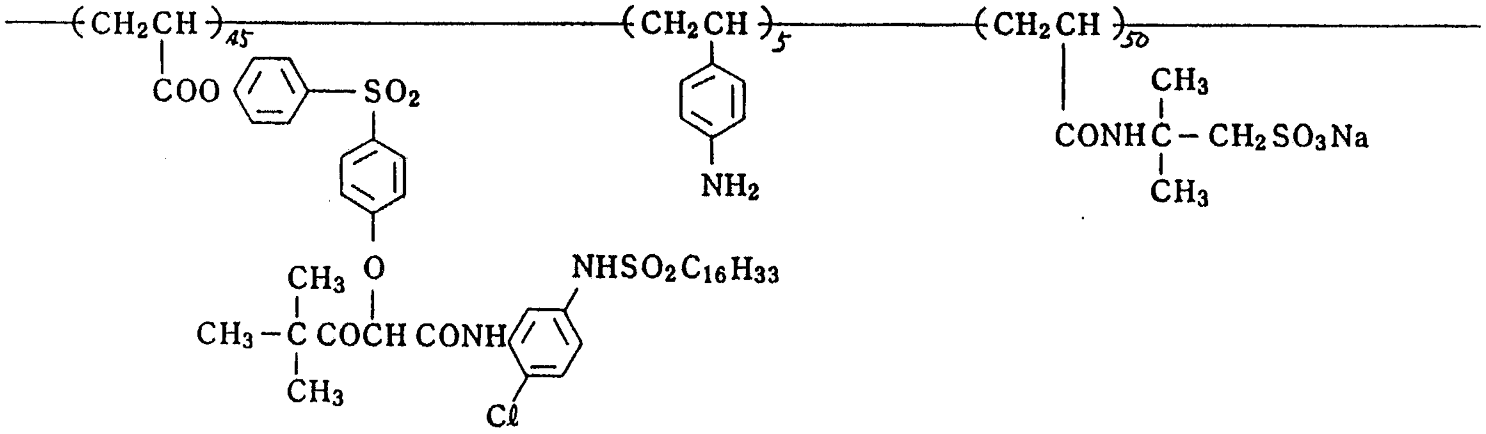
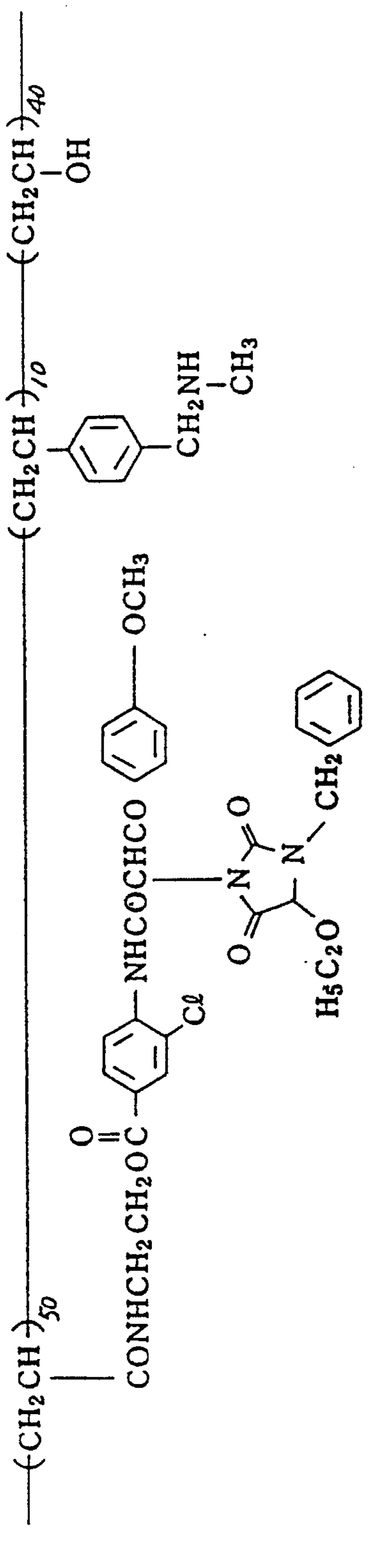
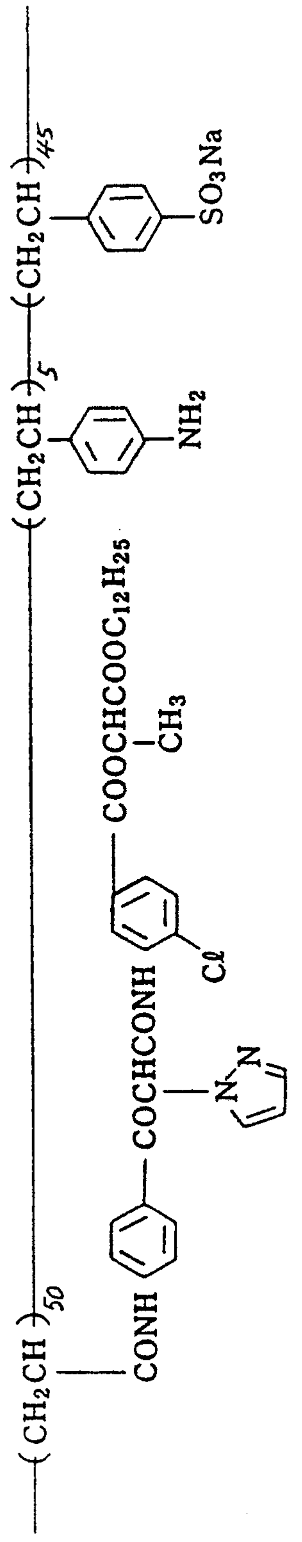


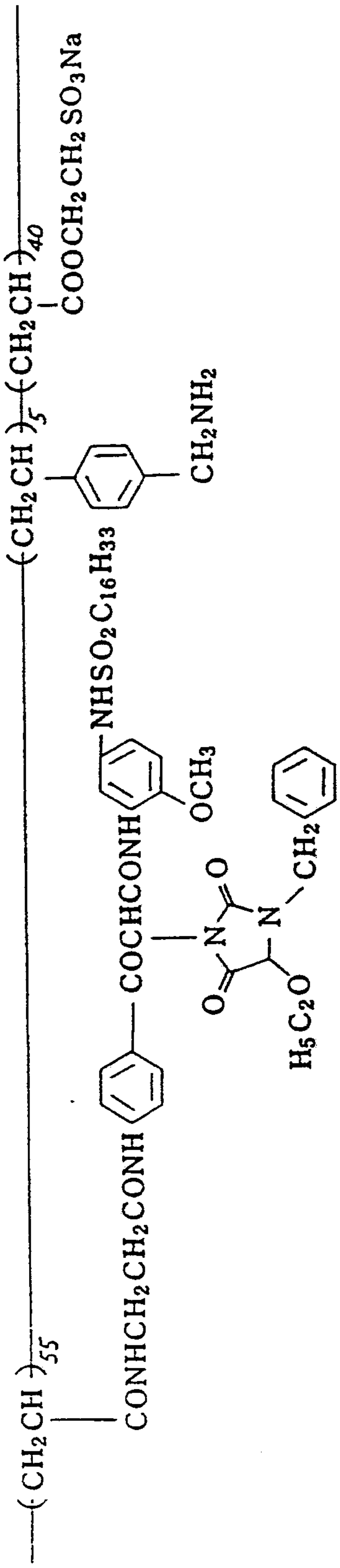
Y − 8



Y − 9

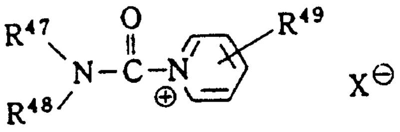


Y – 10



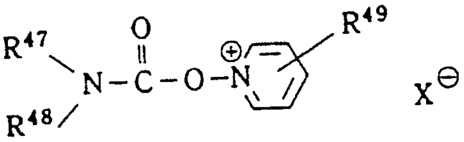
As preferable examples of carboxyl-group-activating-type hardeners in the present invention can be mentioned compounds represented by the following formulae (XXV) to (XXXIII) :

Formula (XXV)



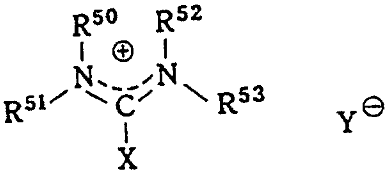
wherein R^{47} and R^{48}, which may be the same or different, each represent an alkyl group having 1 to 10 carbon atoms (e.g., methyl, ethyl, and 2-ethylhexyl), an aryl group having 6 to 15 carbon atoms (e.g., phenyl and naphthyl), or an aralkyl having 7 to 15 carbon atoms (e.g., benzyl and phenetyl). It is preferably that R^{47} and R^{48} bond together with the nitrogen atom to form a heterocyclic ring, such as a pyrrolidine ring, a piperazine ring, and a morpholine ring. R^{49} represents a substituent such as a hydrogen atom, a halogen atom, a carbamoyl group, a sulfo group, a ureido group, an alkoxy group and an alkyl group having 1 to 10 carbon atoms. If R^{49} represents an alkoxy group or an alkyl group, then the group may further have a substituent such as a halogen atom, a carbamoyl group, a sulfo group, and a ureido group. $X^{\ominus}$ represents an anion and becomes a counter ion to the N-carbamoylpyridinium salt. If the substituent of R^{49} contains a sulfo group, an inner salt is formed and $X^{\ominus}$may not be present. Preferably examples of the anions include halide ions, a sulfonic ion, a sulfonate ion, $ClO^{4\ominus}$, $BF^{4\ominus}$ and $PF^{6\ominus}$.

Formula (XXVI)



wherein R^{47}, R^{48}, R^{49} and $X^{\ominus}$ have the same meaning as defined in formula (XXVII).

Formula (XXVII)



wherein R^{50}, R^{51}, R^{52}, and R^{53}, which may be the same or different, each represent an alkyl group having 1 to 20 carbon atoms (e.g., methyl, ethyl, butyl, 2-ethylhexyl, and dodecyl), an aralkyl having 6 to 20 carbon atoms (e.g., benzyl, phenetyl, and 3-pyridylmethyl) or an aryl group having 5 to 20 carbon atoms (e.g., phenyl, naphthyl, and pyridyl), and each may have a substituent such as a halogen atom, an alkoxy group having 1 to 20 carbon atoms, an aryloxy group having 6 to 20 carbon atoms, and an N,N-disubstituted carbamoyl group.

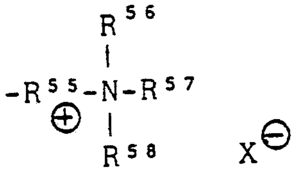
It is also preferable that any two of R^{50}, R^{51}, R^{52}, and R^{53} bond together to form a ring. Examples of rings formed by bonding R^{50} and R^{51} and R^{53} together with the nitrogen atom include a pyrrolidine ring, a piperazine ring, a perhydroazepine, and a morpholine ring. Examples of rings formed by bonding R^{50} and R^{52} or R^{51} and R^{53} together with the two nitrogen atoms and the carbon atom between them include an imidazoline ring, a tetrahydropyrimidine ring, and a tetrahydrodiazepine ring.

X represents a group that can split off when the compound represented by formula (XXVII) reacts with a nucleophilic reagent, preferable examples being a halogen atom, a sulfonyloxy group, and a 1-pyridiniumyl group.

$Y^{\ominus}$ represents an anion, preferably a halide ion, a sulfonate ion, a sulfuric acid ion, $C\ell O^{4\ominus}$, $BF^{4\ominus}$ or $PF^{6\ominus}$, and if $Y^{\ominus}$ represents a sulfonate ion, it may bond to X, R^{50}, R^{51}, R^{52} or R^{53} to form an inner salt.

Formula (XXVIII) $R^{54}\text{-}N=C=N\text{-}R^{54'}$

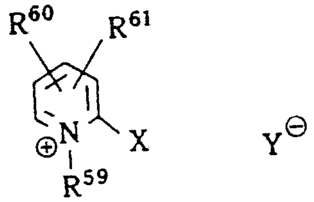
wherein R^{54} represents an alkyl group having 1 to 10 carbon atoms (e.g., methyl, ethyl, and 2-ethylhexyl), a cycloalkyl group having 5 to 8 carbon atoms (e.g., cyclohexyl), an alkoxyalkyl group having 3 to 10 carbon atoms, (e.g., methoxyethyl), an aralkyl group having 7 to 15 carbon atoms (e.g., benzyl and phenetyl); $R^{54'}$ represent the groups defined for R^{54}, or preferably



$$-R^{55}\text{-}\underset{\oplus\ \ R^{58}}{\overset{R^{56}}{N}}\text{-}R^{57} \qquad X^{\ominus}$$

R^{55} represents an alkylene group having 2 to 4 carbon atoms (e.g, ethylene, propylene, and trimethylene); R^{56} and R^{57}, which may be the same or different, each represent an alkyl group having 1 to 6 carbon atoms (e.g., methyl and ethyl). It is also preferable that R^{56} and R^{57} bond together with the nitrogen atom to form a heterocyclic ring (e.g., pyrrolidine, piperazine, and morpholine). R^{58} represents an alkyl group having 1 to 6 carbon atoms (e.g., methyl, ethyl, and butyl), wherein it is also preferable if it is substituted by a substituted or unsubstituted carbamoyl group or a sulfo group; $X^{\ominus}$ represents an anion, preferably a halide ion, a sulfonate ion, a sulfuric acid ion, $C\ell O^{4\ominus}$, $BF^{4\ominus}$ or $PF^{6\ominus}$; and if R^{58} is substituted by a sulfo group, an inner salt is formed and $X^{\ominus}$ may not be present.

Formula (XXIX)

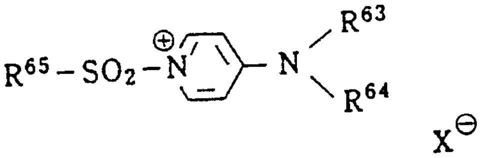


R^{59} represents an alkyl group having 1 to 10 carbon atoms (e.g., methyl, ethyl, and butyl), an aryl group having 6 to 15 carbon atoms (e.g., phenyl and naphthyl), or an aralkyl group having 7 to 15 carbon atoms (e.g., benzyl and phenetyl), which may be substituted, for example, by a carbamoyl group, a sulfamoyl group, or sulfo group; R^{60} and R^{61}, which may be the same or different, each represent a substituent such as a hydrogen atom, a halogen atom, an acylamido group, a nitro group, a carbamoyl group, a uredio group, an alkoxy group, an alkyl group, an alkenyl group, an aryl group, and an aralkyl group. It is also preferable that R^{60} and R^{61} bond together with the pyridinium ring skeleton to form a condensed ring.

X represents a group that can split off when the compounds represented by formula (XXIX) react with a nucleophilic reagent, preferable examples being a halogen atom, a sulfonyloxy group, or a group represented by $-\underset{\underset{O}{\|}}{O}P(OR^{62})^2$, in which R^{62} represents an alkyl group or an aryl group. If X represents a sulfonyloxy group, it is preferable that X and R^{59} bond together.

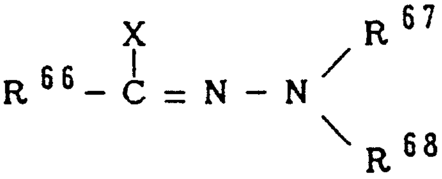
Y represents an anion, preferably a halide ion, a sulfonate ion, a sulfuric acid ion, $C\ell O^{4\ominus}$, $BF^{4\ominus}$ or $PF^{6\ominus}$, and if R^{59} is substituted by a sulfo group, an inner salt is formed and $Y^{\ominus}$ may not be present.

Formula (XXX)



wherein R^{63} and R^{64} have the same meaning as defined for R^{47} and R^{48} of formula (XXV), R^{65} represents an alkyl group having 1 to 10 carbon atoms (e.g., methyl, ethyl, and butyl), an aryl group having 6 to 15 carbon atoms (e.g, phenyl and naphthyl), or an aralkyl group having 7 to 15 carbon atoms, and $X^{\ominus}$ represents an anion, preferably a halide ion, a sulfonate ion, a sulfuric acid ion, $C\ell O^{4\ominus}$, $BF^{4\ominus}$, or $PF^{6\ominus}$.

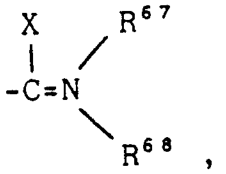
Formula (XXXI)



$$R^{66}-\overset{X}{\overset{|}{C}}=N-N\begin{matrix} R^{67} \\ R^{68} \end{matrix}$$

wherein R^{66} represents preferably a straight-chain or branched alkyl group having 1 to 20 carbon atoms (e.g., methyl, ethyl, butyl, 2-ethylhexyl, and dodecyl), an aralkyl group having 7 to 20 carbon atoms (e.g., benzyl and phenetyl), an aryl group having 6 to 20 carbon atoms (e.g., phenyl and naphthyl), an alkenyl group having 2 to 20 carbon atoms (e.g., vinyl and propenyl), or a heteroaromatic ring group (e.g., pyridyl and quinolyl), and it may have a substituent such as a halogen atom, a nitro group, an alkoxy group having 1 to 20 carbon atoms, and an aryloxy group having 2 to 20 carbon atoms. If R^{66} represents a heteroaromatic ring group, it bonds via its carbon atom

to

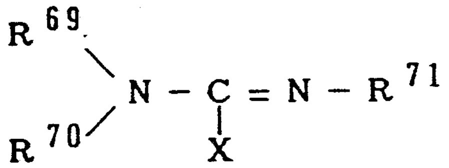


$$-\overset{X}{\overset{|}{C}}=N\begin{matrix} R^{67} \\ R^{68} \end{matrix},$$

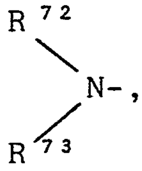
in which R^{67} and R^{68} represent preferably a straight-chain or branched alkyl group having 1 to 20 carbon atoms (e.g., methyl, ethyl, butyl, 2-ethylhexyl, or dodecyl), an aralkyl group having 7 to 20 carbon atoms (e.g., benzyl and phenetyl), an aryl group having 6 to 20 carbon atoms (e.g., phenyl group and naphthyl), an alkenyl group having 2 to 20 carbon atoms (e.g., vinyl and propenyl), or an heteroaromatic ring group (e.g., pyridyl and quinolyl), and each may have a substituent such as a halogen atom, a nitro group, an alkoxy group having 1 to 20 carbon atoms, an aryloxy group having 6 to 20 carbon atoms, an alkyl group having 1 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms, and they may bond together with the nitrogen atom to form a heterocyclic ring, preferable examples of being a pyrrolidine ring, a piperidine ring, and a morpholine ring.

X represents a group that can split off when the compounds represented by formula (XXXI) react with a nucleophilic reagent, examples being a halogen atom (e.g., chlorine and bromine), a phthalimidyloxy group, a succinimidyloxy group, a glutarimidyloxy group, an azoryloxy group (e.g., 1-benzotriazolyloxy), an ammonio group (e.g., 1-pyridinio and 1-quinolinio), an alkylsulfonyloxy group having 1 to 20 carbon atoms, and an arylsulfonyloxy group having 6 to 20 carbon atoms, and X may be substituted by a substituent, preferably, for example, by a halogen atom, a nitro group, a sulfo group, a carbamoyl group, an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, or an aryloxy group having 6 to 20 carbon atoms.

Formula (XXXII)



wherein R^{69} and R^{70} preferably represent a straight-chain or branched alkyl group having 1 to 20 carbon atoms (e.g., methyl, ethyl, butyl, 2-ethylhexyl, and dodecyl), a cycloalkyl group having 3 to 20 carbon atoms (e.g., cyclopropyl and cyclohexyl), an aralkyl group having 7 to 20 carbon atoms (e.g., benzyl and phenetyl), an aryl group having 6 to 20 carbon atoms (e.g., phenyl and naphthyl), an alkenyl group having 2 to 20 carbon atoms (e.g, vinyl and propenyl), or a heterocyclic group (e.g., pyridyl), and they may have a substituent such as a halogen atom, a nitro group, an alkoxy group having 1 to 20 carbon atoms, and an aryloxy group having 6 to 20 carbon atoms. The ring formed by bonding R^{69} and R^{70} together preferably should be a pyrrolidine ring, a piperidine ring, or a morpholine ring,

R^{71} represents preferably a straight-chain or branched alkyl group having 1 to 20 carbon atoms (e.g., methyl, ethyl, butyl, 2-ethylhexyl, and dodecyl), a cycloalkyl group having 3 to 20 carbon atoms (e.g., cyclopropyl and cyclohexyl), an aralkyl group having 7 to 20 carbon atoms (e.g., benzyl and phenetyl), an aryl group having 6 to 20 carbon atoms (e.g., phenyl and naphthyl), an alkenyl group having 2 to 20 carbon atoms (e.g., vinyl and propenyl), a heterocyclic group (e.g., pyridyl and quinolyl), or a group  , and it may have a substituent such as a halogen atom, a nitro group, an alkoxy group having 1 to 20 carbon atoms, and an aryloxy group having 6 to 20 carbon atoms,

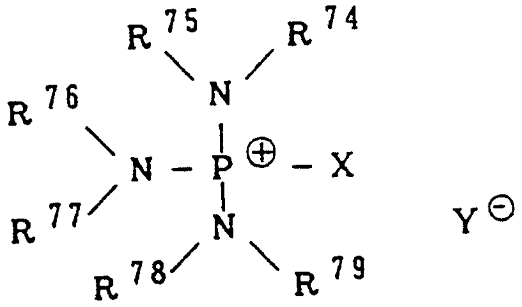
R^{72} and R^{73} represent preferably a straight-chain or branched alkyl group having 1 to 20 carbon atoms (e.g., methyl, ethyl, butyl, 2-ethylhexyl, and dodecyl), an aralkyl group having 7 to 20 carbon atoms (e.g., benzyl and phenetyl), an aryl group having 6 to 20 carbon atoms (e.g., phenyl and naphthyl), or an alkenyl having 2 to 20 carbon atoms (e.g., vinyl and propenyl),

R^{69} and R^{70} or R^{72} and R^{73} may bond together with the nitrogen atom to form a ring, such as a pyrrolidine ring, a piperidine ring, or a morpholine ring,

X represents a group that can split off when the compounds represented by formula (XXXII) react with a nucelophilic reagent, examples being a halogen atom (e.g., chlorine and bromine), a phthalimidyloxy group, a succinimidyloxy group, a glutarimidyloxy group, an azoryloxy group (e.g., 1-benzotriazolyloxy), an ammonio group (e.g., 1-pyridinio), an alkylsulfonyloxy group having 1 to 20 carbon atoms, and an arylsulfonyloxy group having 6 to 20 carbon atoms, and X may be substituted.

The compound represented by formula (XXXII) may form a salt with an acid, for example, preferably with $HC\ell$, HBr, HBF_4, HPF_6, $HC\ell O_4$, H_2SO_4, an alkylsulfonic acid having 1 to 20 carbon atoms, or an aryl (heteroaromatic ring) sulfonic acid having 5 to 20 carbon atoms.

Formula (XXXIII)



wherein R^{74}, R^{75}, R^{76}, R^{77}, R^{78}, and R^{79}, which may be the same or different, each represent preferably a straight-chain or branched alkyl group having 1 to 20 carbon atoms (e.g., methyl, ethyl, butyl, 2-ethylhexyl, and dodecyl), an aralkyl group having 6 to 20 carbon atoms (e.g., benzyl, phenetyl, and 3-pyridylmethyl), or an aryl group having 5 to 20 carbon atoms (e.g., phenyl, naphthyl, and pyridyl), and they may have a substituent such as a halogen atom, an alkoxy group having 1 to 20 carbon atoms, an aryloxy group having 6 to 20 carbon atoms, and an N,N-disubstituted carbamoyl group.

It is also preferable that any two of R^{74}, R^{75}, R^{76}, R^{77}, R^{78}, and R^{79} bond together to form a ring. For example, R^{74} and R^{75}, R^{76} and R^{77}, or R^{78} and R^{79} bond together with the nitrogen atom to form a pyrrolidine ring, a piperazine ring, a perhydroazepine ring, a morpholine ring, or a pyrrole ring.

X represents a group that can split off when the compounds represented by formula (XXXIII) react with a nucleophilic reagent, preferable examples being a halogen atom, a sulfonyloxy group, a 1-pyridiniumyl group, an imidyloxy group (e.g., succinimidyloxy, glutarimidyloxy, and phthalimidyloxy), an azoryloxy group (e.g, 1-benzotriazolyloxy).

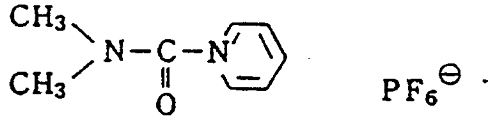
$Y^{\ominus}$ represents an anion such as a halide ion, a sulfonate ion, a sulfuric acid ion, a phosphonate ion, a phosphoric acid ion, $BF^{4\ominus}$, $C\ell O^{4\ominus}$, and $PF^{6\ominus}$, with the more preferable being $C\ell^{\ominus}$, $BF^{4\ominus}$, $C\ell O^{4\ominus}$, $PF^{6\ominus}$, and a sulfonate ion.

In addition to the compounds represented by formulae (XXV) to (XXXIII), as carboxyl-group-activating-type hardeners used in the invention, preferable example compounds are described in Japanese Patent Application (OPI) Nos. 38540/1975, 93470/1977, 43353/1981, and 113929/1983, and U.S. Patent No. 3,321,313.

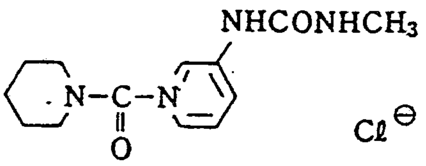
Compound examples to be used in the present invention are shown below, but the invention is not limited to them.

a. Exemplified compounds represented by formula (XXV) (The methods for synthesis of these compounds are described in detail in U.S. Patent Nos. 3,880,665 and 4,063,952)

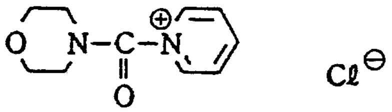
H-1



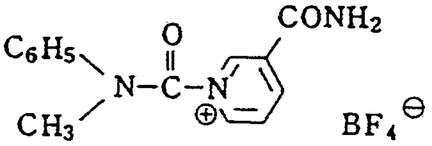
H-2



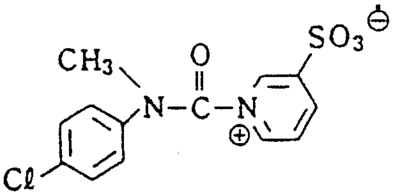
H-3



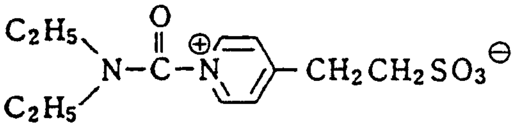
H-4



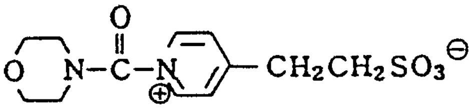
H-5



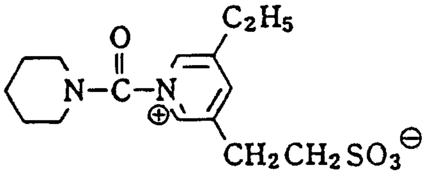
H-6



H-7

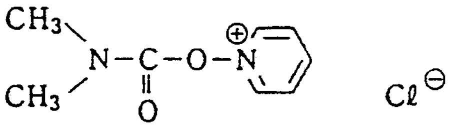


H-8



b. Exemplified compounds represented by formula (XXVI) (The methods for synthesis of these compounds are described in detail in U.S. Patent No. 4,055,427.)

H-9



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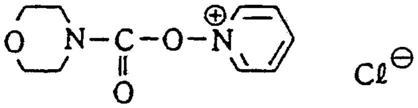

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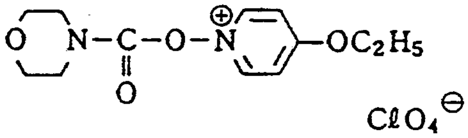
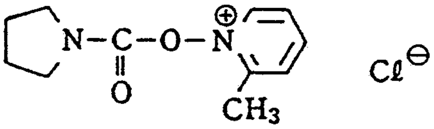
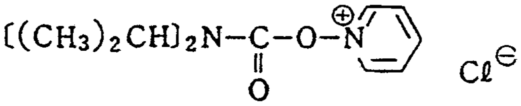


H-12

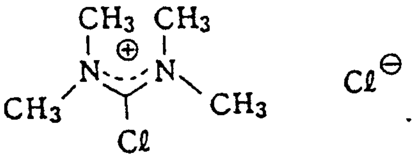


H-13



c. Exemplified compounds represented by formula (XXVII) (The methods for synthesis of these compounds are described in detail in U.S. Patent No. 4,673,632.)

H-14



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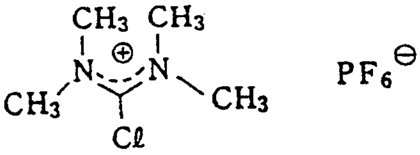

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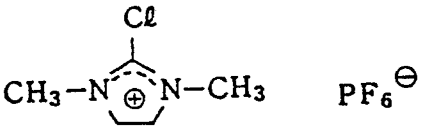
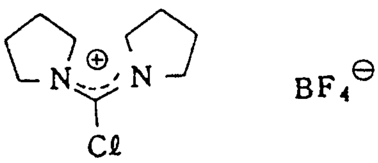


H-17



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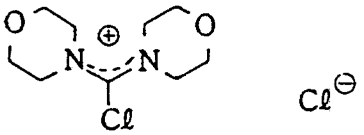

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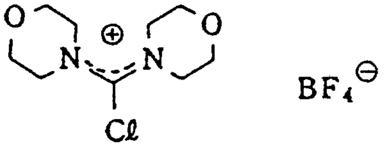

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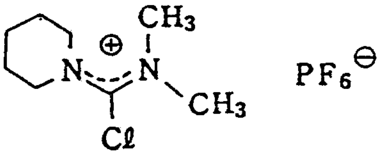

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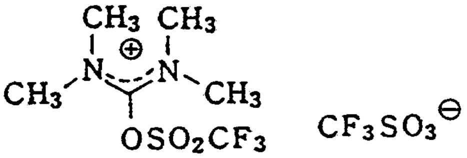
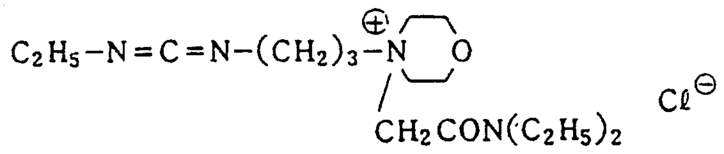
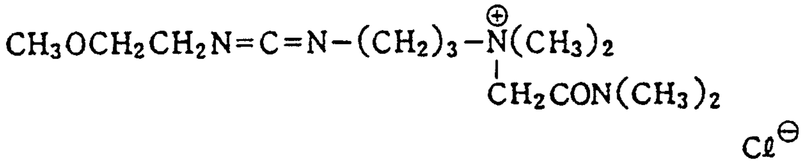


d. Exemplified compounds represented by formula (XXVIII) (The methods for synthesis of these compounds are described in detail in German Patent Nos. 2,439,553 and 2,545,477.)

H-22

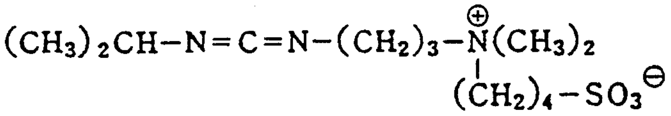


H-23



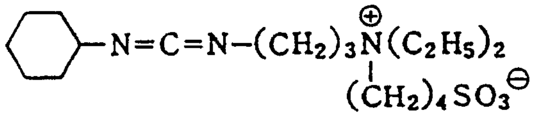
$$CH_3OCH_2CH_2N=C=N-(CH_2)_3-\overset{\oplus}{N}(CH_3)_2(CH_2CON(CH_3)_2)\ Cl^{\ominus}$$

H-24

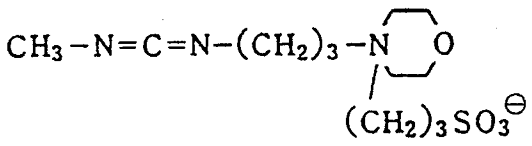


$$(CH_3)_2CH-N=C=N-(CH_2)_3-\overset{\oplus}{N}(CH_3)_2-(CH_2)_4-SO_3^{\ominus}$$

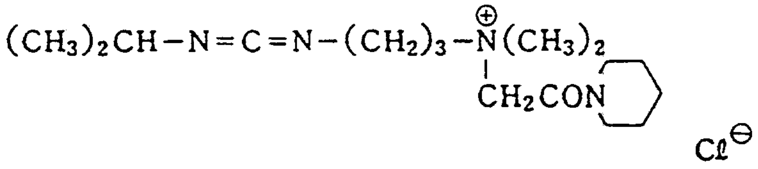
H-25



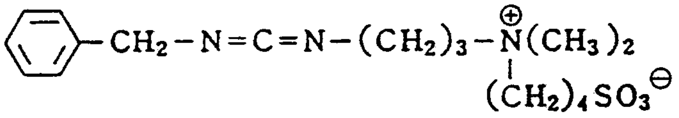
H-26



H-27

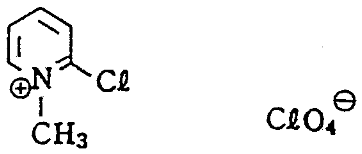


H-28

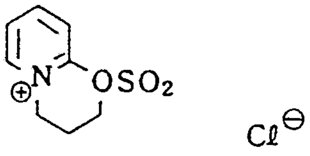


e. Exemplified compounds represented by formula (XXIX) (The methods for synthesis of these compounds are described in detail in British Patent No. 1,462,789, Japanese Patent Application (OPI) No. 46538/1982, and Japanese Patent Publication No. 50669/1983.)

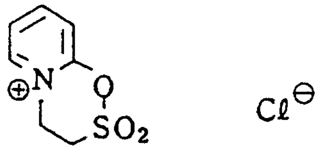
H-29



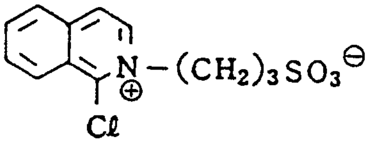
H-30



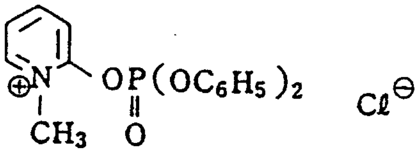
H-31



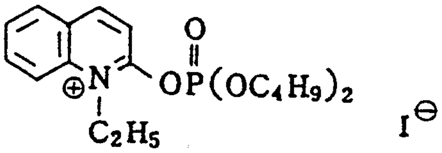
H-32



H-33

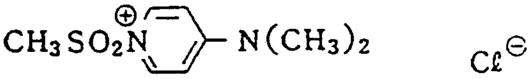


H-34

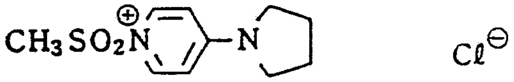


f. Exemplified compounds represented by formula (XXX) (The methods for synthesis of these compounds are described in detail in U.S. Patent No. 4,067,741.)

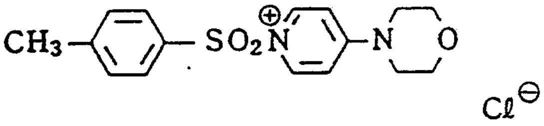
H-35



H-36

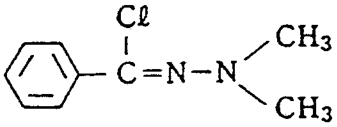


H-37

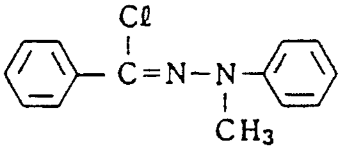


g. Exemplified compounds represented by formula (XXXI) (The methods for synthesis of these compounds are described in detail in Japanese Patent Application (OPI) No. 68866/1987.)

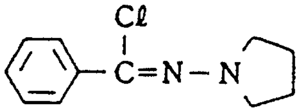
H-38



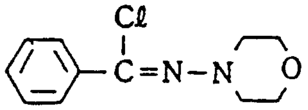
H-39



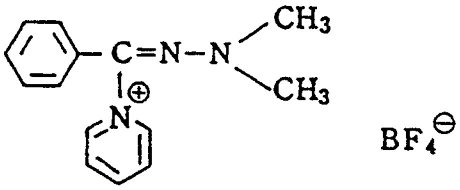
H-40



H-41

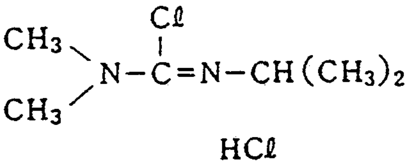


H-42

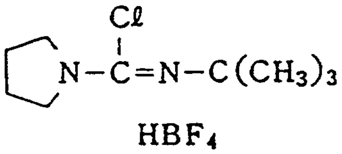


h. Exemplified compounds represented by formula (XXXII) (The methods for synthesis of these compounds are described in detail in Japanese Patent Application (OPI) No. 68867/1987.)

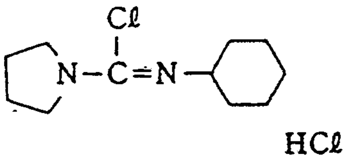
H−43



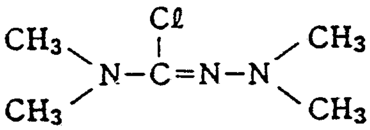
H−44



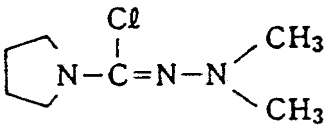
H−45



H−46



H−47



i. Exemplified compounds represented by formula (XXXIII) (The methods for synthesis of these compounds are described in detail in U.S. Patent No. 4,668,616.)

H-48

$\{(CH_3)_2N\}_3P^{\oplus}-C\ell \qquad C\ell^{\ominus}$

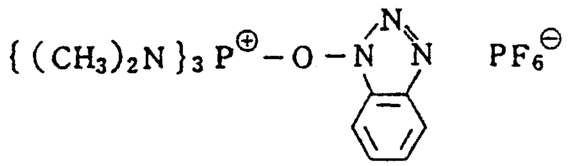
H-49

$\{(CH_3)_2N\}_3P^{\oplus}-C\ell \qquad BF_4^{\ominus}$

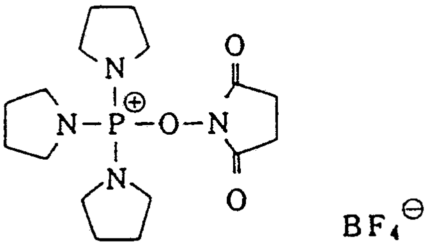
H-50

$\{(CH_3)_2N\}_3P^{\oplus}-C\ell \qquad PF_6^{\ominus}$

H-51

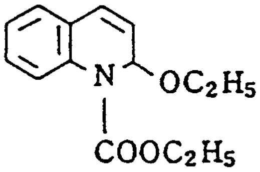


H-52

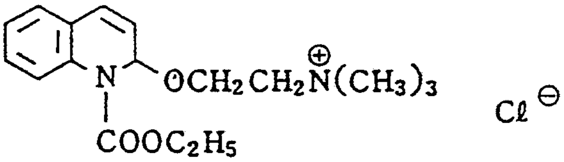


j. Compounds described in U.S. Patent No. 4,013,468.

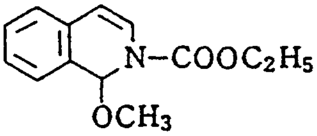
H-53



H-54

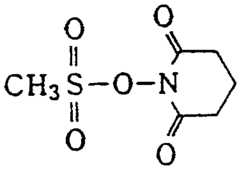


H-55

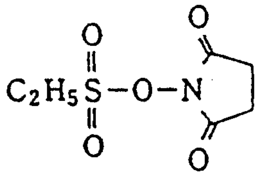


k. Compounds described in U.S. Patent No. 4,111,926.

H-56

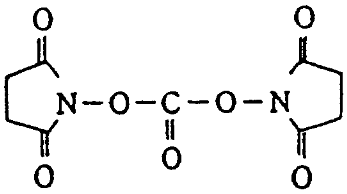


H-57

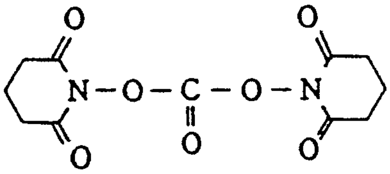


ℓ. Compounds described in U.S. Patent No. 4,427,768.

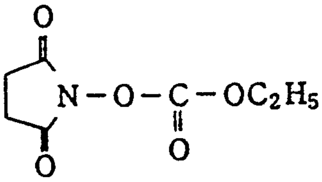
H-58



H-59

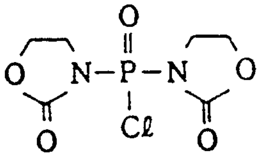


H-60

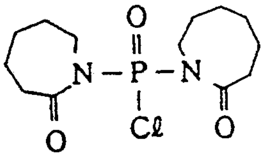


m. Compounds described in Japanese Patent Application (OPI) No. 113929/1983.

H-61

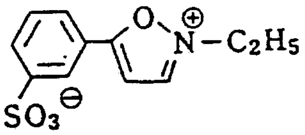


H-62

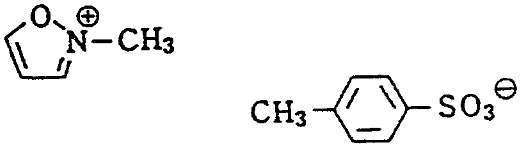


n. Compounds described in U.S. Patent No. 3,321,313.

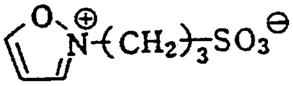
H-63



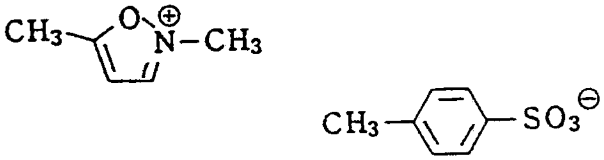
H-64



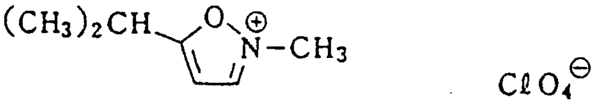
H-65



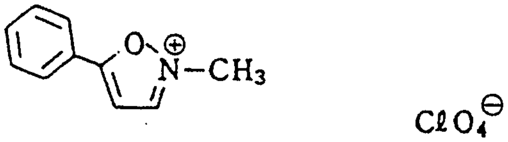
H-66



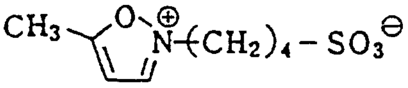
H-67



H-68



H-69



When the hardeners represented by formulae (XXV) to (XXXIII), which act by activating a carboxyl group in gelatin, are used in photographic layers, unfavorable phenomenon such as reactions with couplers contained in color photographic materials, the occurrence of stain, photographic deterioration such as fogging, and desensitization are hardly observed. Further, the progress of the hardening is quick, the final hardness is attained within a few days, and a further increase of the hardness thereafter, that is, posthardening, is not substantially observed.

These compounds have excellent affinity for water and do not require organic solvents when added. Therefore problems such as uneven coating due to the organic solvent do not arise. Also, there no concern necessary regarding a possible explosion or the like. These compounds have no particular physiological action, and since they are of low vapor pressure, unfavorable effects on the human body are reduced.

The amount of hardener used in the invention can be selected depending on the purpose. Generally the amount can be in the range of 0.01 to 20 wt. %, more preferably in the range of 0.05 to 10 wt. % for dried gelatin.

The hardeners of the present invention can be used for a method of extending the chain length of gelatin by partial hardening, as described in Japanese Patent Application (OPI) No. 2324/1981. The hardeners of the invention can also be used for hardening gelatin whose chain has thus been lengthened.

The hardeners of the present invention can be used in any photographic materials that uses gelatin, for example, color negative film, color reversal film, color positive film, color photographic paper, color reversal photographic paper, color photographic materials used in the color diffusion transfer reversal process or in the silver dye bleaching process, and black and white photographic materials such as black and white film, X-ray film, process film, black and white photographic paper, aerial film, microfilm, facsimile film, photocomposing film, photocomposing photographic paper, and film for graphs.

There is no particular limit on photographic layers in which the hardener of the present invention is used, and the hardener can be used not only in a silver halide emulsion layer, but also in any gelatin-containing photographic layer, including such nonphotosensitive layers as an undercoat layer, a back layer, a filter layer, an intermediate layer, and an overcoat layer.

The hardeners of the present invention can be used alone or in combination, and they also can be combined with other hardeners known to the art, such as aldehyde-type compounds, for example formaldehyde and glutaraldehyde; ketone compounds, such as diacetyl, cyclopentanedione, bis(2-chloroethylurea), 2-hydroxy-4,6-dichloro-1,3,5-triazine, divinyl sulfon, 5-acetyl-1,3-diacryloylhexahydro-1,3,5-triazine; compounds having a reactive halogen described, for example, in U.S. Patent Nos. 3,288,775 and 2,732,303 and British Patent Nos. 974,723 and 1,167,207; N-hydroxymethylphthalimide; compounds having a reactive olefin described, for example, in U.S. Patent Nos. 3,635,718 and 3,232,763, British Patent No. 994,869, and Japanese Patent Application (OPI) Nos. 41221/1978 and 57257/1979; N-methylol compounds described, for example, in U.S. Patent Nos. 2,732,316 and 2,586,168; isocyanates described, for example, in U.S. Patent No. 3,103,437; aziridine compounds described, for example, in U.S. Patent No. 3,017,280 and 2,983,611 acid derivatives described, for example, in U.S. Patent Nos. 2,725,294 and 2,725,295; carbodiimide-type compounds described, for example, in U.S. Patent No. 3,100,704; epoxy-compounds described, for example, in U.S. Patent No. 3,091,537; halogenocarboxyaldehydes, such as mucochloric acid; dioxane derivatives, such as dihydroxydioxane, and dichlorodioxane; the above-mentioned dihydroquinoline-type compounds; compounds having a phosphorus-halogen bond, N-sulfonyloxyimide-type compounds; N-acyloxyimide-type compounds; isooxazole-type compounds described in U.S. Patent Nos. 3,321,313 and 3,543,292; N-carbamoylpyridinium salts; 2-sulfonyloxypyridinium salts or N-carbonyloxyimide-type compounds described in Japanese Patent Application (OPI) No. 43353/1981; or hardeners of inorganic compounds such as chrome alum and zirconium sulfate. The hardeners of the present invention can also be used in combination with, instead of the above compounds, precursors for them, such as alkali metal bisulfite aldehyde adducts, methylol derivatives of hydantoin, primary aliphatic nitroalcohols, methyloxyethyl-sulfonyl-type compounds, and chloroethylsulfonyl-type compounds. When the present hardener is used in combination with another hardener, although the proportion of the present hardener used can be chosen depending on the purpose or desired effect, it is preferable that the proportion of the present hardener is 50 mol % or greater.

In addition to the hardener of the present invention, a compound that can facilitate the hardening of gelatin can also be used. Examples of such agents for facilitating hardening include nonprotonic solvents described in German Patent Application (OLS) No. 2,417,586, betain-type surface active agents described in Japanese Patent Application (OPI) No. 62045/1982, tertiary amines or their salts (e.g., those described, for example, in Japanese Patent Application (OPI) Nos. 1043/1981 and 9434/1986, German Patent Application (OLS) No. 2,138,305, and British Patent No. 1,284,305, and 1,269,983), various inorganic salts, and polyvalent alcohols. Naturally these agents for facilitating hardening can be used in combination with the present hardener plus the above-mentioned known hardener. For example, as an agent for facilitating hardening, a polymer containing a sulfinic acid group described in Japanese Patent Application (OPI) No. 4141/1981 can be additionally used in a system containing the present hardener and a vinylsulfonic-type hardener.

The gelatin to which the polymer coupler of the present invention will be applied may be any one of the so-called alkali-treated gelatins (lime-processed gelatins), obtained by immersion into an alkali bath before the extraction of gelatin during its production; acid-treated gelatin, obtained by immersion into an acid bath; double-immersion gelatin, obtained by immersion into an alkali bath and an acid bath; and enzyme-processed gelatin. Further, the hardener of the present invention may be applied to gelatin having a low molecular weight obtained by heating the above gelatin in a water bath or allowing a proteolytic enzyme to act on the above gelatin, which action thereby partially hydrolyzes the gelatin.

Although it is advantageous to use gelatin, as a binder or a protective colloid that can be used in the emulsion layer or an intermediate layer of the present photographic material, other synthetic binders can also be used.

The silver halide emulsion of the color photographic material to be used in this invention may be any type of halogen composition, including silver bromide, silver iodobromide, silver bromochloroiodide, silver chlorobromide, or silver chloride.

The silver halide grains of the silver halide emulsion may be regular grains comprising regular crystals such as cubes, octahedrons, or tetradecahedrons, or irregular crystals such as spherical crystals or plate-like crystals, crystals having defects such as twin planes, or composites thereof.

The grain diameter of the silver halide may be fine grains about 0.2 µm or less, or coarse grains wherein the diameter of the projected area is about 10 µm, and a polydisperse emulsion or a monodisperse emulsion can be used.

The silver halide photographic emulsions that can be used in this invention may be prepared suitably by known means, for example by the methods described in "I. Emulsion Preparation and Types" in Research Disclosure (RD), No. 17643 (December 1978), pp. 22-23, and in RD, No. 18716 (November 1979) p. 648; the methods described in P. Glafkides "Chemie et Phisique Photographique", Paul Montel (1967), in G.F. Duffin "Photographic Emulsion Chemistry", Focal Press (1966), and in V.L.Zelikman et al. "Making and Coating of Photographic Emulsion", Forcal Press (1964).

A monodisperse emulsion, such as described in U.S. Patent Nos. 3,574,628 and 3,655,394, and in British Patent No. 1,413,748, is preferable.

Tabular grains having an aspect ratio of 5 or greater can be used in the emulsion. Tabular grains can be easily prepared by the methods described in Gutoff "Photographic Science and Enggineering", Vol. 14, pp 248-257 (1970), U.S. Patent Nos. 4,434,226, 4,414,310, 4,433,048, and 4,439,520, and British Patent No. 2,112,157.

The crystal structure of the emulsion grains may be uniform, the outer halogen composition of the crystal structure may be different from the inner halogen composition, or the crystal structure may be layered. Silver halides whose compositions are different may be joined by the epitaxial joint, or a silver halide may be joined, for example, to a compound other than silver halides, such as silver rhodanide, lead oxide, etc.

Further, the silver halide may be a mixture of grains having various crystal shapes.

The silver halide emulsion may generally be physically ripened, chemically ripened, and spectrally sensitized. Additives that will be used in these steps are described in Research Disclosure No. 17643 and ibid. No. 18716, and the involved sections are listed in the Table below.

Known photographic additives that can be used in this invention are also described in the above-mentioned two Research Disclosures, and the involved sections are listed in the same Table below.

Additive	RD 17643	RD 18716
1 Chemical sensitizer	p. 23	p.648 (right column)
2 Sensitivity-enhancing agents	-	ditto
3 Spectral sensitizers and Supersensitizers	pp.23-24	pp.648 (right column) -649 (right column)
4 Brightening agents	p. 24	-
5 Antifogging agents and Stabilizers	pp.24-25	p.649 (right column)
6 Light absorbers, Filter dyes, and UV Absorbers	pp.25-26	pp.649 (right column) -650 (left column)
7 Stain-preventing agents	p. 25 (right column)	p.650 (left to right column)
8 Image dye stabilizers	p. 25	-
9 Hardeners	p. 26	p.651 (left column)
10 Binders	p. 26	ditto
11 Plasticizers and Lubricants	p. 27	p. 650 (right column)
12 Coating aids and Surface-active agents	pp.26-27	ditto
13 Antistatic agents	p. 27	ditto

Various color couplers can be used in this invention, and typical examples are described in the patents in the above-mentioned Research Disclosure No. 17643, VII-C - G.

As yellow couplers, those described, for example, in U.S. Patent Nos. 3,933,501, 4,022,620, 4,326,024, and 4,401,752, Japanese Patent Publication No. 10739/1983, and British Patent Nos. 1,425,020 and 1,476,760 are preferable.

As magenta coupers, the 5-pyrazolone type and pyrazoloazole type are preferable, and those described in U.S. Patent Nos. 4,310,619 and 4,351,897, European Patent No. 73,636, U.S. Patent Nos. 3,061,432 and 3,725,067, Research Disclosure No. 24220 (June 1984), Japanese Patent Application (OPI) No. 33552/1985, Research Disclosure No. 24230 (1984), Japanese Patent Application (OPI) No. 43659/1985, and U.S. Patent Nos. 4,500,630 and 4,540,654 are more preferable.

The cyan couplers that can be used in this invention include phenol-type couplers and naphthol-type couplers, and those described in U.S. Patent Nos. 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011, and 4,327,173, German Patent Application(OLS) No. 3,329,729,European Patent No. 121,365A, U.S. Patent Nos. 3,446,622, 4,333,999, 4,451,559, and 4,427,767, and European Patent No. 161,626A are more preferable.

As a colored coupler to rectify the unnecessary absorption of color-forming dyes, those couplers described in paragraph VII-G of Research Disclosure No. 17643, U.S. Patent No. 4,163,670, Japanese Patent Publication No. 39413/1982, U.S. Patent Nos. 4,004,929 and 4,138,258, and British Patent No. 1,146,368 can be preferably used in the present invention.

As a coupler which forms a dye having moderate diffusibility, those described in U.S. Patent No. 4,366,237, British Patent No. 2,125,570, European Patent No. 96,570, and German Patent Application (OLS) No. 3,234,533 are preferable.

Examples of a polymerized dye-forming coupler are described in U.S. Patent Nos. 3,451,820, 4,080,211, and 4,367,282, and British Patent No. 2,102,173.

A coupler that releases a photographically useful residue can be used favorably in this invention. As a DIR coupler that releases a development retarder, those described in Japanese Patent Application (OPI) Nos. 151944/1982, 154234/1982, and 184248/1985, and U.S. Patent No. 4,248,962, which are cited in paragraph VII-F of the above-mentioned Research Disclosure No. 17643, are preferable.

As a coupler which releases, imagewise, a nucleating agent or a development accelerator upon developing, those described in British Patent Nos. 2,097,140, 2,131,188, and Japanese Patent Application (OPI) No. 157638/1984, and 170840/1984 are preferable.

Other couplers that can be incorporated in the photographic material of this invention include competitive couplers described in U.S. Patent No. 4,130,427, multi-equivalent couplers described in U.S. Patent Nos. 4,283,472, 4,338,393, and 4,310,618, DIR coupers which release a redox compound, as described in Japanese Patent Application (OPI) No. 185950/1985, and couplers which release a dye to regain a color after releasing, as described in European Patent No. 173,302A.

Couplers to be used in this invention may be incorporated in the photographic material by means of various known dispersion processes.

Examples of high boiling solvents for use in an oil-in-water type dispersion process are illustrated, for example, in U.S. Patent No. 2,322,027.

Processes and effects of the latex dispersion process and concrete examples of latex for impregnation are described, for example, in U.S. Patent No. 4,199,363 and German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

Adequate substrate that can be used in this invention are described, for example, on page 28 of the above-mentioned RD No. 17643, and on p. 647 (right column) to p. 648 (left column) of ibid. No. 18716.

The color photograhic material according to this invention can be processed for development by conventional methods, such as described on pp. 28-29 of the above-mentioned RD No. 17643 and on page 651 of ibid. No. 18716.

The silver halide color photographic material of the present invention is generally passed through a washing step and/or a stabilizing step after the desilvering process of fixing or bleach-fixing.

The amount of washing water in the washing step can be set in a wide range depending on the properties of the photographic material (due to the material used, for example, such as the couplers), the uses of the photographic material, the temperature of the washing water, the number of washing tanks (number of steps), the type of replenishing mode, such as counter-current mode or concurrent mode, as well as other conditions. The relationship between the number of washing tanks and the amount of water in the multistage counter-current mode can be determined according to a method described in Journal of the Society of Motion Picture and Television Engineers, Vol. 64, pp. 248-253 (May 1955). The number of steps of the multistage counter-current washing mode is preferably 2 to 6, more preferably 2 to 4.

With the multistage counter-current method the amount of washing water can be decreased considerably. However, bacteria propagate due to the increased time the water remains in the tanks, causing problems such as the adhesion of resulting suspended matter on the photographic material. To solve such problems in the method of processing of the present invention a color photographic material, a method of decreasing calcium and magnesium described in Japanese Patent Application No. 131632/1986 can be effectively used. Other agents that can be used include isothiazolone and cyabendazole compounds, described in Japanese Patent Application (OPI) No. 8542/1982, chlorine-type bactericides such as sodium chlorinated isocyanurate, benzotriazole, and other bactericides, described in Hiroshi Horiguchi Bokinbobai no Kagaku, Biseibutsu no Mekkin, Sakkin, Bobai Gijutsu, edited by Eiseigijutsu kai, and Bokinbobaizai Jiten, edited by Nihon Bokinbobai-gakkai.

The pH of the washing water for processing a photographic material according to the present invention is 4 to 9, preferably 5 to 8. Although the temperature of the washing water and the period for washing are set differently according, for example, to the uses and properties of the photographic material, generally the temperature of the washing water and the period for washing are selected in the range of 15 to 45°C for 20 sec. to 10 min., preferably 25 to 40°C for 30 sec. to 5 min.

Further, in the present invention a photographic material can be processed by using a stabilizing solution directly, instead of the above-mentioned washing water. In such a process of stabilizing, known methods are described, for example, in Japanese Patent Application (OPI) Nos. 8543/1982, 14834/1983, 184343/1984, 220345/1985, 238832/1985, 239784/1985, 239749/1985, 4054/1986, and 118749/1986. Particularly preferable for use is a stabilizing bath containing 1-hydroxyethylidene-1,1-diphosphonic acid, 5-chloro-2-methyl-4-isothiazoline-3-one, bismuth compounds, ammonium compounds, or the like.

In some cases a stabilizing process is carried out after the above-mentioned washing process, an example of which is a stabilizing bath containing formalin and a surface-active agent used as a final bath.

According to the silver halide color photographic material of the present invention, there are attained a superior fastness to diffusion of the employed couplers, a good color reproduction and a high level color-forming property. Further, according to the invention, there are attained a rapid hardening-reaction of gelatin and less posthardening of the film not to soften by swelling even in the rapid and higher-temperature processing over normal temperature to afford a photograph having a excellent preservability.

In addition the silver halide color photographic material of the present invention can afford a photograph with a remarkably inproved sharpness of an image because of high film-strength so as to make the coating layers thinner.

Next, the present invention will be described in detail in accordance with examples, but it should be understood that these examples are not intended to limit the scope of the invention.

Example 1

A color photograhic material (Sample 101) consisting of layers of the following composition was prepared on an undercoated triacetate cellulose film base. (Composition of photosensitive layers).

In the following compositions, the coating amount of silver halide and colloidal silver are each indicated in g/m^2 in terms of silver, the coating amount of the coupler, additive and gelatin are each indicated in g/m^2, and the coating amount of the sensitizing dye is indicated in mol per mol of silver halide in the same layer.

First layer: Emulsion layer Monodisperse silver iodobromide emulsion (fluctuation coefficient: about 15%, silver iodide: 3 mol%, average grain size: 0.5 µm) silver: 0.6

Gelatin	1.0
Coupler E-1	1.0

Second layer: Protective layer Gelatin 0.8

Poly(methyl methacrylate) particles (diameter: 1.0 µm)	0.2
Hardener HT-1	0.1

A surface-active agent was added to each layer as a coating aid.

Preparation of Samples 102 - 116

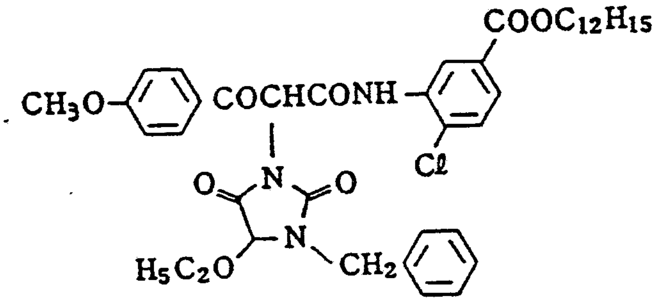
Samples 102 to 116 were prepared by repeating the same procedure as Sample 101, except that the coupler E-1 and the hardener HT-I in Sample 101 were changed to those shown respectively in Table 1. In all samples, a high boiling organic solvent was not used.

On the other hand, in order to determine the film strength of the respective emulsion layers, samples corresponding to Samples 101 to 116 but not coated the second layer (protective layer) were prepared, and the Vickers hardness of each thus-prepared sample was measured by a Terasawa's micro-hardness tester (MM-2 type) (using a Knoop indenter). Vickers hardness is described in D. Talor "The Physical Meaning of Indentation and Scratch. Hardness.", British Journal of Applied Physics Vol. 7 p 260 (1956).

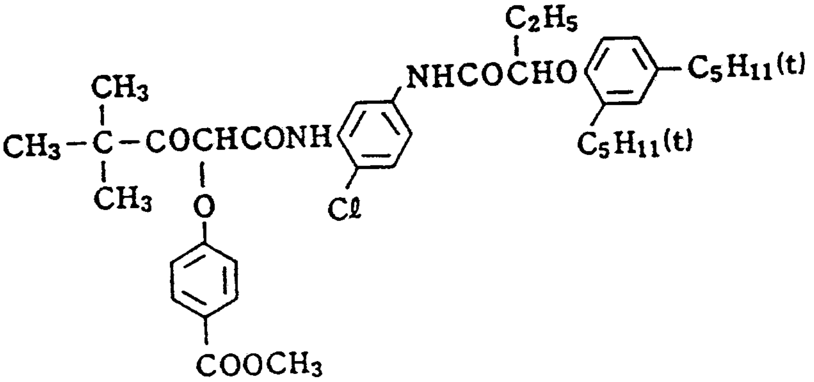
In the preparation of Samples 101 to 116, the oil-soluble coupler (E-1 or E-2) was heated and dissolved in ethyl acetate of an 8-times amount by weight of the coupler. The resulting solution was then mixed with an 8% gelatin aqueous solution (2 times the volume of the coupler solution) containing a surface-active agent W-1, and it was emulsified by a homogenizer. After removing ethyl acetate from the thus-prepared emulsion, it was added to the coating solution. The water-soluble polymer coupler was dissolved in water so as to be a 5 wt. percent solution, and it was then added to the coating solution. The coating amount for Samples 101 to 116 was the same.

The constitution of the materials used are shown below.

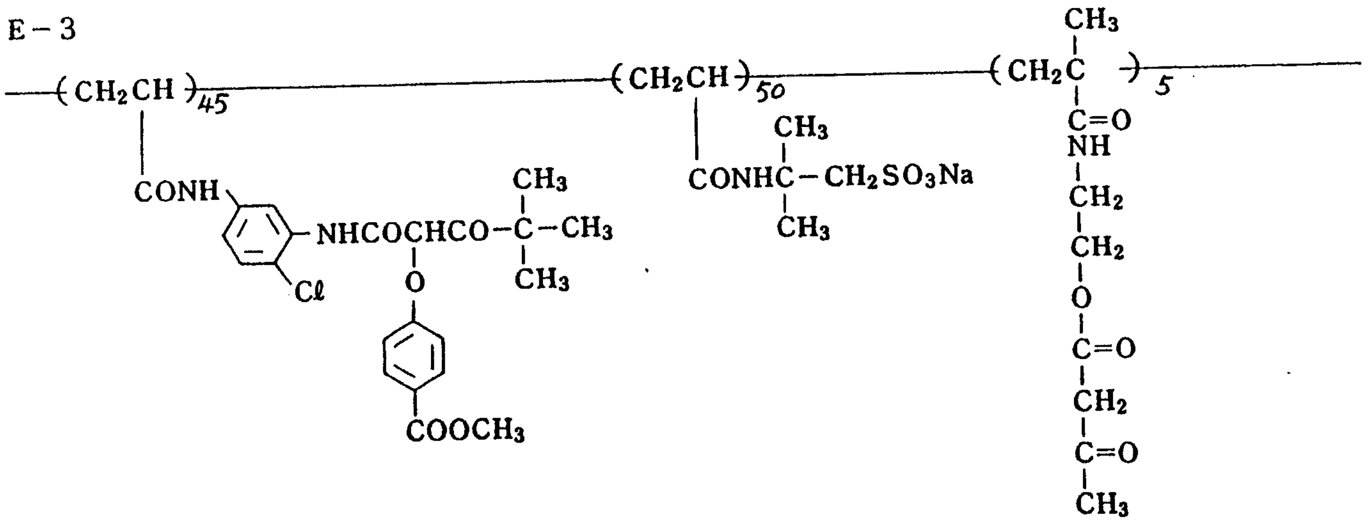
E-1



E-2

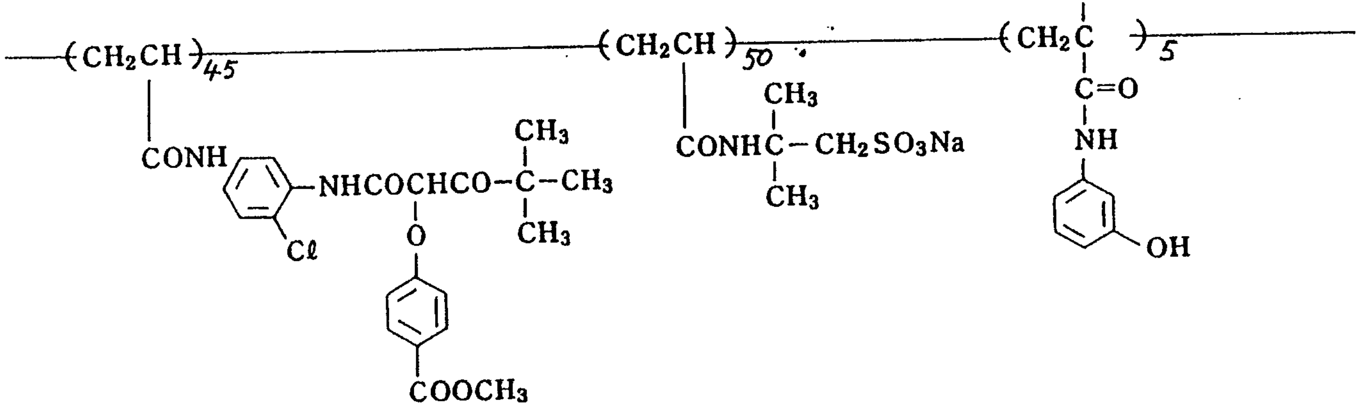


E - 3



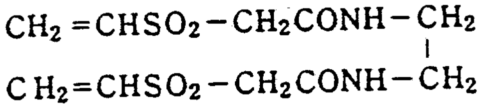
(Compound described in U.S. Patent No. 4,215,195, ratio of instituents is shown in weight ratio.)

E - 4



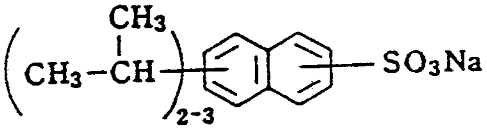
(Compound described in U.S. Patent No. 4,207,109, ratio of instituents is shown in weight ratio.)

HT-1



$$\begin{array}{l} CH_2{=}CHSO_2{-}CH_2CONH{-}CH_2 \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2{=}CHSO_2{-}CH_2CONH{-}CH_2 \end{array}$$

W-1



Each of Samples 101 to 116 was subjected to a light exposure of an Wolfram light source at a color temperature of 4,800°K through a filter so that maximum exposure amount might be 25 CMS, and it was then subjected to development processing at 38°C according to the following process (I).

Processing process (I)	
Color developing	3 min. 15 sec.
Bleaching	6 min. 30 sec.
Water washing	2 min. 10 sec.
Fixing	4 min. 20 sec.
Water washing	3 min. 15 sec.
Stabilizing	1 min. 05 sec.

The composition of each processing solution was as follows:

<u>Color Developing Solution</u>

Diethylenetriaminetetraacetate	1.0 g
1-Hydroxyethylidene-1,1-diphosphonate	2.0 g
Sodium sulfite	4.0 g
Potassium carbonate	30.0 g
Potassium bromide	1.4 g
Potassium iodide	1.3 mg
Hydroxylamine sulfate	2.4 g
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfonate	4.5 g
Water to make	1000 ml
pH 10.0	

<u>Bleaching Solution</u>

Iron (III) ammonium ethylenediaminetetraacetate	100.0 g
Disodium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Ammonium nitrate	10.0 g
Water to make	1000 ml
pH 6.0	

Fixing Solution Disodium ethylenediaminetetraacetate 1.0 g
Sodium sulfite 4.0 g
Ammonium thiosulfite (70%) 175.0 ml
Sodium hydrogensulfite 4.6 g
Water to make 1000 ml
pH 6.6

Stabilizing Solution Formalin (40%) 2.0 ml
Polyoxyethylene-p-monononylphenyl ether (average polymerization degree: 10) 0.3 g
Water to make 1000 ml

A density measurement was conducted on each of the thus-processed samples, and the highest density was shown as D^1.

Further, color photographic materials (Samples 101′ -116′) were prepared by repeating the same procedure as in Samples 101 - 116, except that the composition of the multi-layers was changed as hereinbelow described. These samples were subjected to the same exposure of light and then the same development processing as Samples 101 - 116. A density measurement was conducted on each of the thus-processed samples, and the highest density was shown as D^2. The value D^2/D^1 is indicative of the fastness to diffusion.

(Composition of photosensitive layers)

In the following compositions, each ingredient is indicated as in Sample 101.

First layer: Emulsion layer Monodisperse silver iodobromide emulsion (fluctuation coefficient: about 15%, silver iodide: 3 mol%, average grain size: 0.5 μm) silver: 0.6
Gelatin 1.0

Second layer: Coupler layer Coupler 1.0
Gelatin 1.0

Third layer Gelatin 0.8
Poly(methyl methacrylate) particles (diameter: 1.0 μm) 0.2
Hardener HT-1 0.1

In each layer a surface-active agent was added as a coating aid.
Results are shown in Table 1.

Table 1

Sample No.	Coupler	Film Hardener	Max. Density (D_1)	Film Strength (kg/mm^2)	D_2/D_1
101 (Comparative example)	E-1	HT-1	2.13	13	0
102 (")	E-2	"	1.48	15	0
103 (")	E-3	"	1.17	25	0.25
104 (")	E-4	"	1.12	22	0.23
105 (")	CY-1	"	1.62	25	0.26
106 (")	CY-5	"	1.25	25	0.22
107 (")	E-1	H-3	1.96	11	0
108 (")	E-2	"	1.28	12	0
109 (")	E-3	"	1.16	24	0.25
110 (")	E-4	"	1.10	22	0.24
111 (This invention)	CY-1	"	1.92	27	0.06
112 (")	CY-5	"	1.46	26	0.05
113 (")	CY-1	H-7	1.96	27	0.02
114 (")	CY-2	"	2.03	25	0.04
115 (")	CY-6	H-17	2.10	26	0.02
116 (")	CY-7	"	1.52	26	0.05

Although the water soluble polymer coupler is excellent in film strength as compared to the oil soluble coupler, the degree of diffusion to the other layer is large, as shown in the data of the comparative sample.

In contrast with this, as in the present invention (Samples 111 to 116), when using the hardener acting by activation of the water soluble polymer containing a non-color-forming repeating unit having a carboxyl group and with activation of the carboxyl group, the film strength is excellent and the color-developing property is improved by restraining the diffusion of coupler to the other layers.

Example 2

A color photographic material (Sample 201) was prepared by multi-coatings composed of the following composition on an undercoated triacetate cellulose film base.

(Composition of photosensitive layers)

In the following compositions, each ingredient is indicated as in Example 1.

First layer: Antihalation layer Black colloidal silver 0.2
Gelatin 1.3
Color coupler C-1 0.06
UV absorber UV-1 0.1
UV absorber UV-2 0.2
High-boiling organic solvent Oil-1 0.01
High-boiling organic solvent Oil-2 0.01

Second layer: Intermediate layer Fine particle silver bromide emulsion (average grain size: 0.07 µm) 0.15
Gelatin 1.0
Colored coupler C-2 0.02
High-boiling organic solvent Oil-1 0.1

Third layer: First red-sensitive emulsion layer Silver iodobromide emulsion (silver iodide: 2 mol%, average grain size: 0.3 µm) Silver: 0.4
Gelatin 0.6
Sensitizing dye I 1.0×10^{-4}
Sensitizing dye II 3.0×10^{-4}
Sensitizing dye III 1.0×10^{-5}
Coupler C-3 0.06
Coupler C-4 0.06
Coupler C-8 0.04
Coupler C-2 0.03
High-boiling organic solvent Oil-1 0.03
High-boiling organic solvent Oil-3 0.012

Fourth layer: Second red-sensitive emulsion layer Silver iodobromide emulsion (silver iodide: 5 mol%, average grain size: 0.5 µm) silver: 0.7
Sensitizing dye I 1×10^{-4}
Sensitizing dye II 3×10^{-4}
Sensitizing dye III 1×10^{-5}
Coupler C-3 0.24
Coupler C-4 0.24
Coupler C-8 0.04
Coupler C-2 0.04
High-boiling organic solvent Oil-1 0.15
High-boiling organic solvent Oil-3 0.02

Fifth layer: Third red-sensitive emulsion layer Monodisperse cubic silver iodobromide emulsion (silver iodide: 10 mol%, average grain size: 0.7 µm) silver: 1.0
Gelatin 1.0
Sensitizing dye I 1×10^{-4}
Sensitizing dye II 3×10^{-4}
Sensitizing dye III 1×10^{-5}
Coupler C-6 0.05

Coupler C-7	0.1
High-boiling organic solvent Oil-1	0.01
High-boiling organic solvent Oil-2	0.05

Sixth layer: Intermediate layer Gelatin 1.0

Compound Cpd-A	0.03
High-boiling organic solvent Oil-1	0.05

Seventh layer: First green-sensitive emulsion layer Silver iodobromide emulsion (silver iodide: 4 mol%, average grain size: 0.3 µm) Silver: 0.30

Sensitizing dye IV	5×10^{-4}
Sensitizing dye VI	0.3×10^{-4}
Sensitizing dye V	2×10^{-4}
Gelatin	1.0
Coupler C-9	0.2
Coupler C-5	0.03
Coupler C-1	0.03
High-boiling organic solvent Oil-1	0.5

Eighth layer: Second green-sensitive emulsion layer Silver iodobromide emulsion (silver iodide: 5 mol%, average grain size: 0.5 µm) Silver: 0.4

Gelatin	1.0
Sensitizing dye IV	5×10^{-4}
Sensitizing dye V	2×10^{-4}
Sensitizing dye VI	0.3×10^{-4}
Coupler C-9	0.25
Coupler C-1	0.03
Coupler C-10	0.015
Coupler C-5	0.01
High-boiling organic solvent Oil-1	0.2

Ninth layer: Third green-sensitive emulsion layer Monodisperse cubic silver iodobromide emulsion (silver iodide: 6 mol%, average grain size: 0.7 µm) silver: 0.85

Gelatin	1.0
Sensitizing dye VII	3.5×10^{-4}
Sensitizing dye VIII	1.4×10^{-4}
Coupler C-11	0.01
Coupler C-12	0.03
Coupler C-13	0.20
Coupler C-1	0.02
Coupler C-15	0.02
High-boiling organic solvent Oil-1	0.20
High-boiling organic solvent Oil-2	0.05

Tenth layer: Yellow filter layer Gelatin 1.2

Yellow colloidal silver	0.08
Compound Cpd-B	0.1
High-boiling organic solvent Oil-1	0.3

Eleventh layer: First blue-sensitive emulsion layer Monodisperse silver iodobromide emulsion (silver iodide: 4 mol%, average grain size: 0.3 µm) silver: 0.4

Gelatin 1.0
Sensitizing dye IX 2×10^{-4}
Coupler E-1 0.9
Coupler C-5 0.07

Twelfth layer: Second blue-sensitive emulsion layer Monodisperse cubic silver iodobromide emulsion (silver iodide: 10 mol%, average grain size: 1.5 µm) silver: 0.5

Gelatin 0.6
Sensitizing dye IX 1×10^{-4}
Coupler E-1 0.25

Thirteenth layer: First protective layer Gelatin 0.8

UV absorber UV-1 0.1
UV absorber UV-2 0.2
High-boiling organic solvent Oil-1 0.01
High-boiling organic solvent Oil-2 0.01

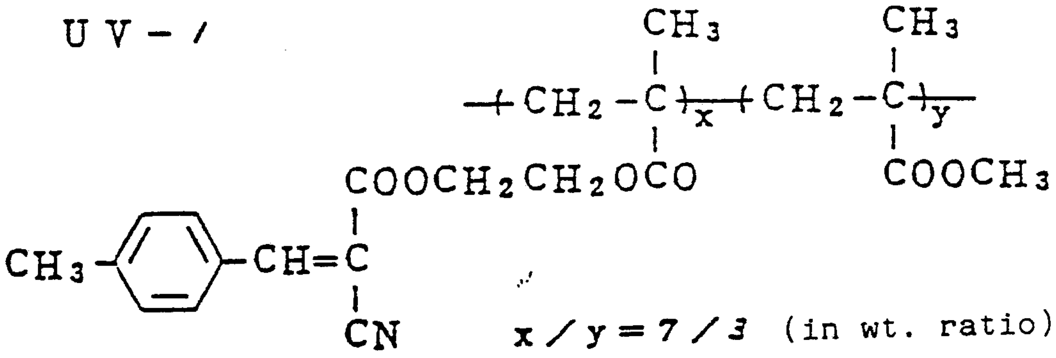
Fourteenth layer: Second protective layer Fine-particle silver bromide (average grain size: 0.07 µm) 0.5

Gelatin 0.45
Poly(methyl methacrylate) particles (average particle diameter: 1.5 µm)0.2
Hardener HT-1 0.4
Formaldehyde-scavenger FO-1 0.5
Formaldehyde-scavenger FO-2 0.5

In each layer described above, a surface-active agent was added as a coating aid.

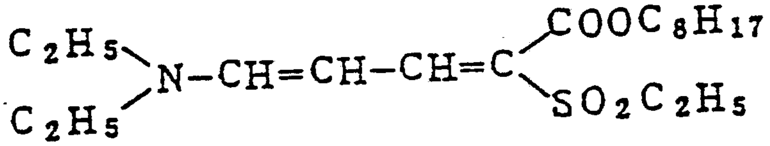
The structural formula or chemical name of the compound used in this Example are shown below.

UV - 1



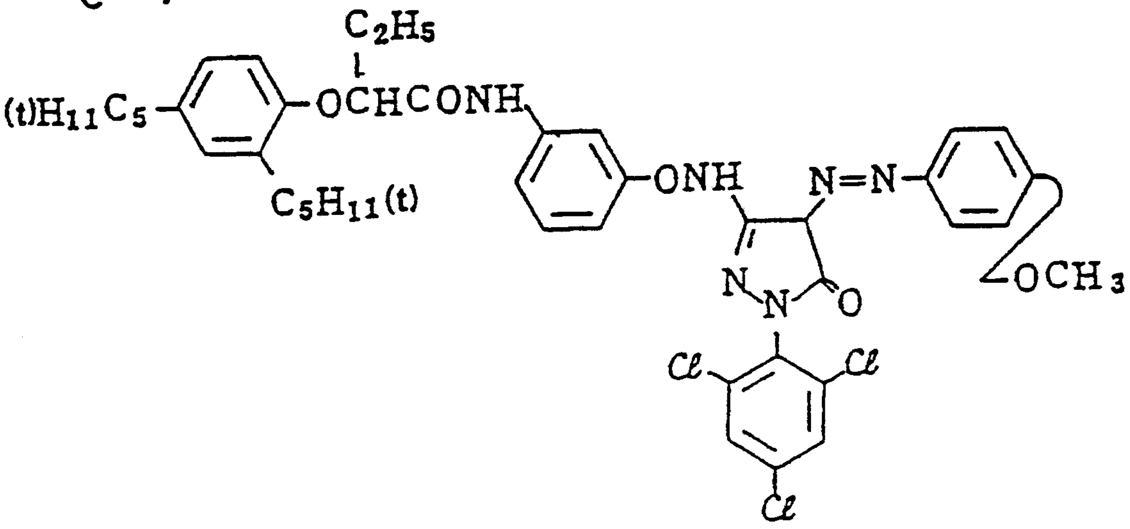
x / y = 7 / 3 (in wt. ratio)

UV - 2

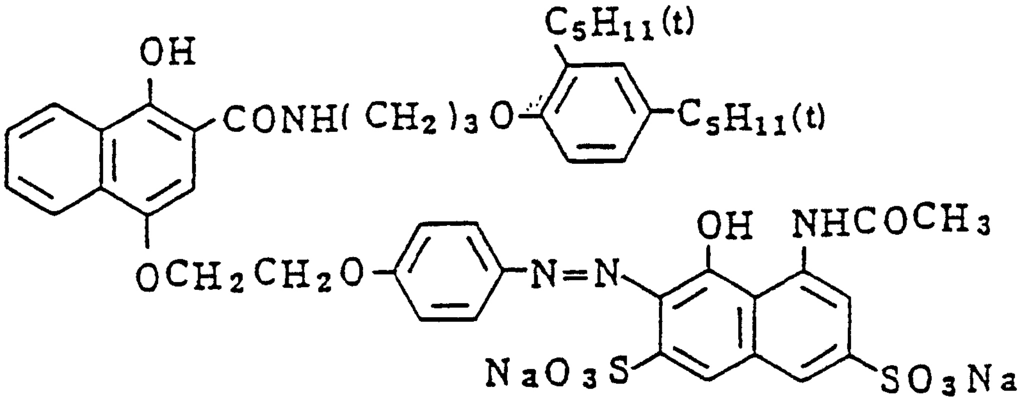


Oil - 1	Tricresyl phosphate
Oil - 2	Dibutyl phthalate
Oil - 3	Bis(2-ethylhexyl)phthalate

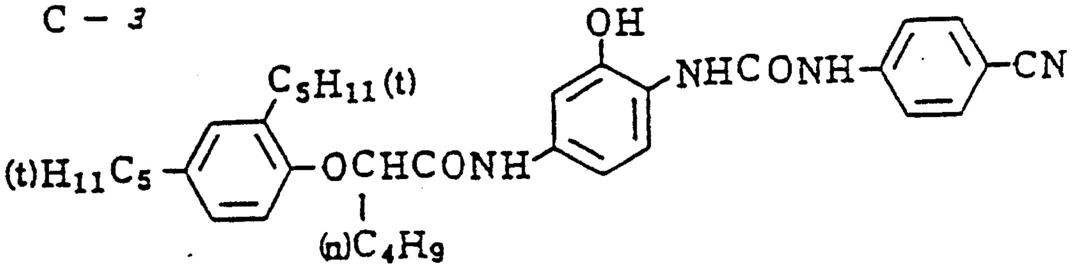
C - 1



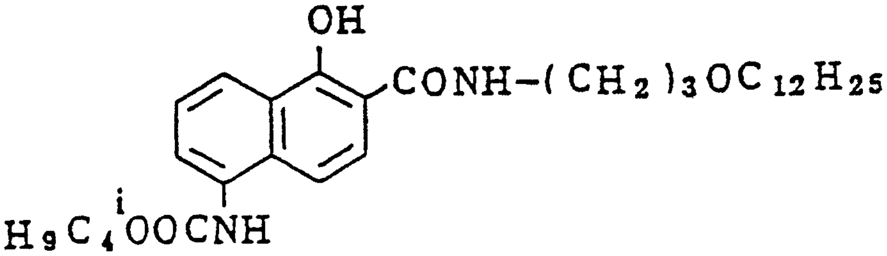
C - 2



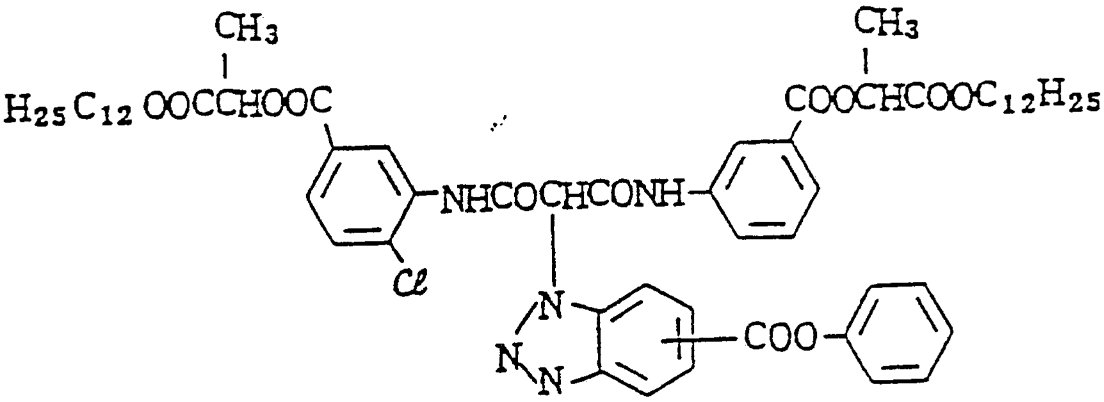
C - 3



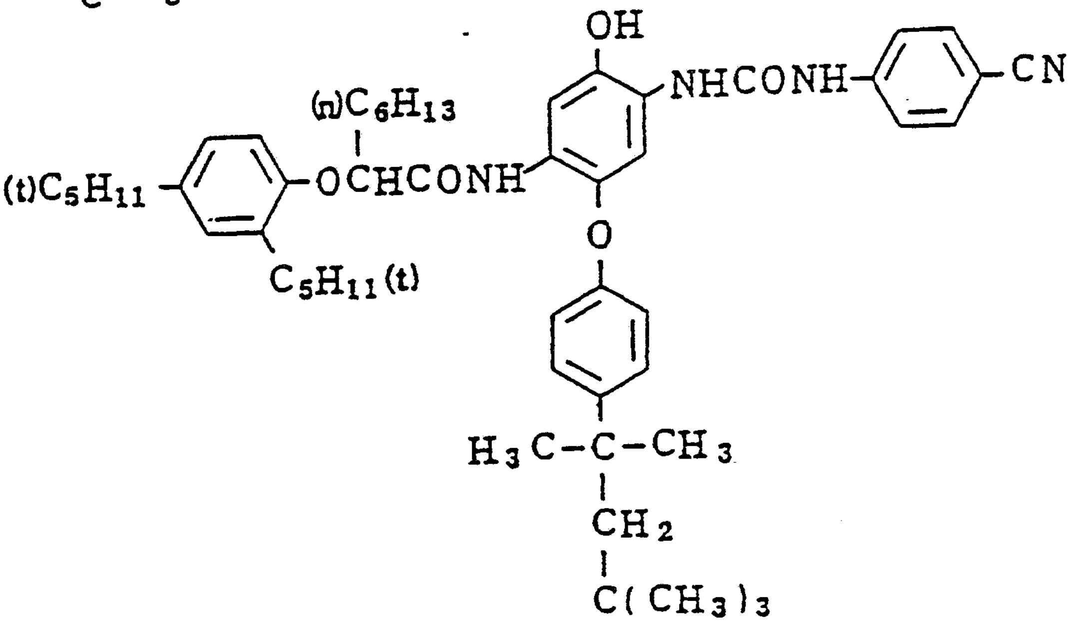
C - 4



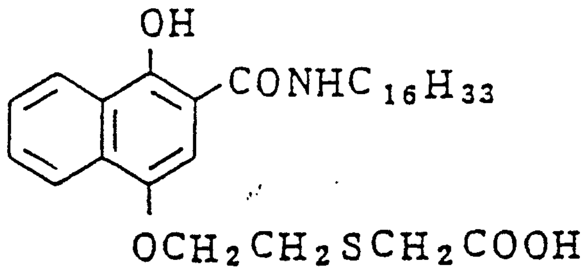
C - 5


CH3
H25C12 OOCCHOOC
NHCOCHCONH
CH3
COOCHCOOC12H25
Cl
N
N
N
COO

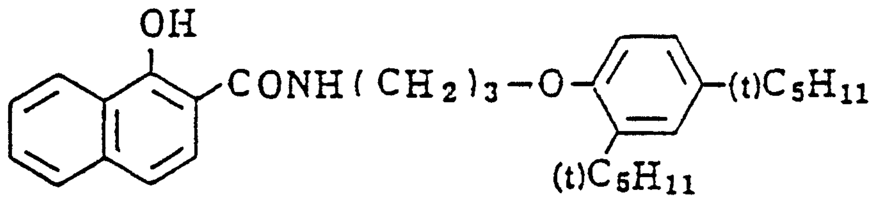
C - 6


OH
NHCONH
CN
(n)C6H13
(t)C5H11
OCHCONH
C5H11(t)
O
H3C-C-CH3
CH2
C(CH3)3

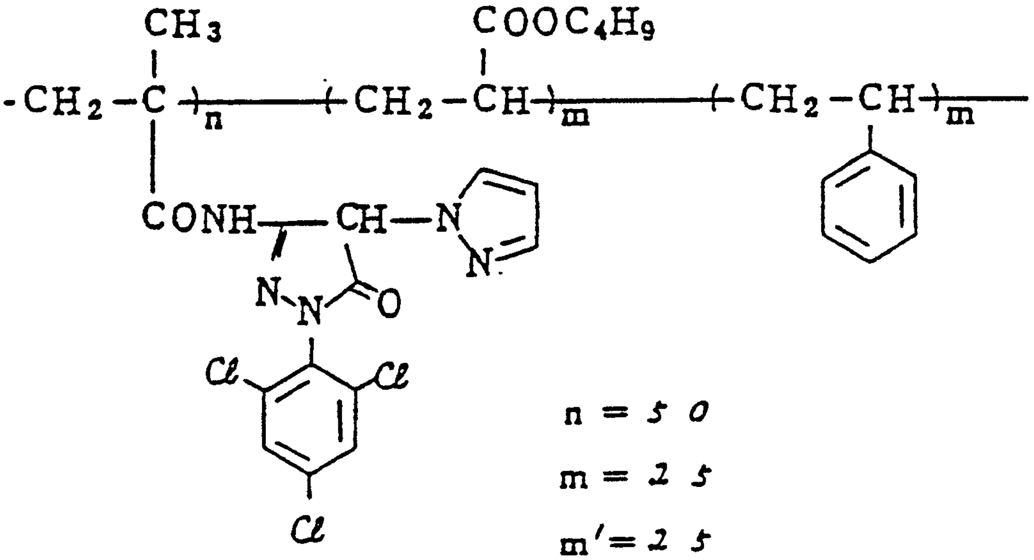
C - 7



C - 8



C - 9



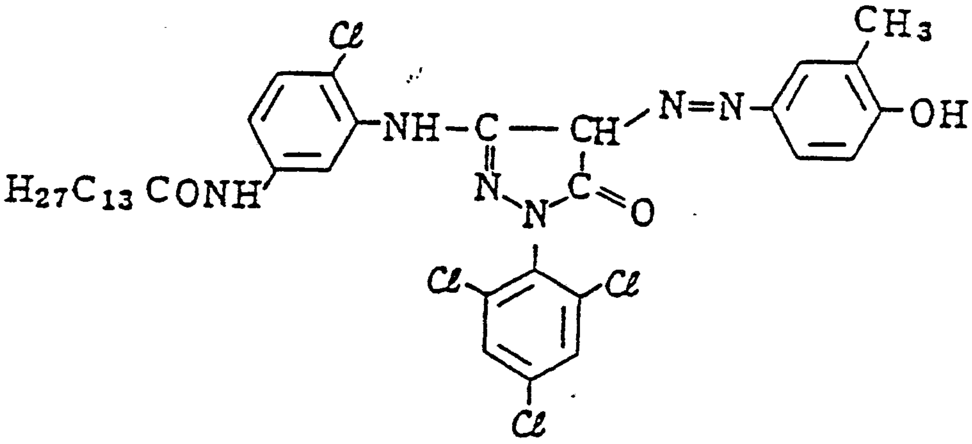
n = 50

m = 25

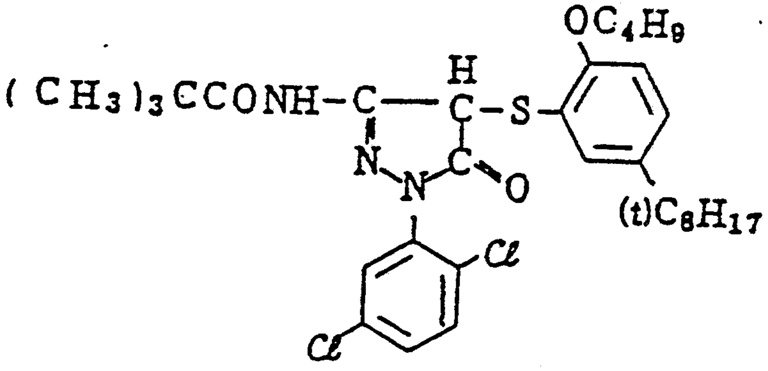
m′ = 25

molecular weight : about 20,000

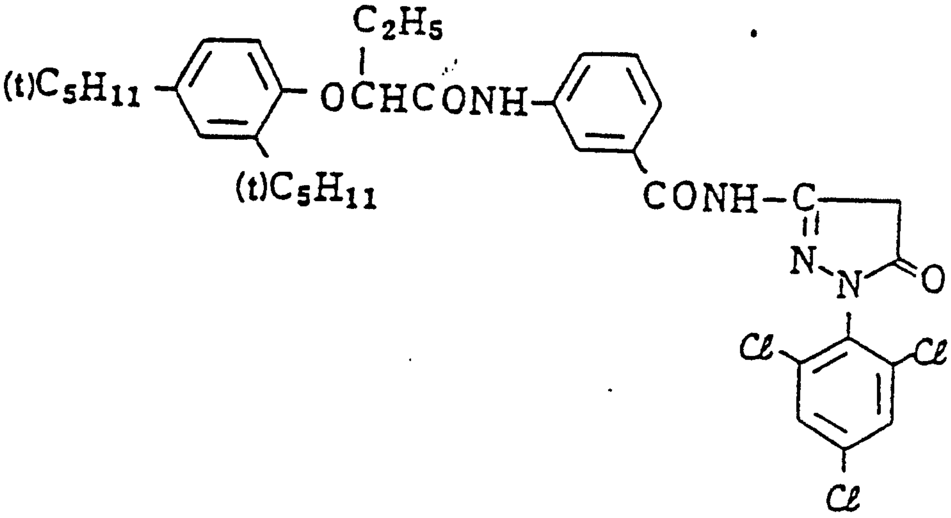
C-10


Cl
CH3
NH-C
CH
N=N
OH
H27C13 CONH
N
N
C
O
Cl
Cl
Cl

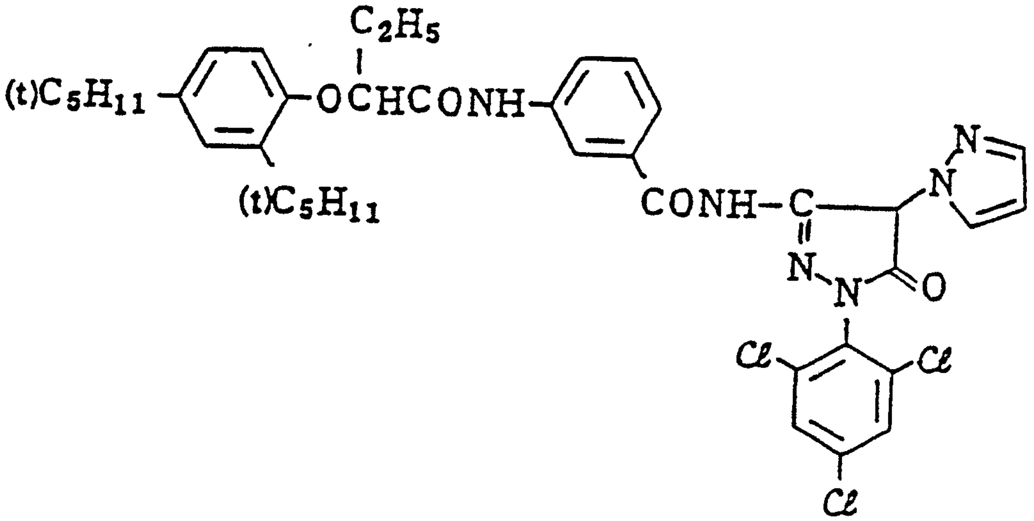
C-11


OC4H9
H
(CH3)3CCONH-C
C-S
N
N
C
O
(t)C8H17
Cl
Cl

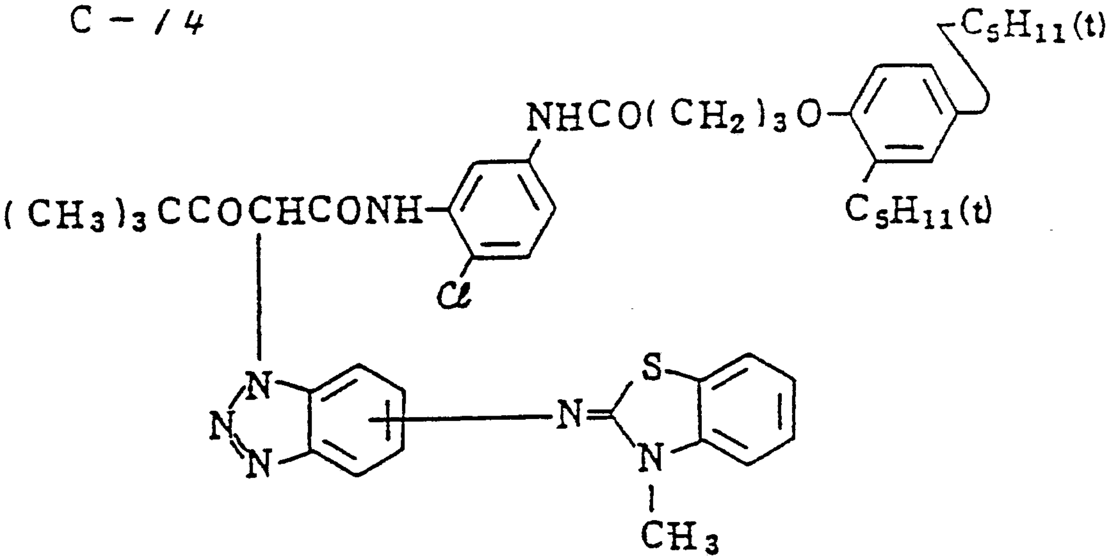
C－12



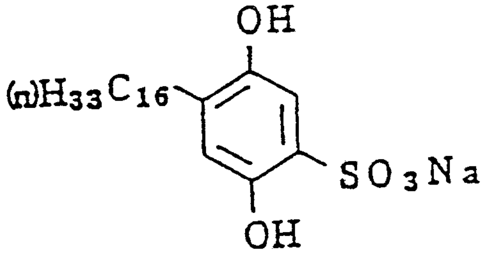
C－13



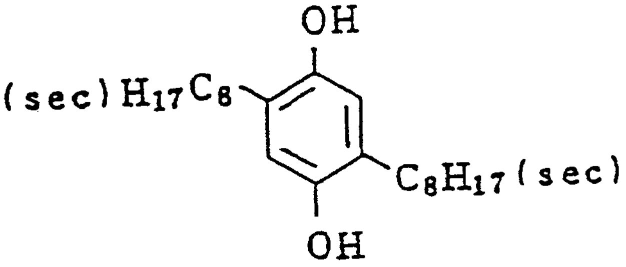
C－14



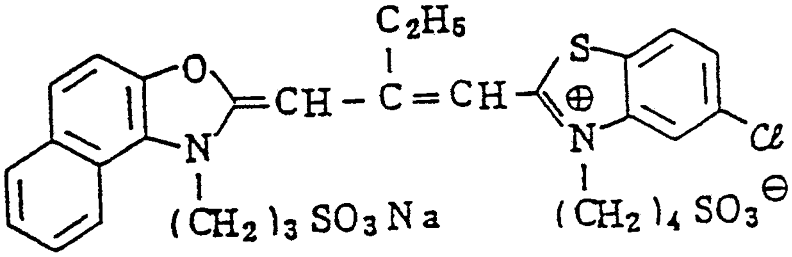
Cpd A



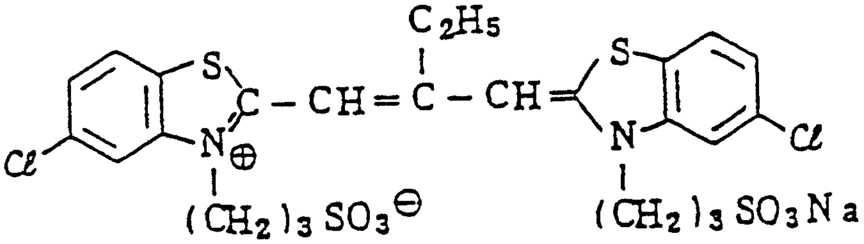
Cpd B



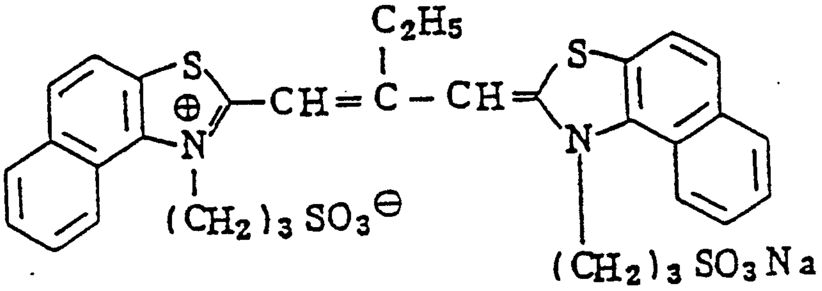
Sensitizing dye I



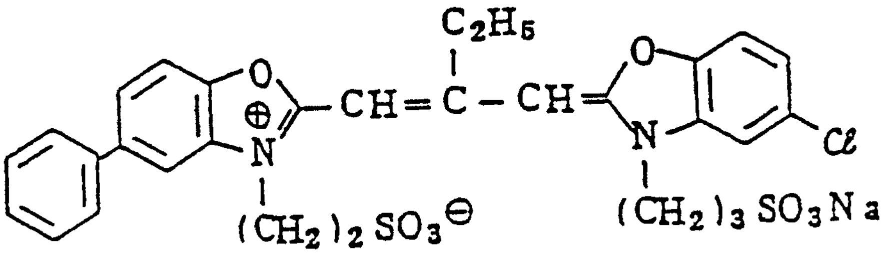
Sensitizing dye II



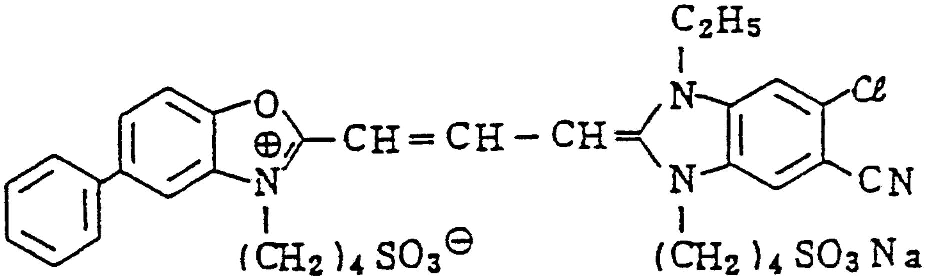
Sensitizing dye III



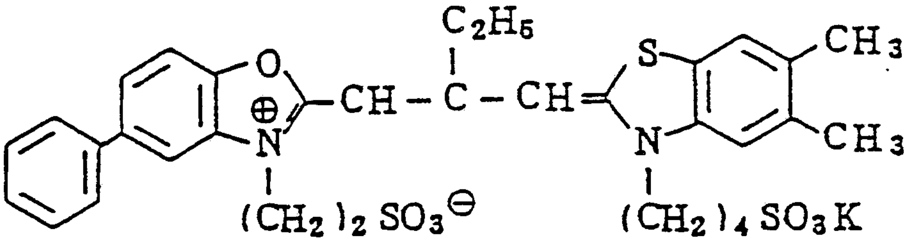
Sensitizing dye IV



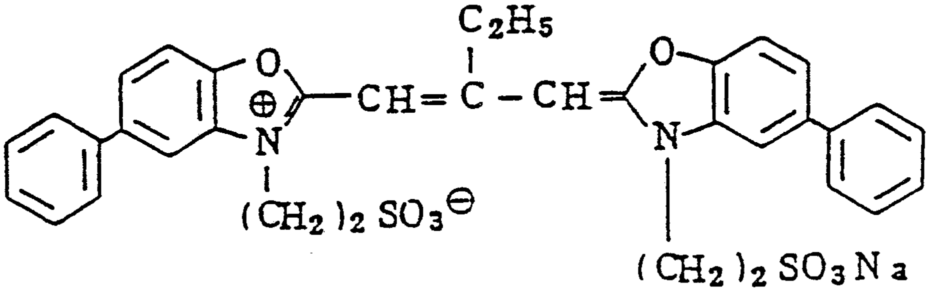
Sensitizing dye V



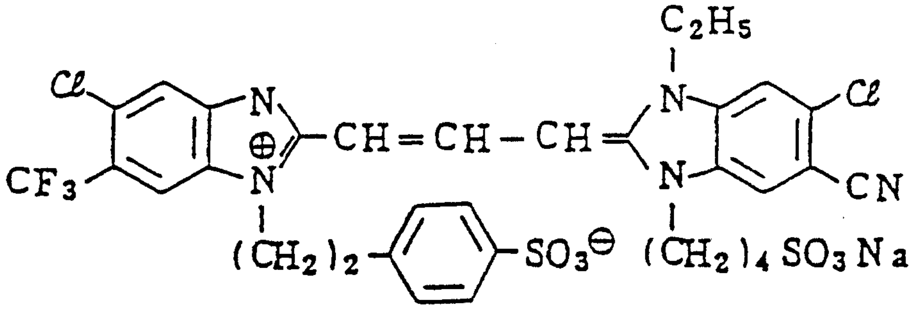
Sensitizing dye VI



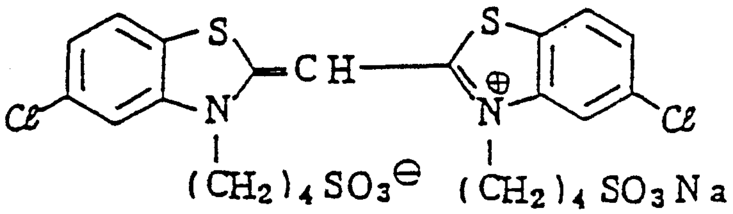
Sensitizing dye VII



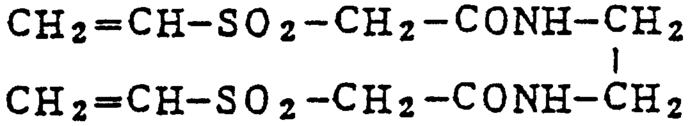
Sensitizing dye VIII



Sensitizing dye IX

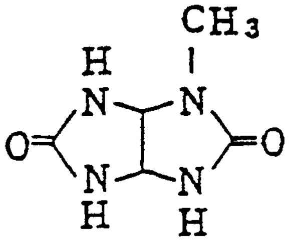


HT-1

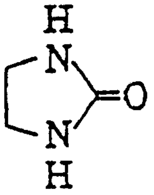


$$\begin{array}{l} CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \end{array}$$

FO-1



FO-2



Preparation of Samples 202 to 209

The same procedure as for Sample 201 was repeated, except that the coupler E-1 in the 11th layer and the 12th layer and the hardener HT-1 in the 14th layer were changed to those shown in Table 2 at equal molar ratios, thus preparing Samples 202 to 209. These samples were each subjected to an exposure of green light through a wedge and then to development processing according to the following processing process (II).

The density of each thus-processed sample was measured, and the density of yellow at the magenta color-forming layer was evaluated as a criterion for coupler diffusion from the blue-sensitive layer to the green-sensitive layer.

Processing process (II)

Color developing	3 min. 15 sec.	38°C
Bleaching	30 sec.	"
Bleach-fixing	1 min. 30 sec.	"
Rinsing	1 min. 40 sec.	"
Stabilizing	40 sec.	"

The composition of each processing solution was as follows:

Color developing solution

Same as processing process (I).

Bleaching solution

Ammonium bromide	100 g
Iron (III) ammonium ethylenediaminetetraacetate	120 g
Disodium ethylenediaminetetraacetate	10.0 g
Ammonium nitrate	10.0 g
Bleach accelerator	2.0 g
Aqueous ammonia	17.0 ml
Water to make	1000 ml
pH: 6.5	

Bleach-fixing solution

Ammonium bromide	50.0 g
Iron (III) ammonium ethylenediaminetetraacetate	50.0 g
Disodium ethylenediaminetetraacetate	5.0 g
Ammonium nitrate	5.0 g
Sodium sulfite	12.0 g
Ammonium thiosulfite (70% of aqu. solution)	240 ml
Aqueous ammonia	10.0 ml
Water to make	1000 ml
pH: 7.3	

Rinsing Solution

Disodium ethylenediaminetetraacetate	0.4 g
Water to make	1000 ml
By sodium hydroxide	pH: 7.0

Stabilizing solution Formalin (40%) 2.0 ml
Poly(oxyethylene-p-monononylphenyl ether) (average polymerization degree: about 10) 0.3 g
Water to make 1000 ml

Table 2

Sample No.	Coupler	Film Hardener	Yellow density* at Magenta Density ** 1.0
201 (Comparative example)	E-1	HT-1	± 0
202 (")	E-3	"	+ 0.14
203 (")	CY-1	"	+ 0.19
204 (")	E-1	H-3	± 0
205 (")	E-3	"	+ 0.15
206 (This invention)	CY-1	"	+ 0.02
207 (")	CY-5	"	+ 0.01
208 (")	CY-2	H-7	+ 0.02
209 (")	CY-6	H-17	+ 0.03

*, ** : Each is shown the value when $D_{min} = 0$.

The thus-obtained samples according to the present invention were all of excellent film strength. As is apparent from the results in Table 2, the diffusion of couplers to other layers of samples of the present invention is restrained to such a degree as to present no practical problem.

Example 3

A color photographic material was prepared by multi-coatings composed of the following composition on an undercoated triacetate cellulose film base as Sample 301.

First layer: Antihalation layer

Gelatin layer (dry film thickness: 2 µm) comprising the following ingredients:

Black colloidal silver	0.25 g/m^2
UV absorber U-1	0.04 g/m^2
UV absorber U-2	0.1 g/m^2
UV absorber U-3	0.1 g/m^2
High-boiling organic solvent Oil-2	0.11 ml/m^2

Second layer: Intermediate layer

Gelatin layer (dry film thickness: 1 µm) comprising the following ingredients:
Compound Cpd-C 0.05 g/m^2
Compound I-1 0.05 g/m^2
High-boiling organic solvent Oil-1 0.05 ml/m^2

Third layer: First red-sensitive emulsion layer

Gelatin layer (dry film thickness: 1 µm) comprising the following ingredients:
Silver bromide emulsion spectral-sensitized by sensitizing dyes S-1 and S-2 (average grain size: 0.3 µm, AgI: 4 mol%) silver: 0.8 g/m^2
Coupler F-1 0.2 g/m^2
Coupler F-2 0.05 g/m^2
Compound I-2 2×10^{-3} g/m^2
High-boiling organic solvent Oil-1 0.12 ml/m^2

Fourth layer: Second red-sensitive emulsion layer

Gelatin layer (dry film thickness: 2.5 µm) comprising the following ingredients:
Silver bromide emulsion spectral-sensitized by sensitizing dye S-1 and S-2 (average grain size: 0.6 µm, AgI: 3 mol%) silver: 0.8 g/m^2
Coupler F-1 0.55 g/m^2
Coupler F-2 0.14 g/m^2
Compound I-2 1×10^{-3} g/m^2
High-boiling organic solvent Oil-1 0.33 ml/m^2
Dye D-1 0.2 g/m^2

Fifth Layer: Intermediate layer

Gelatin layer (dry film thickness: 1 µm) comprising the following ingredients:
Compound Cpd-C 0.1 g/m^2
High-boiling organic solvent Oil-1 0.1 ml/m^2
Dye D-2 0.02 g/m^2

Sixth Layer: First green-sensitive emulsion layer

Gelatin layer (dry film thickness: 1 µm) comprising the following ingredients:
Silver iodobromide emulsion containing the sensitizing dyes S-3 and S-4 (average grain size: 0.3 µm, AgI: 4 mol%) silver: 0.7 g/m^2
Coupler F-3 0.20 g/m^2
Coupler F-5 0.10 g/m^2
High-boiling organic solvent Oil-1 0.26 ml/m^2

Seventh layer: Second green-sensitive emulsion layer

Gelatin layer (dry film thickness; 2.5 µm) comprising the following ingredients:
Silver iodobromide emulsion containing the sensitizing dyes S-3 and S-4 (average grain size: 0.6 µm, AgI: 2.5 mol%) silver: 0.7 g/m^2
Coupler F-4 0.10 g/m^2
Coupler F-5 0.10 g/m^2
High-boiling organic solvent Oil-2 0.05 ml/m^2
Dye D-3 0.05 g/m^2

Eighth layer: Intermediate layer

Gelatin layer (dry film thickness: 1 µm) comprising the following ingredients:

Compound Cpd-C	0.05 g/m^2
High-boiling organic solvent Oil-2	0.1 ml/m^2
Dye D-4	0.01 g/m^2

Ninth layer: Yellow filter layer

Gelatin layer (dry film thickness; 1 µm) comprising the following ingredients:

Yellow colloidal silver	0.1 g/m^2
Compound Cpd-C	0.02 g/m^2
Compound Cpd-B (same as Example 1)	0.03 g/m^2
High-boiling organic solvent Oil-1	0.04 ml/m^2

Tenth layer: First blue-sensitive emulsion layer

Gelatin layer (dry film thickness: 1.5 µm) comprising the following ingredients:

Silver iodobromide emulsion containing the sensitizing dye S-5 (average grain size: 0.3 µm, AgI: 2 mol%)	silver 0.6 g/m^2
Coupler F-6	0.5 g/m^2

Eleventh layer: Second blue-sensitive emulsion layer

Gelatin layer (dry film thickness: 3 µm) comprising the following ingredients:

Silver iodobromide emulsion containing the sensitizing dye S-6 (average grain size: 0.6 µm, AgI: 2 mol%)	silver: 1.1 g/m^2
Coupler F-6	1.3 g/m^2
Dye D-5	0.02 g/m^2

Twelfth layer: First protective layer

Gelatin layer (dry film thickness: 2 µm) comprising the following ingredients:

UV absorbent U-1	0.02 g/m^2
UV absorbent U-2	0.32 g/m^2
UV absorbent U-3	0.03 g/m^2
High-boiling organic solvent Oil-2	0.28 ml/m^2

Thirteenth layer: Second protective layer

Gelatin layer (dry film thickness: 2.5 µm) comprising the following ingredients:

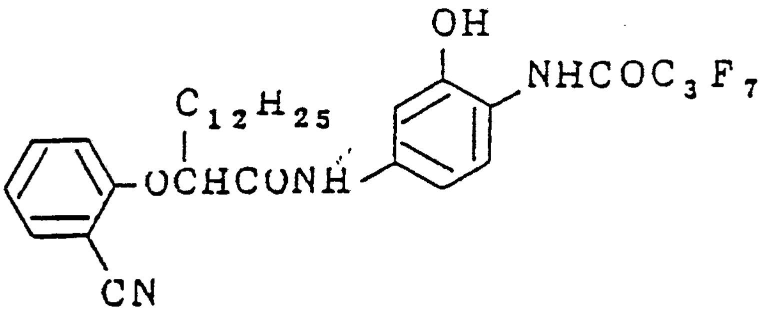
Surface fogged fine-particle silver iodobromide emulsion (average grain size: 0.06 µm, I: 1 mol%) silver: 0.1 g/m^2

Poly(methyl methacrylate) particles (average particle diameter: 1.5 µm)

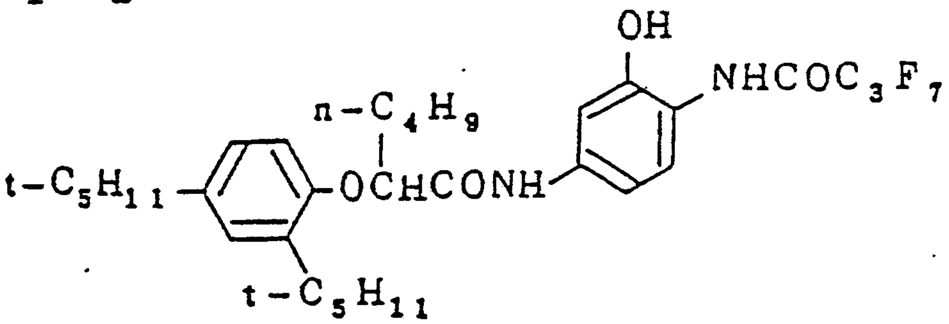
In each layer described above, a gelatin hardener HT-1 (Same as in Example 1) and a surfactant were added.

The compounds used in the above layers were as follows:

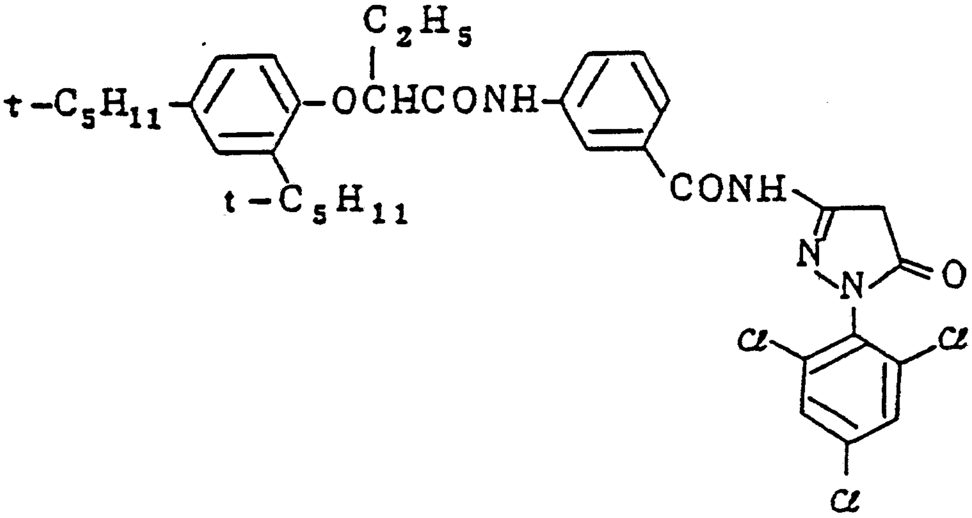
F - 1



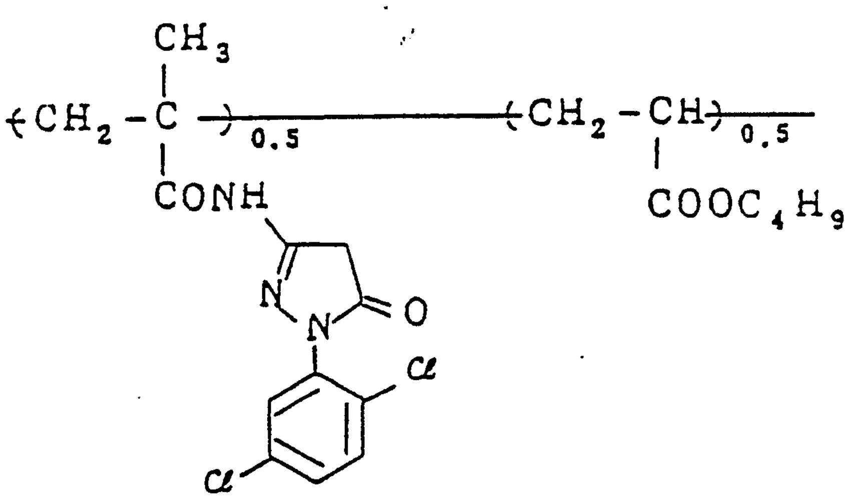
F - 2



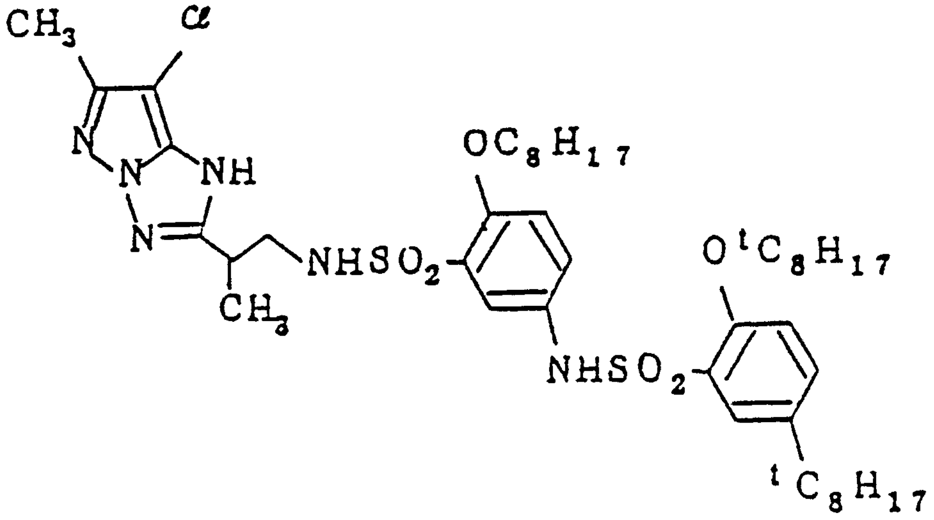
F - 3



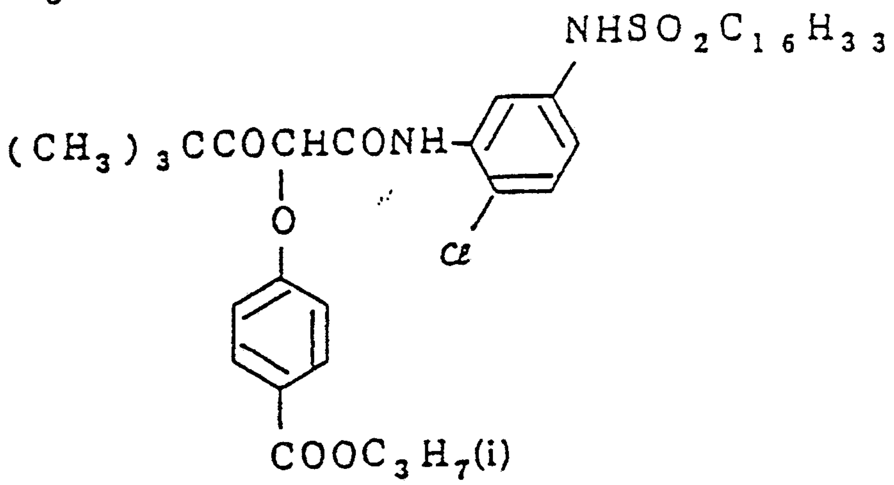
F - 4


CH3
CH2
C
0.5
CH2
CH
0.5
CONH
COOC4H9
N
N
O
Cl
Cl

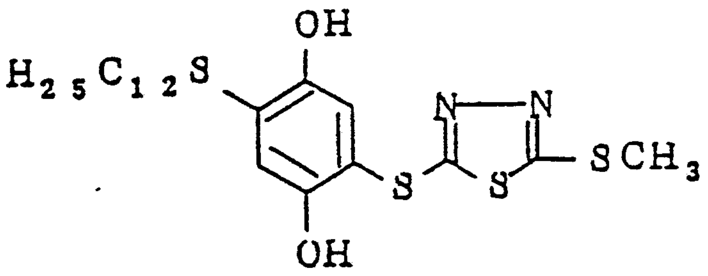
F - 5


CH3
Cl
N
N
NH
N
CH3
NHSO2
OC8H17
NHSO2
OtC8H17
tC8H17

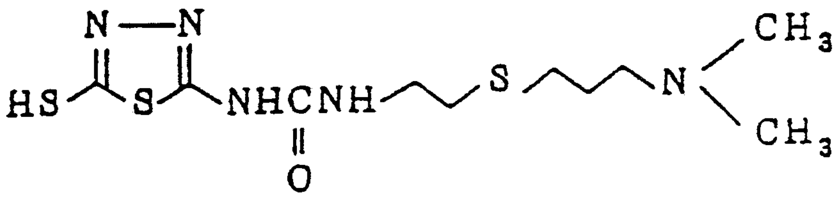
F - 6



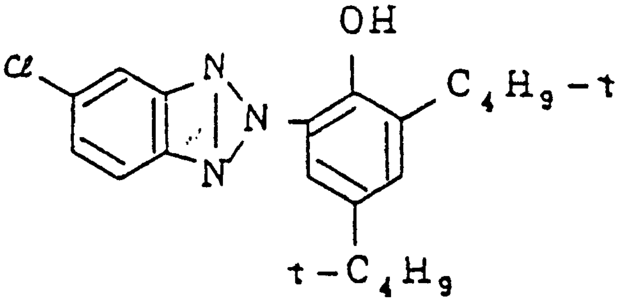
Compound I-1



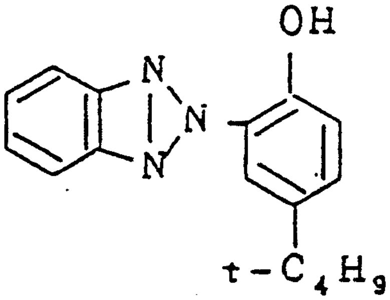
Compound I-2



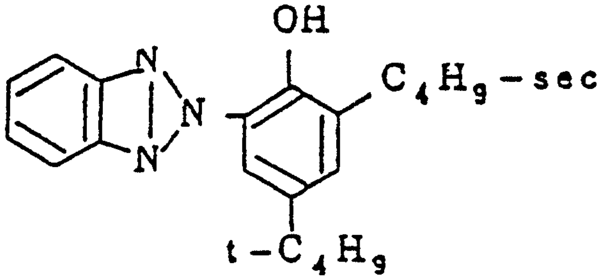
U - 1



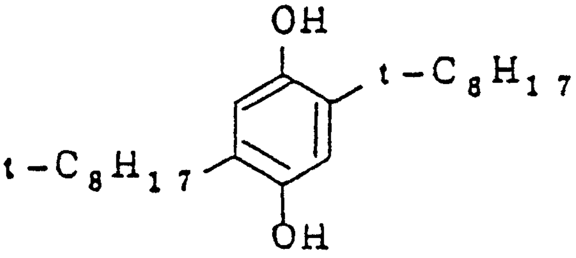
U - 2



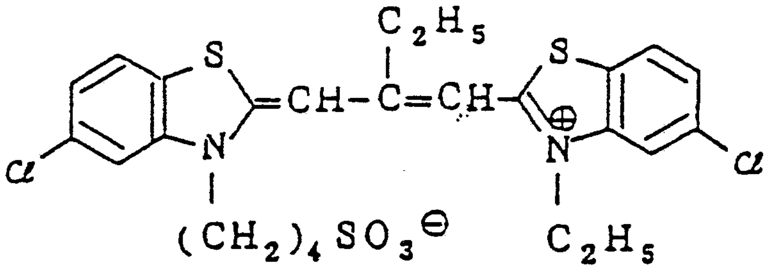
U - 3



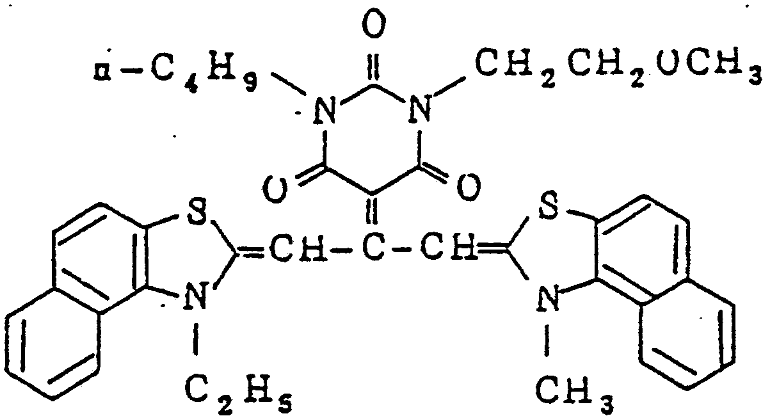
Cpd C



S - 1



S - 2



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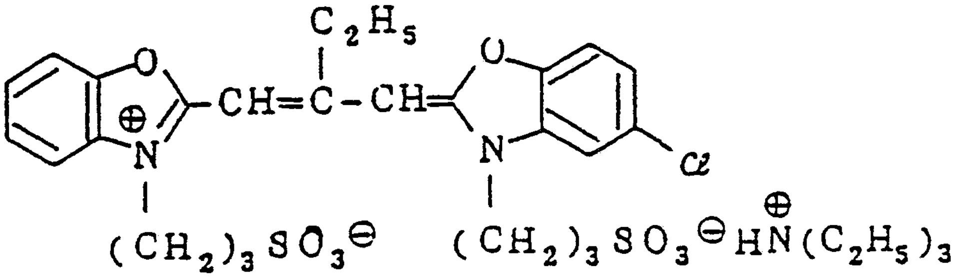
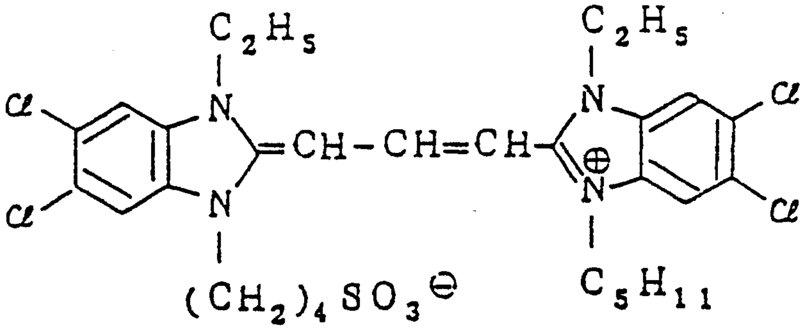
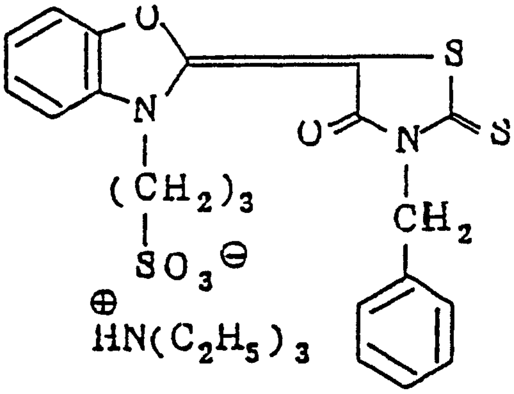


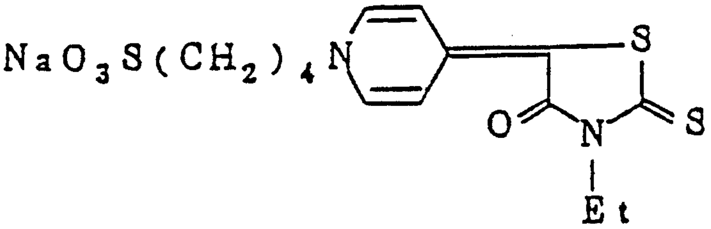
S - 4



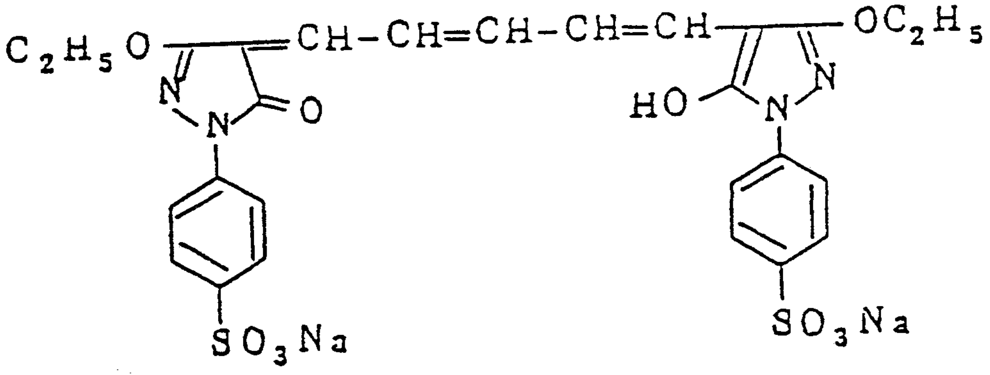
S - 5



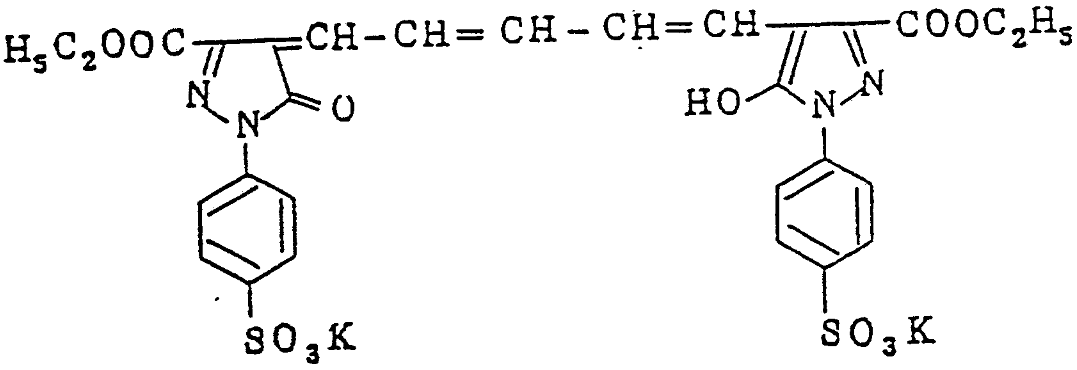
S - 6



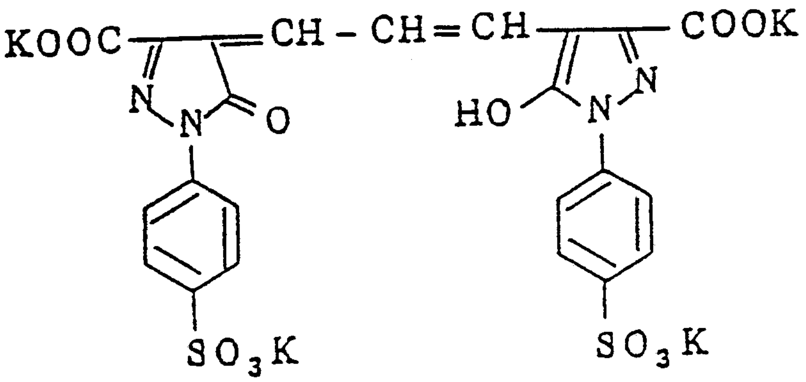
D - 1



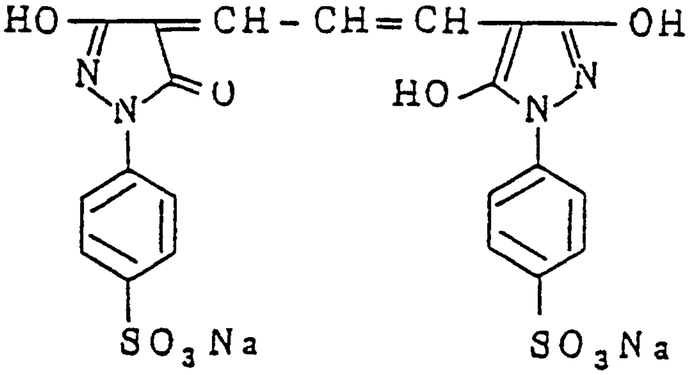
D - 2



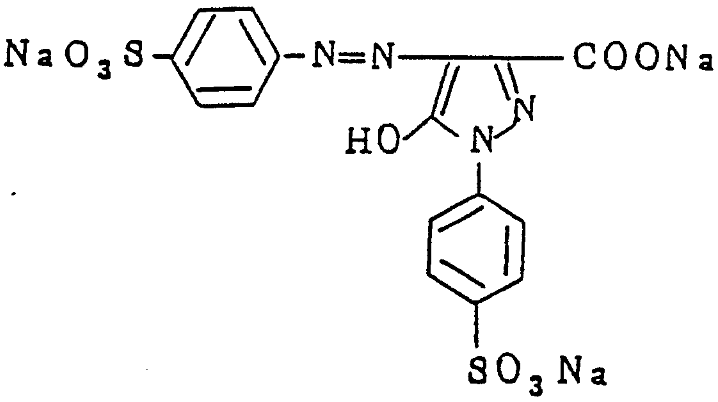
D - 3



D - 4



D - 5



The high-boiling organic solvents Oil-1 and Oil-2 are the same as in Example 2.

The emulsion grains used in the 10th layer and 11th layer of Sample 301 are both plate-twin type, having an aspect ratio of 8.

Preparation of Samples 302 to 310

The same procedure as for Sample 301 was repeated, except that the coupler F-6 in the 10th layer and the 11th layer and the film hardener HT-1 in the 13th layer were changed to those shown in Table 3, thus preparing Samples 302 to 310. Each of Samples 301 to 310 were subjected to an exposure of white light through a wedge and then to processing as described below.

The same density measurement as in Example 2 was conducted on each of the thus-processed samples, and the results are shown in Table 3. The samples according to the present invention were of excellent film strength, and as is apparent from the results in this Table, the diffusion of couplers to other layers of these samples are restrained to such a level as to present no practical problem.

Processing process (III)

Step	Time	Temperature
First developing	6 min.	38°C
Water washing	2 min.	"
Reversal	2 min.	"
Color developing	6 min.	"
Conditioning	2 min.	"
Bleaching	6 min.	"
Fixing	4 min.	"
Water washing	4 min.	"
Stabilizing	1 min.	Room temperature
Drying		

The composition of each processing solution was as follows:

First developing solution	
Water	700 ml
Pentasodium nitrilo-N,N,N-trimethylenephosphonate	2 g
Sodium sulfite	20 g
Hydroquinone monosulfonate	30 g
Sodium carbonate monohydrate	30 g
1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolydone	2 g
Potassium bromide	2.5 g
Potassium thiocyanate	1.2 g
Potassium iodide (0.1 % aqu. solution)	2 ml
Water to make	1000 ml

Reversal solution	
Water	700 ml
Pentasodium nitrilo-N,N,N-trimethylene phosphonate	3 g
Stannous chloride dihydrate	1 g
p-Aminophenol	0.1 g
Sodium hydroxide	8 g
Glacial acetic acid	15 ml
Water to make	1000 ml

Color developing solution	
Water	700 ml
Pentasodium nitrilo-N,N,N-trimethylene phosphonate	3 g
Sodium sulfite	7 g
Trisodium phosphate (12 H^2O)	36 g
Potassium bromide	1 g
Potassium iodide (0.1% aqu. solution)	90 ml

Sodium hydroxide	3 g
Citrazinic acid	1.5 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	11 g
3,6-Dithiaoctane-1,8-diol	1 g
Water to make	1000 ml

Conditioner		
	Water	700 ml
	Sodium sulfite	12 g
	Sodium ethylenediaminetetraacetate dihydrate	8 g
	Thioglycerol	0.4 ml
	Glacial acetic acid	3 ml
	Water to make	1000 ml

Bleaching solution		
	Water	800 ml
	Sodium ethylenediaminetetraacetate dihydrate	2 g
	Iron (III) ammonium ethylenediaminetetraacetate dihydrate	120 g
	Potassium iodide	100 g
	Water to make	1000 ml

Fixing solution		
	Water	800 ml
	Sodium thiosulfate	80.0 g
	Sodium sulfate	5.0 g
	Sodium bisulfite	5.0 g
	Water to make	1000 ml

Stabilizing solution		
	Water	800 ml
	Formalin 37 wt.%)	5.0 ml
	Fuji Driwel (tradename, surfactant, made by Fuji Photo Film Co.)	5.0 ml
	Water to make	1000 ml

Table 3

Sample No.	Coupler	Film Hardener	Yellow density* at Magenta Density ** 1.0
301 (Comparative example)	F-6	HT-1	± 0
302 (")	E-3	"	+ 0.18
303 (")	CY-5	"	+ 0.22
304 (")	F-6	H-3	± 0
305 (")	E-3	"	+ 0.17
306 (This invention)	CY-5	"	+ 0.02
307 (")	CY-3	"	+ 0.01
308 (")	CY-4	H-7	+ 0.01
309 (")	CY-5	H-17	+ 0.02
310 (")	CY-7	H-38	+ 0.02

*, ** : Each is shown the value when $D_{min} = 0$.

Example 4

Samples 401 to 416 were prepared by repeating the same procedure as in Example 1, except that the polymer couplers were changed to those shown in Table 4.

The thus-prepared samples were subjected to the same treatments as Example 1 and then the same measurements as Example 1 were conducted.

Results are shown in Table 4.

Table 4

Sample No.	Coupler	Film Hardener	Max. Density (D_1)	Film Strength (kg/mm^2)	D_2/D_1
401 (Comparative example)	E-1	HT-1	2.13	13	0
402 (")	E-2	"	1.48	15	0
403 (")	E-3	"	1.17	25	0.25
404 (")	E-4	"	1.12	22	0.23
405 (")	Y-1	"	1.62	25	0.26
406 (")	Y-5	"	1.25	25	0.22
407 (")	E-1	H-3	1.96	11	0
408 (")	E-2	"	1.28	12	0
409 (")	E-3	"	1.16	24	0.25
410 (")	E-4	"	1.10	22	0.24
411 (This invention)	Y-1	"	1.92	27	0.05
412 (")	Y-5	"	1.46	26	0.04
413 (")	Y-1	H-7	1.96	27	0.02
414 (")	Y-2	"	2.03	25	0.03
415 (")	Y-6	H-17	2.10	26	0.02
416 (")	Y-7	"	1.52	26	0.02

As is evident from the results in Table 4, when using the coupler of the present invention (Samples 411 to 416), the film strength is excellent and the color-forming property is improved by restraining the diffusion of coupler to the other layers.

Example 5

Samples 501 to 509 were prepared by repeating the same procedure as Example 2, except that the polymer couplers were changed to those shown in Table 5.

The thus-prepared Samples were subjected to the same treatments as Example 2 and then the same measurements as Example 2 were conducted.

Results are shown in Table 5.

Table 5

Sample No.	Coupler	Film Hardener	Yellow density* at Magenta Density ** 1.0
501 (Comparative example)	E-1	HT-1	± 0
502 (")	E-3	"	+ 0.14
503 (")	Y-1	"	+ 0.19
504 (")	E-1	H-3	± 0
505 (")	E-3	"	+ 0.15
506 (This invention)	Y-1	"	+ 0.01
507 (")	Y-5	"	+ 0.02
508 (")	Y-2	H-7	+ 0..02
509 (")	Y-6	H-17	+ 0.02

*, ** : Each is shown the value when $D_{min} = 0$.

The thus-obtained samples according to the present invention (Samples 506 to 509) were all of excellent film strength. As is apparent from the results in Table 5, the diffusion of couplers to other layers of samples of the present invention is restrained to such a degree as to present no practical problem.

Example 6

Samples 601 to 610 were prepared by repeating the same procedure as Example 3, except that the polymer couplers were changed to those shown in Table 6.

The thus-prepared samples were subjected to the same treatments as Example 3 and then the same measurements as Example 3 were conducted.

Results are shown in Table 6.

Table 6

Sample No.	Coupler	Film Hardener	Yellow density* at Magenta Density ** 1.0
601 (Comparative example)	F-6	HT-1	± 0
602 (")	E-3	"	+ 0.18
603 (")	Y-5	"	+ 0.22
604 (")	F-6	H-3	± 0
605 (")	E-3	"	+ 0.17
606 (This invention)	Y-5	"	+ 0.01
607 (")	Y-3	"	+ 0.02
608 (")	Y-4	H-7	+ 0.01
609 (")	Y-5	H-17	+ 0.02
610 (")	Y-7	H-38	+ 0.01

*, ** : Each is shown the value when $D_{min} = 0$.

The samples according to the present invention (Samples 606 to 610) were of excellent film strength, and as is apparent from the results in Table 6, diffusion of couplers to other layers of these samples are restrained to such a level as to present no practical problem.

Having described our invention as related to the embodiment, it it our intention that the invention be not limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

Claims

1. A silver halide color photographic material which comprises a hardener that acts by activating a carboxyl group and water-soluble polymer couplers comprising at least one of repeating units represented by the following formula (I):

Formula (I) $—\!\!(\!-A-\!)\!\!—$

wherein A represents a vinyl polymer unit having a color coupler residue capable of coupling with the oxidized product of an aromatic primary amine developing agent,

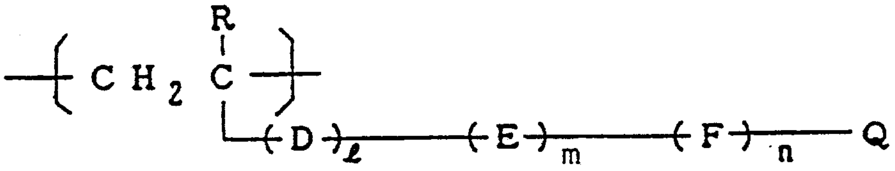
and at least one of repeating units represented by the following formula (II):

Formula (II) $-\!(B)\!-$

wherein B represents a vinyl monomer unit having at least one group selected from -COOM, in which M represents a hydrogen atom, an alkali metal or ammonium, and amino group.

2. The silver halide color photographic material as claimed in Claim 1, wherein the monomer units represented by formula (I) capable of coupling with the oxidized product of an aromatic primary amine developing agent to form a dye are those represented by formula (III):

Formula (III)

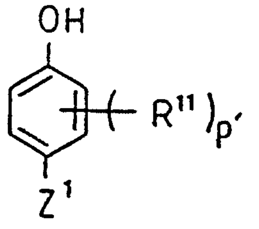


$$-\!\left(CH_2-\overset{R}{\underset{|}{C}}\right)\!- \quad \text{with } C-(D)_{\ell}-(E)_{m}-(F)_{n}-Q$$

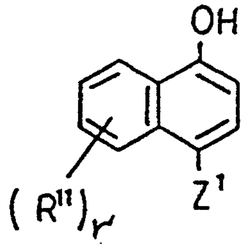
wherein R represents a hydrogen atom, a chlorine atom, or an alkyl group having 1 to 4 carbon atoms; D represents -COO-, -CONR'-, or a substituted or unsubstituted phenyl group; E represents a substituted or unsubstituted alkylene group, phenylene group, or aralkylene group; F represents -CONR'-, -NR'CONR'-, -NR'-COO-, -NR'CO-, -OCONR'-, -NR'-, -COO-, -OCO-, -OCO-, -CO-, -O-, -SO^2-, -NR'SO^2-, or -SO^{2}NR'-, in which R' represents a hydrogen atom or a substituted or unsubstituted alkyl group or aryl group, and if R' is present two or more in number in the same molecule, they may be the same or different;

ℓ, m, and n are 0 or 1, provided that ℓ, m, and n are not 0 at the same time, and Q represents cyan, magenta, or yellow dye-forming coupler residue capable of coupling with the oxidized product of an aromatic primary amine developing agent to form a dye.

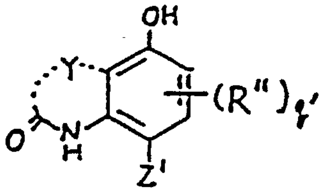
3. The silver halide color photographic material as claimed in Claim 2, wherein the color coupler residue represented by Q is selected from those represented by phenol type (IV) or (V), or naphthol type (VI) or (VII) (a hydrogen atom other than one positioned at the coupling position or the 1-positioned OH group will split off to join with F of formula (III))



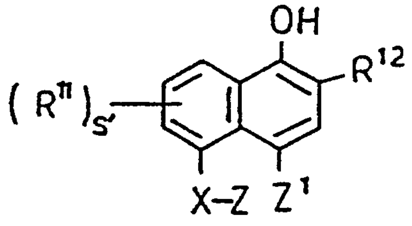
······ (IV)



······ (V)



······ (V')



······ (VI)

wherein R^{11} represents a group capable of substitution onto a phenol ring or a naphthol ring;

R^{12} represents $-CONR^{12}R^{14}$, $-NHCOR^{13}$, $-NHCOOR^{15}$, $-NHSO^2R^{15}$, $-NYCONR^{13}R^{14}$, or $-NHSO^2R^{13}R^{14}$, in which R^{13} or R^{14} represents a hydrogen atom, an aliphatic, an aromatic group, a heterocyclic group, R^{15} represents an aliphatic group, an aromatic group, or a heterocyclic group, R^{13} and R^{14} may bond together to form a heterocyclic ring;

p' is an integer of 0 to 3, q' is an integer of 0 to 2, r' and s' are each integers of 0 to 4;

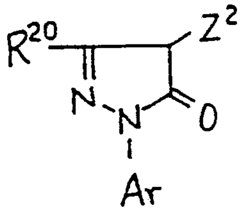
X represents an oxygen atom, a sulfur atom, or $R^{16}N<$, in which R^{16} represents a hydrogen atom or a monovalent substituent;

Z represents a hydrogen atom, or a group that can split off by the coupling reaction; and

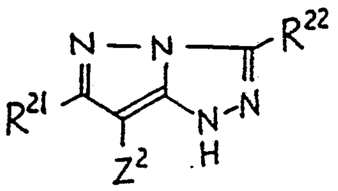
Y represents a group of atoms required to form a 5-, 6-or 7-membered ring together with the carbon atom.

4. The silver halide color photographic material as claimed in Claim 2, wherein the color forming coupler residue represented by Q is selected from those represented by the following formulas (VII), (VIII), (IX), (X), (XI), (XII), and (XIII), and they are connected to F of formula (III) at a part of Ar, Z^2, and R^{20} to R^{32}

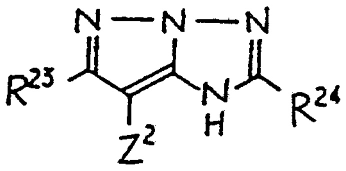
Formula (VII)



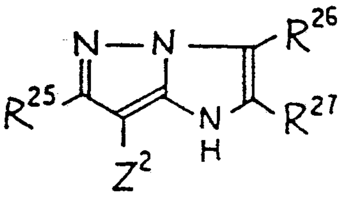
Formula (VIII)



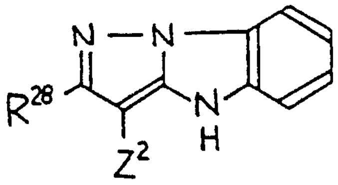
Formula (IX)



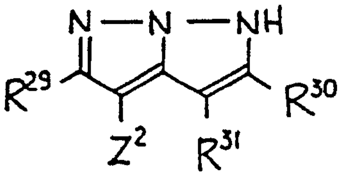
Formula (X)



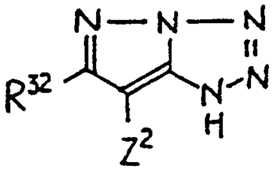
Formula (XI)



Formula (XII)



Formula (XIII)



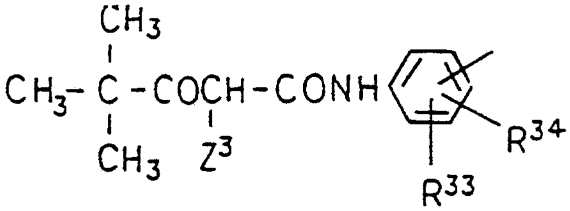
wherein Ar represents a substituent capable of substitution at the first position of a 2-pyrazoline-5-on coupler;

R^{20} represents an unsubstituted or substituted anilino group, an unsubstituted or substituted acylamino group, or an unsubstituted or substituted ureido group;

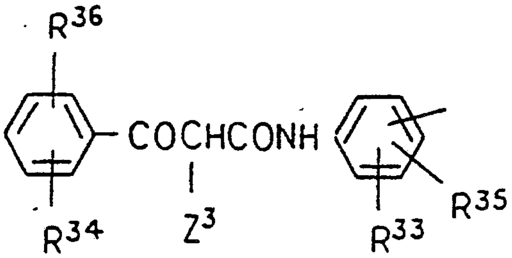
R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}, R^{28}, R^{29}, R^{30}, R^{31} and R^{32} each represent a hydrogen atom, hydroxyl group, unsubstituted or substituted alkyl group, unsubstituted or substituted aryl group, unsubstituted or substituted heterocyclic group, alkylamino group, acylamino group, anilino group, alkoxycarbonyl group, alkylcarbonyl group, arylcarbonyl group, alkylthio group, arylthio group, carbamoyl group, sulfamoyl group, or sulfonamido group; and

Z^2 represents a hydrogen atom or a group which can split-off upon a coupling-reaction.

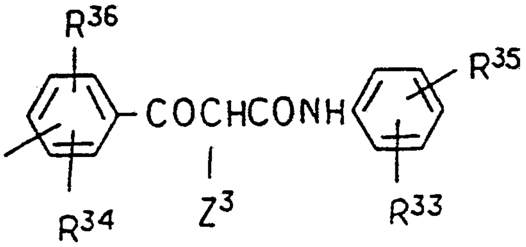
5. The silver halide color photographic material as claimed in Claim 2, wherein the color coupler residue represented by Q is selected from a pivaloylacetoanilido type (XIV), or a benzoylacetoanilido type (XV) or (XVI)



(XIV)



(XV)

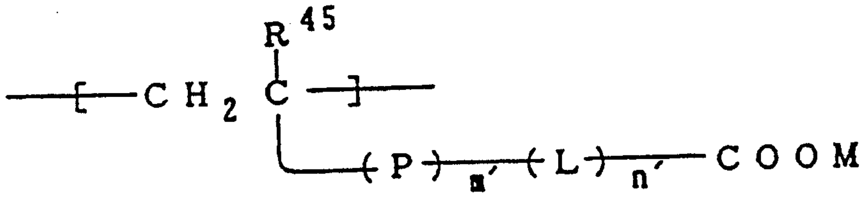


(XVI)

wherein R^{33}, R^{34}, R^{35}, and R^{36}, which may be the same or different, each represent a hydrogen atom or a substituent of the residue of yellow color-forming coupler, and

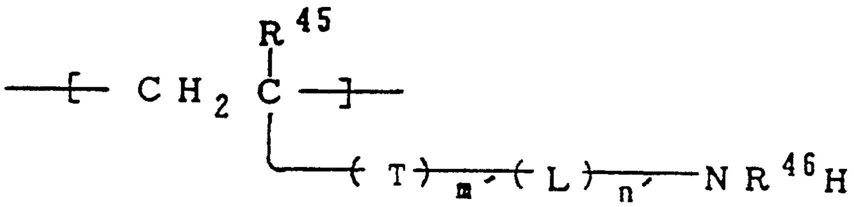
Z^3 represents a hydrogen atom or a group that can split off upon a coupling reaction.

6. The silver halide color photographic material as claimed in Claim 1, wherein the monomer unit represented by formula (II) is selected from the unit represented by the following formula (XXIVa) or (XXIVb):



$$-\!\left[CH_2-\overset{R^{45}}{\underset{|}{C}}\right]\!-\quad \llcorner\!-(P)_{m'}-(L)_{n'}-COOM$$

(XXIVa)



$$-\!\left[CH_2-\overset{R^{45}}{\underset{|}{C}}\right]\!-\quad \llcorner\!-(T)_{m'}-(L)_{n'}-NR^{46}H$$

(XXIVb)

wherein R^{45} represents a hydrogen atom, lower alkyl group having 1 to 4 carbon atoms, or chlorine atom; P represents -COO-, -CONHR$^{46'}$-, or a substituted or unsubstituted phenylene group; T represents -COO-, -CONH-, or a substituted or unsubstituted phenylene group; L represents a substituted or unsubstituted alkylene, a phenylene or an alalkylene group; M represents a hydrogen atom, alkali metal, or ammonium; m′ and n′ each represent 0 or 1; and R^{46} and $R^{46'}$ each represent a hydrogen atom, or a substituted or unsubstituted alkyl or aryl group.

7. The silver halide color photographic material as claimed in Claim 1, wherein the water-soluble polymer coupler contains a non-color-forming ethylenically-unsaturated monomer unit which does not undergo a coupling reaction with the oxidation product of an aromatic primary amine developing agent other than those represented by formulas (I) and (II), and which does not contain -COOM or an amino group in the molecular in an amount of 60% or less in terms of the total of monomer unit represented by formulas (I) and (II).

8. The silver halide color photographic material as claimed in Claim 7, wherein the non-color-forming ethylenically-unsaturated monomer unit other than those represented by formulas (I) and (II) is selected from acrylate esters, methacrylate esters, crotonate esters, vinyl esters, maleate diesters, fumarate diesters, itaconate diesters, acrylamides, methacrylamides, vinyl ethers, and styrenes.

9. The silver halide color photographic material as claimed in Claim 1, wherein the proportion of the color forming moiety correspnoding to formula (I) in the polymer coupler is 5 to 80 wt.%.

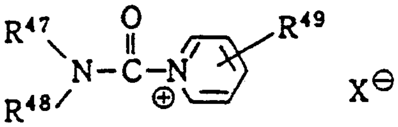
10. The silver halide color photographic material as claimed in Claim 1, wherein the proportion of the component (monomer unit) corresponding to formula (II) in the polymer coupler is 20 to 95 wt.%.

11. The silver halide color photographic material as claimed in Claim 1, wherein the polymer coupler is added in an amount of 0.005 to 0.5 mol, per mol of silver, in terms of the coupler monomer unit represented by formula (1).

12. The silver halide color photographic material as claimed in Claim 1, wherein the molecular weight of the polymer coupler is 5×10^3 to 1×10^7.

13. The silver halide color photographic material as claimed in Claim 1, wherein the molecular weight equivalent of the polymer coupler is about 250 to 4000.

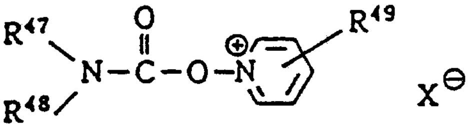
14. The silver halide color photographic material as claimed in Claim 1, wherein the hardener is selected from compounds represented by the following formula (XXV): Formula (XXV)



wherein R^{47} and R^{48}, which may be the same or different, each represent an alkyl group, an aryl group, or an aralkyl group in which R^{47} and R^{48} may bond together with the nitrogen atom to form a heterocyclic ring, R^{49} represents a substituent such as a hydrogen atom, a halogen atom, a carbamoyl group, a sulfo group, a ureido group, an alkoxy group and an alkyl group, and $X^{\ominus}$ represents an anion and becomes a counter ion to the N-carbamoylpyridinium salt.

15. The silver halide color photographic material as claimed in Claim 1, wherein the hardener is selected from compounds represented by the following formula (XXVI):

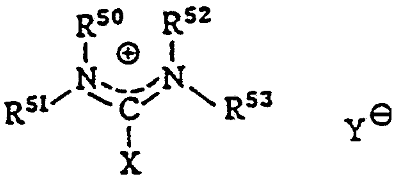
Formula (XXVI)



wherein R^{47} and R^{48}, which may be the same or different, each represent an alkyl group, an aryl group, or an aralkyl group in which R^{47} and R^{48} may bond together with the nitrogen atom to form a heterocyclic ring, R^{49} represents a substituent such as a hydrogen atom, a halogen atom, a carbamoyl group, a sulfo group, a ureido group, an alkoxy group and an alkyl group, and $X^{\ominus}$ represents an anion and becomes a counter ion to the N-carbamoylpyridinium salt.

16. The silver halide color photographic material as claimed in Claim 1, wherein the hardener is selected from compounds represented by the following formula (XXVII):

Formula (XXVII)



wherein R^{50}, R^{51}, R^{52}, and R^{53}, which may be the same or different, each represent an alkyl group, an aralkyl or an aryl group, in which R^{50}, R^{51}, R^{52}, and R^{53} may bond together to form a ring,

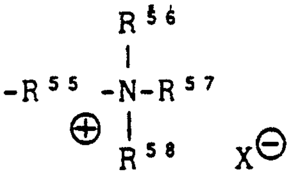
X represents a group that can split off when the compound represented by formula (XXVII) reacts with a nucleophilic reagent, and

$Y^{\ominus}$ represents an anion, and if $Y^{\ominus}$ represents a sulfonate ion, it may bond to X, R^{50}, R^{51}, R^{52} or R^{53} to form an inner salt.

17. The silver halide color photographic material as claimed in Claim 1, wherein the hardener is selected from compounds represented by the following formula (XXVIII):

Formula (XXVIII) $R^{54}-N=C=N-R^{54'}$

wherein R^{54} represents an alkyl group, a cycloalkyl group, an alkoxyalkyl group, or an aralkyl group; $R^{54'}$ represents the groups defined for R^{54}, or

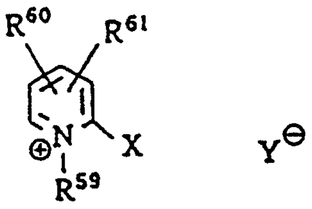


$$-R^{55}-\underset{\oplus\ \ R^{58}}{\overset{R^{56}}{N}}-R^{57}\qquad X^{\ominus}$$

wherein R^{55} represents an alkylene group; R^{56} and R^{57}, which may be the same or different, each represent an alkyl group (R^{56} and R^{57} may bond together with the nitrogen atom to form a heterocyclic ring); R^{58} represents an alkyl group; $X^{\ominus}$ represents an anion, and if R^{58} is substituted by a sulfo group, an inner salt is formed.

18. The silver halide color photographic material as claimed in Claim 1, wherein the hardener is selected from compounds represented by the following formula (XXIX):

Formula (XXIX)



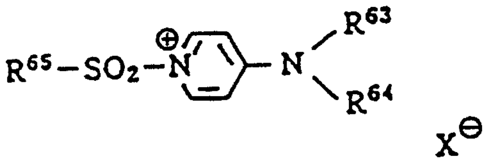
R^{59} represents an alkyl group, an aryl group or an aralkyl group, R^{60} and R^{61}, which may be the same or different, each represent a substituent, (R^{60} and R^{61} may bond together with the pyridinium ring skeleton to form a condensed ring),

X represents a group that can split off when the compounds represented by formula (XXIX) react with a nucleophilic reagent, and

$Y^{\ominus}$ represents an anion, and if R^{59} is substituted by a sulfo group, an inner salt is formed.

19. The silver halide color photographic material as claimed in Claim 1, wherein the hardener is selected from compounds represented by the following formula (XXX):

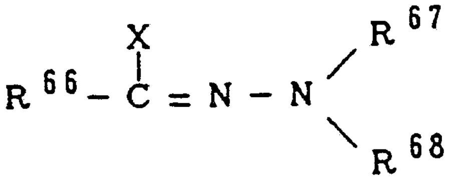
Formula (XXX)



wherein R^{63} and R^{64}, which may be the same or different, each represent an alkyl group, an aryl group, or an aralkyl in which R^{63} and R^{64} may bond together with the nitrogen atom to form a heterocyclic ring, R^{65} represents an alkyl group, an aryl group, or an aralkyl group, and $X^{\ominus}$represents an anion.

20. The silver halide color photographic material as claimed in Claim 1, wherein the hardener is selected from compounds represented by the following formula (XXXI):

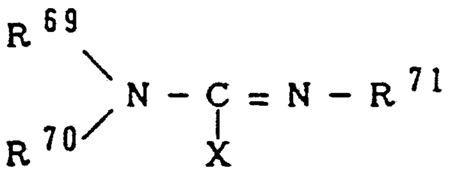
Formula (XXXI)



wherein R^{66} represents a straight-chain or branched alkyl group, an aralkyl group, an aryl group, an alkenyl group, or a heteroaromatic group, and X represents a group that can split off when the compounds represented by formula (XXXI) react with a nucleophilic reagent.

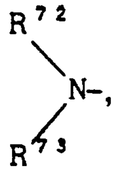
21. The silver halide color photographic material as claimed in Claim 1, wherein the hardener is selected from comounds represented by the following formula (XXXII):

Formula (XXXII)



wherein R^{69} and R^{70} represent a straight-chain or branched alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, an alkenyl group, or a heterocyclic group, R^{69} and R^{70} may bond together to form a heterocyclic ring;

R^{71} represents a straight-chain or branched alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, an alkenyl group, a heterocyclic group, or a group



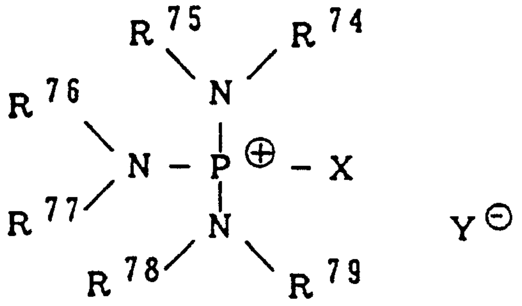
in which R^{72} and R^{73} represent a straight-chain or branched alkyl group, an aralkyl group, an aryl group, or an alkenyl group,

R^{69} and R^{70} or ring R^{72} and R^{73} may bond together with the nitrogen atom to form a ring, and

X represents a group that can split off when the compounds represented by formula (XXXII) react with a nucleophilic reagent.

22. The silver halide color photographic material as claimed in Claim 1, wherein the hardener is selected from compounds represented by the following formula (XXXIII):

Formula (XXXIII)



wherein R^{74}, R^{75}, R^{76}, R^{77}, R^{78}, and R^{79}, which may be the same or different, each represent a straight-chain or branched alkyl group, an aralkyl group, or an aryl group (R^{74}, R^{75}, R^{76}, R^{77}, R^{78}, and R^{79} may bond together to form a ring),

X represents a group that can split off when the compounds represented by formula (XXXIII) react with a nucleophilic reagent, and

$Y^{\ominus}$ represents an anion.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 10 4270

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	DE-A-3 516 945 (FUJI PHOTO FILM CO.) * Claims; pages 12-55; page 56, lines 1-18; pages 89-93,98-100; page 101, lines 1-14 * ---	1,2,4,6-19	G 03 C 7/32 G 03 C 1/30
Y	DE-A-3 233 168 (FUJI PHOTO FILM CO.) * Claims; page 21, lines 26-38; pages 22-28,33-47 * ---	1-13	
Y	EP-A-0 161 626 (FUJI PHOTO FILM CO.) * Page 4, lines 5-26; pages 5-35,70-74,85-88; claims * ---	1-3,6-13	
Y	EP-A-0 133 262 (FUJI PHOTO FILM CO.) * Page 3, lines 6-23; pages 4-20; claims * ---	1,2,4,6-13	
Y	PATENT ABSTRACTS OF JAPAN, vol. 10, no. 195 (P-475)[2251], 9th July 1986; & JP-A-61 39 044 (KONISHIROKU PHOTO IND. CO., LTD.) 25-02-1986 * Abstract * ---	1-3,6-13	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
Y,D	PATENT ABSTRACTS OF JAPAN, vol. 10, no. 322 (P-511)[2378], 31st October 1986; & JP-A-61 128 241 (FUJI PHOTO FILM CO., LTD.) 16-06-86 * Abstract * ---	1,22	G 03 C 1/00 G 03 C 7/00
P,A D	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 267 (C-443)[2714], 28th August 1987; & JP-A-62 68 866 (FUJI PHOTO FILM CO., LTD.) 28-03-87 * Abstract * ---	1,20	

-/-

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	31-05-1988	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number

EP 88 10 4270

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,A D	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 267 (C-443)[2714], 28th August 1987; & JP-A-62 68 867 (FUJI PHOTO FILM CO., LTD.) 28-03-87 * Abstract * -----	1,21	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	31-05-1988	MAGRIZOS S.

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