# PATENT SPECIFICATION

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## (54) COLOUR PHOTOGRAPHIC SILVER HALIDE MATERIAL CONTAINING A COUPLER PRECURSOR

(71) We, AGFA-GEVAERT, a Naamloze Vennootschap organised under the Laws of Belgium of Septestraat 27, B 2510 Mortsel, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a colour photographic silver halide material, containing a proteinaceous emulsion and a fast-acting hardener and a 2-pyrazolin-5-one coupler precursor.

It is known to make photographic colour images by the coupling of oxidized aromatic developing agents containing primary amino groups with colour couplers. It is common to use in this process the subtractive method of colour formation and in general cyan, magenta, and yellow are used as complementary colours to the primary colours in the formation of image dyes. It is common practice to use phenol or naphthol colour couplers for the formation of the cyan image, 2-pyrazolin-5-one couplers for the formation of the magenta image, and couplers containing a methylene group linked to one or two carbonyl groups for the formation of the yellow image.

To shorten the processing time photographic colour materials are often processed at temperatures above ambient temperature (20—25°C). Processing temperatures above 30°C are often used. However during processing of photographic silver halide emulsions at these high temperatures the hydrophilic colloids such as gelatin, in which the silver halide, the photographic colour couplers and further additives have been dispersed, soften and swell. In consequence of manipulation these layers may become damaged (or the emulsion layer may become loosened from the support. For these reasons the emulsion layers have to be hardened before the processing at high temperatures. The hardening can be realized by first conducting the emulsion layer through a hardening bath during the processing or by incorporating prehardeners e.g. aldehydes and halogen-containing aldehyde compounds especially formaldehyde, dialdehyde, and mucochloric acid into the photographic silver halide emulsion during its preparation.

It is particularly important for the hardening of photographic layers that maximum hardening be reached as soon as possible after drying so that the material to be hardened does not continuously change its permeability to the developer solution as is the case e.g. with mucochloric acid or formaldehyde.

The use of fast-acting hardeners for photographic purposes instead of hardeners, which act over a prolonged period, has recently become increasingly important. With the rapid progress of the hardening reaction it is possible to avoid changes in the photographic materials during storage, more particularly to avoid a continuous decrease in permeability of the photographic layers to photographic baths.

The term "fast-acting hardeners" is hereby defined as compounds which bring about crosslinking of the protein e.g. gelatin of emulsions of the photographic material by activation of carbonyl groups, e.g. during the drying process, so as to provide maximum cross-linking within 24 hours.

Particular fast-acting hardeners are carbodiimides such as those described in the

U.S. Patent Specifications 2,938,892 and 3,098,693, in the paper of E. Schmidt, F. Hitzler, and E. Lahde in Ber 71, 1933 (1938), and in the paper by G. Amiard and R. Heynes in Bull Soc. Chim. France 1360 (1956), the dihydroquinoline compounds described in the published German Patent Application 2,322,317, the carbamoylpyridinium compounds described in the published German Patent Applications 2,225,230, 2,317,677 and 2,439,551, and the carbamoyloxypyridinium compounds described in the published German Patent Application 2,408,814.

A common feature of all these fast-acting hardeners is that they activate carboxyl groups. This action can be illustrated by the example of the known reaction of carbodiimides with carboxylic acids. In this reaction N-acylureas or acid anhydrides are used as activating groups. With proteins containing carboxyl and amino groups, the reaction proceeds further and the activated carboxyl groups form peptide bonds with the amino groups. These compounds are therefore also known as peptide reagents (Chem. Rev. *67*, (1967), pages 107—152).

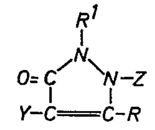
The use of these fast-acting hardeners in colour photographic silver halide materials is limited, because compounds of these types often give rise to a reduced development of the magenta layers.

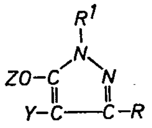
It is an object of the present invention to provide a colour photographic silver halide material containing fast-acting hardeners, in which the formation of the magenta image is substantially unimpaired by rapid hardening before photographic processing.

The invention is directed to colour photographic silver halide material containing a proteinaceous emulsion which is hardened by fast-acting hardeners, wherein the material contains a coupler precursor which in alkaline developer medium is converted into the 2-pyrazolin-5-one coupler, which is then available for the coupling.

The invention provides colour photographic silver halide material containing a fast-acting hardener as hereinbefore defined, wherein the said material contains a 2-pyrazolin-5-one coupler corresponding to one of the following general formulae I and II:

I.





II.

in which

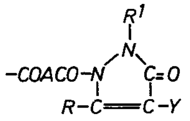
$R^1$ represents (1) an alkyl preferably a $C_1$—$C_{22}$, particularly $C_1$—$C_5$ alkyl group, or such an alkyl group which is substituted, e.g. 2,2,2-trifluoroethyl, cyanoethyl, benzyl, substituted benzyl e.g. chlorobenzyl; (2) a heterocyclic group e.g. furanyl, 2-benzothiazolyl; or (3) an aryl group, e.g. a phenyl group, which aryl group may carry one or more substituents for example alkyl e.g. methyl, halogen, particularly chloro and bromo, sulpho, alkoxy e.g. methoxy, aryloxy e.g. phenoxy, alkylsulphonyl e.g. methylsulphonyl, alkylthio e.g. methylthio, carbalkoxy, haloalkoxy, haloalkylthio, haloalkylsulphonyl, sulphamyl or carbamyl including substituted sulphamyl or carbamyl, cyano or nitro. Representative examples for substituted phenyl are for example 2 - chlorophenyl, 2 - bromophenyl, 2,6 - dichlorophenyl, 2,4,6 - trichlorophenyl, 3,5 - dibromophenyl, 4 - chlorophenyl, 2 - cyanophenyl, 4 - cyanophenyl, 4 - nitrophenyl, 2 - nitrophenyl, 4 - methylphenyl, 2,6 - dimethylphenyl, 4 - butylphenyl, 2 - trifluoromethylphenyl, 2 - ethoxyphenyl, 2 - butoxyphenyl, 4 - phenoxyphenyl, N-methylbenzamidophenyl, N,N - diphenylcarbamylphenyl, N - methyl - N - octadecylcarbamylphenyl, phenyl - p - N - methylsulphonamidophenyl, 2 - methyl - 5 - nitrophenyl, 2 - chloro - 5 - cyanophenyl, 5 - chloro - 2 - methylphenyl, 2,6 - dichloro - 4-methoxyphenyl, 2,4 - dichloro - 6 - methylphenyl, 2,6 - dichloro - 4 - nitrophenyl, 2-chloro - 4,6 dimethylphenyl or 2,6 - dichloro - 4 - methylsulphonylphenyl,

R represents (1) an alkyl group, preferably a $C_1$—$C_{22}$ alkyl group or such an alkyl group which is substituted; (2) an aryl group or substituted aryl group; (3) either anilino or substituted anilino e.g. anilino with one or more common substituents e.g. alkyl, alkoxy, alkylthio, aryloxy, halogen e.g. chloro, nitro,, cyano, sulpho, amino and substituted amino, carbonamido, sulphonamido, sulphamyl or carbamyl including substituted sulphamyl or carbamyl or (4) an acylamino group or a substituted acylamino group, derived from carboxylic or sulphonic acids e.g. acetamido, propionamido, acrylamido, methacrylamido, palmitamido, butylsulphonamido, docosylsulphonamido, phenylethylsulphonamido, benzamido or phenylsulphonamido including benzamido and phenylsulphonamido carrying one or more common substituents e.g. halogen e.g. chloro and bromo, alkyl e.g. methyl, alkoxy e.g. methoxy, ethoxy, hexadecyloxy, aroxy e.g.

phenoxy and substituted phenoxy, carbonamido e.g. acetamido, phenoxyacetamido or α-(2,4-di-t-amylphenoxy) acetamido,

Y represents hydrogen, a group or atom that is capable of being split off during development in which instance the colour precursor is a colour-forming coloured or colourless 2-pyrazolin-5-one coupler precursor, which group or atom may be for example halogen e.g. chloro, a sulpho group in acid or salt form, alkoxy e.g. methoxy, an aryloxy group e.g. phenoxy, an acyloxy group, an alkylthio or an arylthio group, e.g. phenylthio, a heterocyclic thio group e.g. 1 - phenyl - 5 - tetrazolylthio, 2 - benzothiazolylthio, and 2 - benzimidazolylthio, an arylazo group e.g. phenylazo, chlorophenylazo, and methoxyphenylazo, or a benzotriazolyl group; or a group that cannot be so split off in which instance the colour precursor is a 2-pyrazolin-5-one competing coupler precursor e.g. an alkyl group e.g. methyl;

Z represents (1) an acyl group deriving from an organic carboxylic acid e.g. an acyl group deriving from saturated or unsaturated aliphatic, cycloaliphatic, aliphatic-aromatic, aromatic or heterocyclic carboxylic acids, e.g. acetyl, propionyl, palmitoyl, alkoxyacetyl e.g. methoxyacetal and ethoxyacetyl, aryloxyacetyl e.g. phenoxyacetal, β-carboxypropionyl, chloroacetyl, benzoyl, chlorobenzoyl and thienoyl; or (2) the group



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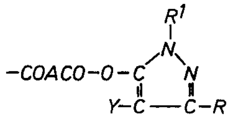


in which R¹, R, and Y have the above described significance, and A represents an alkylene group e.g. ethylene, or an arylene group e.g. phenylene or (3) an alkoxycarbonyl or aryloxycarbonyl group, which groups may carry substituents e.g. methoxycarbonyl, ethoxycarbonyl, trichloroethoxycarbonyl, benzyloxycarbonyl, phenoxycarbonyl, sulphophenoxycarbonyl or alkoxycarbonylphenoxycarbonyl.

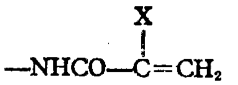
The 2-pyrazolin-5-one coupler precursors according to the general formulae I and II can be prepared from the corresponding known 2-pyrazolin-5-one couplers by reaction with an organic carboxylic acid halide in particular carboxylic acid chloride or with a chloroformate.

Details concerning their preparation can be found in the following American Patent Specifications 2,476,986; 2,476,987; 2,476,988; 2,575,182; 2,706,685 and 2,867,748, in the U.K. Patent Specification 1,057,436, and the published German Patent Applications 2,424,134 and 2,523,882, unless they will be described hereinafter.

In the production of appropriate photographic multilayer materials containing colour couplers for the formation of separation images in the differently sensitized silver halide emulsion layers or containing competing couplers, these couplers have to be incorporated in non-diffusing form into the hydrophilic silver halide emulsion layers or into water-permeable adjacent layers.

In order to reduce the diffusion tendency of the coupler precursors in the photographic colloid layers these compounds may be provided with a ballasting group in the 1- or 3-position. For this purpose groups R¹ and R may e.g. represent or contain an acyclic aliphatic carbon group having 5 to 20 carbon atoms, wherein these groups may be linked via bivalent bridging elements e.g. sulphur, sulphonyl, —NHCO—, —CON(R)—, —SO$_2$N(R)—, wherein R=H or alkyl, —NHSO$_2$— or —N(alkyl)—, to the possibly aromatic groups R¹ and/or R.

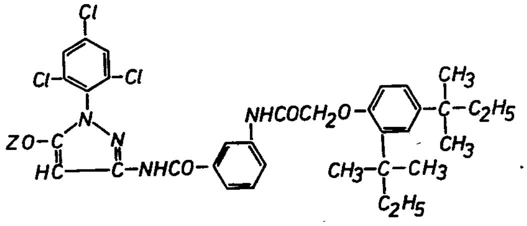
Another valuable method for the non-diffusing incorporation of coupler precursors into photographic colloid layers consists in their use in polymeric form, which can be obtained, e.g. by copolymerization of monomeric couplers according to the above formula I or II, which in the 3-position contain an ethylenic group, e.g. the group



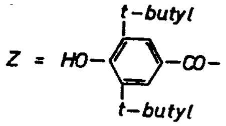
$$—NHCO—\overset{X}{\overset{|}{C}}=CH_2$$

in which X represents hydrogen, halogen, a C$_1$—C$_5$ alkyl group e.g. methyl, an aralkyl group or an aryl group, with one or more non-colour forming monomers containing at least one ethylenic group.

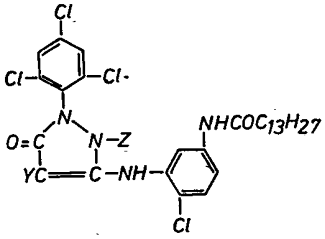
Examples of 2-pyrazolin-5-one coupler precursors according to formulae I and II are the following:



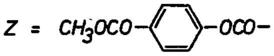
1. $Z=CH_3CO—$
2. $Z=C_2H_5OCO—$
3. $Z=C_6H_5OCO—$
4. $Z=C_6H_5CO—$
5. $Z=C_6H_5OCH_2CO—$
6.



7. $CH_3OCH_2CO—$
8. $4—FSO_2C_6H_4OCH_2CO—$

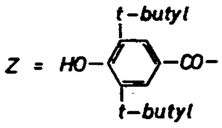


9. $Z=C_6H_5OCO—$ Y=H
10. $Z=C_2H_5OCO—$ Y=H
11. $Z=C_2H_5OCO—$ Y=Cl
12. $Z=CH_3CO—$ Y=H
13.



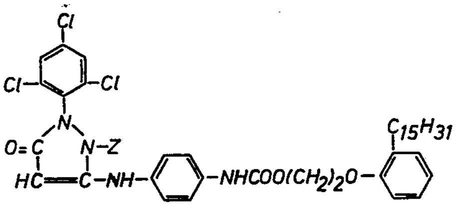
Y=H

14.

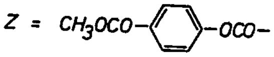


Y=H

15. $4FSO_2C_6H_4OCO—$ Y=H



16. $Z=C_6H_5OCO—$
17.



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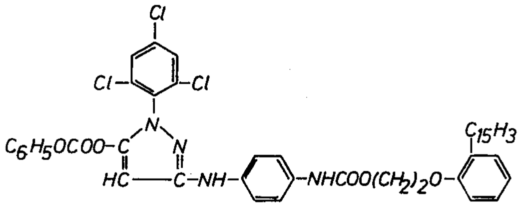

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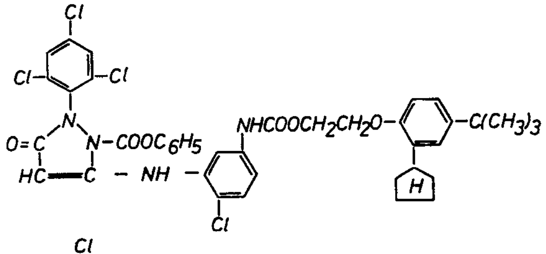

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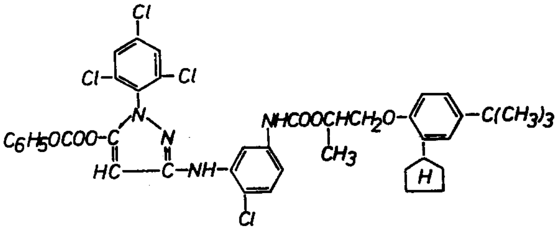

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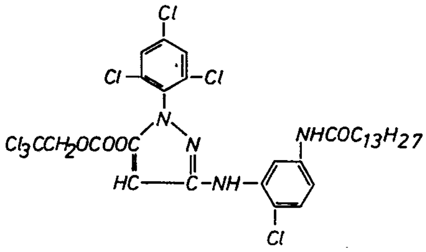

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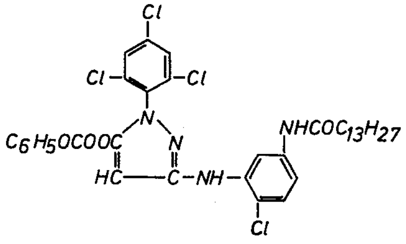

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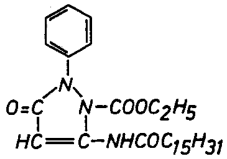

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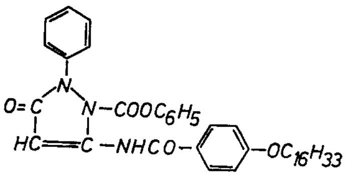

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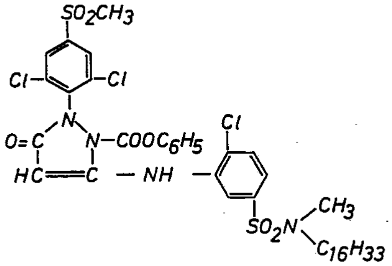

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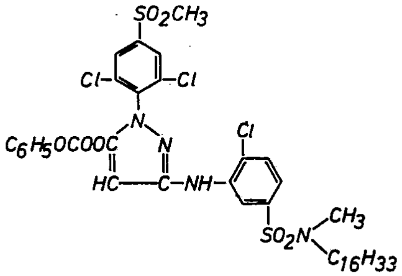

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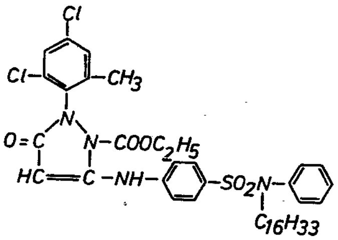

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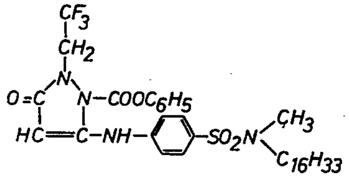

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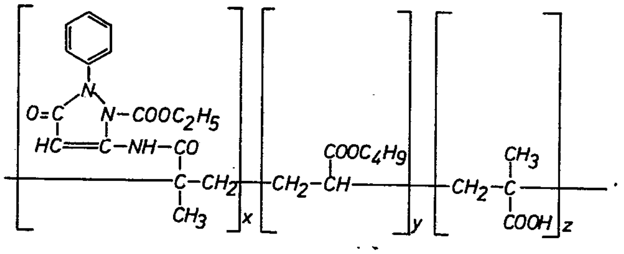

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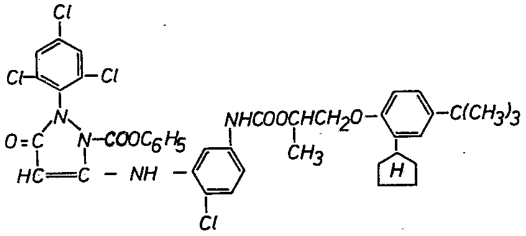

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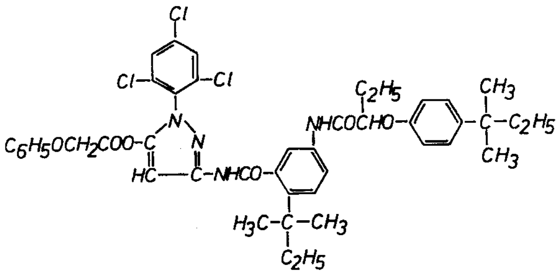


Because of the inactive methylene group the coupler precursors according to the general formulae I and II can take part in undesired side-reactions with the fast-acting hardener activating carboxyl groups during the preparation and the storage of the colour material. This results in a reduced hardening and in smaller amounts of coupler available for coupling with the oxidized developing agent, and consequently in a reduced colour density, which would result in staining. The coupling reaction in alkaline medium is more vigorous, however, than these side-reactions and leads to the splitting off of the 2- or 5-acyl group resulting in the formation of 2-pyrazolin-5-one coupler, which is at the disposal for coupling.

The 2-acyl-3-pyrazolin-5-one compounds for use according to the invention are prepared by reaction of the corresponding 2-pyrazolin-5-ones as starting product with an organic carboxylic acid halide in particular a carboxylic acid chloride or with a chloroformate.

The reaction is carried out preferably in an anhydrous inert organic solvent e.g. nitrobenzene, nitromethane, tetrahydrothiophene-1,1-dioxide, acetonitrile, dioxan or especially in halogenated aliphatic hydrocarbons such as dichloromethane, 1,2-dichloroethane or carbon tetrachloride.

When in the preparation of the compounds according to the invention chloroformate is used as acylating agent, the inert solvent may be replaced wholly or partially by excess chloroformate. The reaction of the 2-pyrazolin-5-one is performed in the presence of a Friedel-Crafts catalyst, especially a metal halide such as aluminium halide, e.g. aluminium chloride and a basic heterocyclic nitrogen-containing condensating agent such as pyridine or a derivative thereof, e.g. lutidine or picoline a. temperatures below 20°C, especially between −20°C and +10C.

When, however, 3-anilino-2-pyrazolin-5-one is used as starting product and chloroformate as acylating agent, it is sufficient to reflux the reagents in the inert solvent.

In the case of an unsubstituted amino group in the 3-position of 2-pyrazolin-5-one the reaction is preferably carried out between −20°C and 0°C, since in this temperature range there is only acylated in the 2-position, whereas at higher temperatures the 3-acylaminopyrazolone compound is formed (see the U.S. Patent Specifications 3,325,482 and 3,846,444). In order to prepare the 2-acyl-3-acylamino-3-pyrazolin-5-one compounds according to the invention the 2-acyl-3-amino-3-pyrazolin-5-one is prepared first by acylation in the presence of a Friedel-Crafts-metal halide and a basic condensation agent at relatively low temperatures preferably below 0°C. The resulting product is then acylated in the 3-position according to known methods e.g. in the presence of a Friedel-Crafts-metal halide, in an anhydrous inert solvent such as those defined hereinbefore.

If Friedel-Crafts-metal halides are used for the preparation of the compounds used in the invention the halide is taken in almost equimolar amounts in respect of the amount of the 2-pyrazolin-5-one. However, to simplify the solution of the pyrazolin-5-one the metal halide may be used in excess with a molar proportion of approximately 1:1.5.

The preferred substituents can be introduced into the groups $R^1$, R, and Y according to known chemical methods prior to or subsequent to the 2-acylation.

The 3-anilino-5-pyrazolylalkylcarbonates or -arylcarbonates to be used according to the invention are prepared by reaction of a 3-anilino-2-pyrazolin-5-one with a chloroformate at a temperature below −20°C, preferably between −40°C and −80°C, in the presence of an inert organic strong base with a pKb-value of at most 5, e.g. an aliphatic tertiary amine such as triethylamine.

The reaction of the 3-anilino-2-pyrazolin-5-one colour coupler with the chloroformate is carried out preferably in an organic solvent e.g. dichloromethane, acetonitrile or dioxane. The molar proportion between pyrazolinone and ester advantageously ranges between 1:1 and 1:5, the molar proportion between pyrazolinone and organic base ranging between 1:1 and 1:5 as well.

The structures of the compounds are determined by IR- and NMR-spectrometry. The alkyl- and aryl-5-pyrazolyl carbonates differ from the 2-aryloxycarbonyl- or 2-alkoxycarbonyl-3-pyrazolin-5-ones by

(1) the IR-absorption frequency (in dichloromethane) of the carbonyl group i.e. 5.70—5.80 μm in the case of the 2-acylated compounds and 5.55—5.60 μm in the case of the 5-acylated compounds and

(2) the chemical shift in $CDCl_3$ of the C-proton of the 4-position, i.e. in the case of 2-acylated compounds less than 6 ppm and in the case of 5-acylated compounds more than 6 ppm as compared with tetraethylsilane.

The four conceivable isomeric structures (acylation in the 2-, 3-, 4-, or 5-position) differ by their IR- and NMR-spectra. The 2- and 5-acylated compounds contain no enolizable active proton in the 4-position.

The following examples illustrate the preparation of the compounds used in the invention.

### Compound 9.

### 1-(2,4,6-trichlorophenyl)-2-phenoxycarbonyl-3-(2-chloro-5-myristoylamino-anilino)-3-pyrazolin-5-one

A solution of 30.7 g (0.05 mole) of 1 - (2,4,6 - trichlorophenyl) - 3 - (2 - chloro-5 - myristoylamino - anilino) - 2 - pyrazolin - 5 - one and 15.6 g (0.1 mole) of phenyl chloroformate in 100 ml of acetonitrile are refluxed for 4 h. The solution is poured out in water and the separated oil is stirred first with water and next with methanol. The precipitate is recrystallized from ethanol.

Yield: 20 g (54%). Melting point: 124°C.

*Structural analysis*

IR $\gamma_{CO}$ 5.73 μm NMR $\delta_{-CH=}$ 5.82 ppm

### Compound 13.

### 1-(2,4,6-trichlorophenyl)-2-(4-methoxycarbonylphenoxycarbonyl)-3-(2-chloro-5-myristoylamino-anilino)-3-pyrazolin-5-one

A solution of 24.5 g (0.04 mole) of 1 - (2,4,6 - trichlorophenyl) - 3 - (2 - chloro-5 - myristoylamino - anilino) - 2 - pyrazolin - 5 - one and 17.16 g (0.8 mole) of 4-methoxycarbonylphenyl chloroformate (Chem. Ztg. 390 (1886)) in 100 ml of dry dichloromethane is refluxed for 8 h. The solution is concentrated by evaporation and the white precipitate is recrystallized from methanol.

Yield: 27 g (69%). Melting point: 156°C.

*Structural analysis*

IR $\gamma_{CO}$ 5.72 μm NMR $\delta_{-CH=}$ 5.85 ppm

### Compound 10.

### 1-(2,4,6-trichlorophenyl)-2-ethoxycarbonyl-3-(2-chloro-5-myristoylamino-anilino)-3-pyrazolin-5-one

a) Analogously to compound 13 16 g (51%) of the above-mentioned compound melting at 136°C are obtained from 30.7 g (0.05 mole) of the 2-pyrazolin-5-one and 10.85 g (0.1 mole) of ethylchloroformate.

*Structural analysis*

IR $\gamma_{CO}$ 5.76 μm NMR $\delta_{-CH=}$ 5.65 ppm

b) 12 ml (0.15 mole) of pyridine are added at 10°C to a solution of 30.7 g (0.05 mole) of the corresponding 2-unsubstituted pyrazolin-5-one, and 150 ml of acetonitrile. 5.25 ml (0.055 mole) of ethylchloroformate are added dropwise in 5 min at 5—10°C to the resulting suspension. 200 ml of dimethylformamide are then added to the solution of the reaction mixture. The mixture is stirred for 1 h and then poured out into a mixture of 100 ml of methanol and 100 ml of 1N aqueous hydrochloric acid. The precipitate is sucked off and recrystallized from methanol.

Yield: 26 g (76%). Melting point: 137°C.

### Compound 19.

1-(2,4,6-trichlorophenyl)-2-phenoxycarbonyl-3-{2-chloro-5-[$\beta$-(2-cyclopentyl-4-t-butyl-phenoxy)-ethoxycarbonylamino]-anilino}-3-pyrazolin-5-one

Analogously to compound 13, 18 g (44%) of the above-mentioned compound melting at 154°C are obtained from 34.6 g (0.05 mole) of the corresponding 2-unsubstituted pyrazolin-5-one and 15.6 g (0.1 mole)of phenylchloroformate after recrystallization from acetonitrile.

*Structural analysis*
IR $\gamma_{oo}$ 5.74 $\mu$m NMR $\delta_{-CH=}$ 5.80 ppm

### Compound 27.

1-(2-methyl-4,6-dichlorophenyl)-2-ethoxycarbonyl-3-[4-(N-phenyl-N-n-hexadecylsulfamyl)-anilino]-3-pyrazolin-5-one

A solution of 28.5 g (0.04 mole) of the corresponding 2-unsubstituted pyrazolin-5-one and 10.85 g (0.1 mole) of ethylchloroformate in 80 ml of acetonitrile is refluxed for 6 hr. The solution is poured out in water and the resulting oil is separated and dissolved in diethylether. Hexane is added to the dried solution and the white precipitate obtained is collected.

Yield: 15 g (39%). Melting point: 85°C.

*Structural analysis*
IR $\gamma_{oo}$ 5.77 $\mu$m NMR $\delta_{-CH=}$ 5.48 ppm

### Compound 20.

1-(2,4,6-trichlorophenyl-3-{2-chloro-5-[$\alpha$-methyl-$\beta$-(2-cyclopentyl-4-t-butyl-phenoxy)-ethoxycarbonylamino]-anilino}-5-pyrazolyl-phenylcarbonate

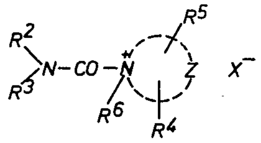
11.75 g (0.075 mole) of phenylchloroformate are added dropwise in 15 min to a solution cooled to −60°C of 35.3 g (0.05 mole) of the corresponding 3-anilino-2-pyrazolin-5-one and 10.35 ml (0.075 mole) of triethylamine in 100 ml of dichloromethane, so that the temperature remains below −60°C. After 15 min 0.1 N hydrochloride acid is poured first on the dichloromethane layer and subsequently it is washed with ice-water until free from acid. After drying the solvent is removed by evaporation and the residue is stirred with hexane. The precipitate is filtered off.

Yield: 24 g (58%). Melting point: 70°C.

*Structural analysis*
IR $\gamma_{oo}$ 5.56 $\mu$m NMR $\delta_{-CH=}$ 6.28 ppm

Particularly suited fast-acting hardeners belong to one of the groups of compounds corresponding to the following general formula A to E.

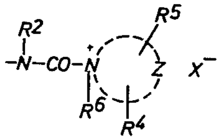
(A)



in which

R² represents an alkyl group, a substituted alkyl group, e.g. an aralkyl group, e.g. benzyl, which may be substituted with $C_1$—$C_5$ alkyl or halogen preferably a $C_1$—$C_3$ alkyl group, an aryl group, which may be substituted with a $C_1$—$C_3$ alkyl group or with halogen, e.g. phenyl, which may be substituted with methyl, ethyl, or propyl, chlorine or bromine,

R³ may have one of the significances given for R² or an alkyl, aryl, aralkyl or alkyl-aryl-alkyl group, e.g. ethyl, propyl, phenyl and xylyl any of which may be substituted, with another carbamoyl ammonium group of the formula



or,

$R^2$ and $R^3$ may together represent the atoms required to complete a substituted or unsubstituted heterocyclic ring,

$R^4$ represents hydrogen, a $C_1$—$C_3$ alkyl group or the group $-\!\!\left[-A-\right]\!\!_{\alpha}-$, in which A represents a vinyl group of a polymerized vinyl compound or a copolymer with other copolymerizable monomers and $\alpha$ denotes a number such that the molecular weight of the compound is greater than 1000,

$R^5$ represents hydrogen, $C_1$—$C_3$ alkyl, or, if Z represents the atoms required to complete a pyridinium ring and $R^4$ is hydrogen, $R^5$ may represent one of the following groups:

—$NR^7$—CO—$R^8$ wherein

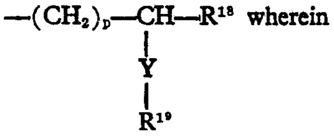
$R^7$=H, Alkyl ($C_1$—$C_4$)
$R^8$=H, Alkyl ($C_1$—$C_4$), $NR^9R^{10}$
$R^9$, $R^{10}$=(same or different) H, Alkyl ($C_1$—$C_4$)

—$(CH_2)_m$—$NR^{11}R^{12}$ wherein

$R^{11}$=—CO—$R^{13}$
$R^{12}$=H, Alkyl ($C_1$—$C_4$)
$R^{13}$=H, Alkyl ($C_1$—$C_4$), $NR^{14}R^{15}$
$R^{14}$=Alkyl ($C_1$—$C_4$), Aryl
$R^{15}$=H, Alkyl, Aryl
m=1—3

—$(CH_2)_n$—$CONR^{16}R^{17}$ wherein

$R^{16}$=H, Alkyl ($C_1$—$C_4$), Aryl
$R^{17}$=H, Alkyl ($C_1$—$C_4$) or
$R^{16}$ and $R^{17}$ together represent the atoms required to complete a 5- or 6-membered aliphatic ring
n=0—3



$-(CH_2)_p-\underset{\underset{R^{19}}{|}}{\underset{Y}{|}}{CH}-R^{18}$ wherein

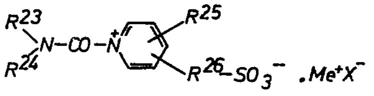
$R^{18}$=H, Alkyl ($C_1$—$C_4$), which may be substituted by halogen
Y=—O—, —$NR^{20}$—
$R^{19}$=H, Alkyl, —CO—$R^{21}$, —CO—$NHR^{22}$
$R^{20}$, $R^{21}$, $R^{22}$=(same or different) H, Alkyl ($C_1$—$C_4$)
p=2—3

$R^6$ represents an alkyl, aryl, or aralkyl group but is absent, if the nitrogen, to which $R^6$ is attached, carries a double-bond in the heterocyclic aromatic ring formed by Z,

Z represents the atoms required to complete a substituted or unsubstituted, 5- or 6-membered, heterocyclic aromatic ring or a condensed system e.g. isoquinoline, which atomic group may contain other hetero atoms in addition to the nitrogen atom, e.g. oxygen or sulphur, and

$X^-$ represents an anion, e.g. halogen$^-$, $BF_4^-$, $NO_3^-$, $SO_4^-$, $ClO_4^-$, or $CH_3OSO_3^-$.

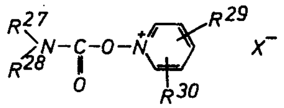
(B)



in which

$R^{23}$, $R^{24}$ have one of the meanings given for $R^2$ and $R^3$,
$R^{25}$ is hydrogen, methyl, or ethyl,
$R^{26}$ is methylene, ethylene, propylene, or a single chemical bond,
$Me^+$ is an alkaline metal cation, e.g. $Li^+$, $Na^+$, $K^+$,
$X^-$ is an anion e.g. $Cl^-$ and $Br^-$.

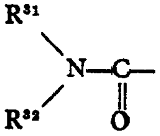
(C)



in which

$R^{27}$ represents $C_1$—$C_8$ alkyl or aryl e.g. phenyl,

$R^{28}$ represents alkyl $C_1$—$C_3$ or the group

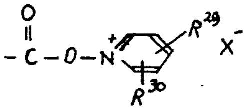


in which

$R^{31}$ represents hydrogen or alkyl e.g. methyl or ethyl, and

$R^{32}$ represents e.g. methyl or ethyl, or

$R^{27}$ and $R^{28}$ together represent the atoms required to complete a heterocyclic ring system such as a pyrrolidine, morpholine, piperidine, perhydroazepine, 1,2,3,4-tetrahydroquinoline imidazolidine-2-OH ring, or a piperazine ring, which by its second nitrogen atom is linked to a similar second molecular group corresponding to the general formula:—



$R^{29}$ represents hydrogen, halogen e.g. chlorine and bromine, $C_1$—$C_3$ alkyl e.g. methyl and ethyl, $C_1$—$C_8$ alkoxy, cyano, —$CONH_2$ or —NH—CO—O alkyl (such as methyl and ethyl),

$R^{30}$ represents hydrogen, or alkyl e.g. methyl and ethyl, and

$X^-$ represents an anion such as $Cl^-$, $BF_4^-$, or $ClO_4^-$.

(D)

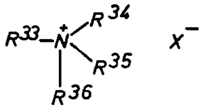
$$R^{31}—N=C=N—R^{32}$$

in which

$R^{31}$ and $R^{32}$ (similar or different) represent alkyl (e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, s-butyl, isobutyl, t-butyl, amyl and hexyl), alkyl, cyclohexyl, methylcyclohexyl, alkoxyalkyl (e.g. methoxy or ethoxyethyl or -propyl), aryl e.g. phenyl or substituted aryl, benzyl, β-phenylethyl, morpholinylethyl, morpholinylpropyl, diethylaminoethyl, pyridylethyl, 2-, 3- or 4-pyridyl methyl or ethyl, N-piperidinyl propyl, or preferably

$R^{31}$ represents $C_1$—$C_5$ alkyl and

$R^{32}$ represents the group



in which

$R^{33}$ represents alkylene having 1 to 5 carbon atoms,

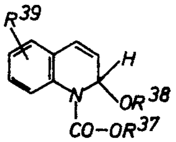
$R^{34}$ and $R^{35}$ represent $C_1$—$C_3$ alkyl or

$R^{34}$ and $R^{35}$ together form a 6-membered heterocyclic ring with one or two hetero atoms e.g. morpholine, piperidine, pyrrolidine,

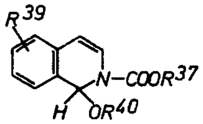
$R^{36}$ represents hydrogen or $C_1$—$C_5$ alkyl, and

$X^-$ represents an anion for example $Cl^-$, $Br^-$, or toluene sulphonate.

(E)



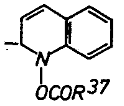
or



in which

$R^{37}$ represents $C_1$—$C_4$ alkyl which may be substituted with alkyloxy e.g. with methoxy or ethoxy; or with halogen e.g. with chlorine or bromine,

$R^{38}$ represents $C_1$—$C_4$ alkyl which may be substituted with alkoxy e.g. methoxy or ethoxy, with halogen e.g. chlorine, with dialkylamino or trialkylammonium, e.g. dimethyl or diethylamino, trimethyl or triethylammonium, with aryl e.g. phenyl, or with alkylsulphonyl e.g. methyl or ethylsulphonyl or $R^{38}$, if $R^{39}$ is hydrogen, represents



$R^{39}$ represents hydrogen, halogen, e.g. chlorine or bromine, alkoxy e.g. methoxy, sulpho or alkyl e.g. methyl, ethyl, or propyl,

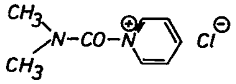
$R^{40}$ represents an alkyl group or a substituted alkyl group.

Details concerning the preparation and properties of these hardeners can be found in the above-mentioned publications. Preferred fast-acting hardeners for use in the colour photographic material according to the invention are the carbamoylpyridinium compounds of formulae A and B, and particularly the carbamoyloxypyridinium compounds of formula C.

The following are examples of fast-acting compounds according to formulae A to E:

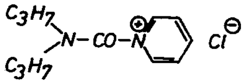
Compounds according to formula (A):

1.



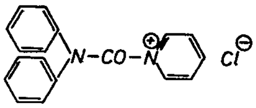
syrup, strongly hygroscopic

2.



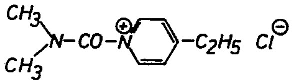
syrup, strongly hygroscopic

3.



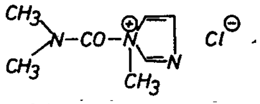
melting point 112°C

4.



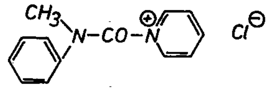
melting point 103°C

5.



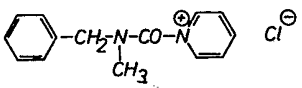
melting point 87—89°C

6.



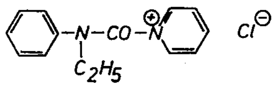
melting point 108—110°C

7.



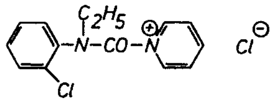
syrup, hygroscopic

8.



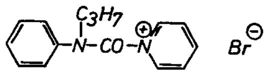
melting point 105—107°C

9.



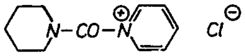
syrup

10.



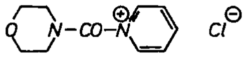
melting point 103—105°C

11.



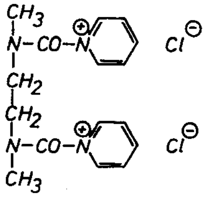
melting point 75—77°C

12.



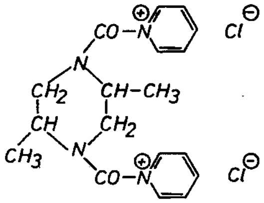
melting point 110—112°C

13.



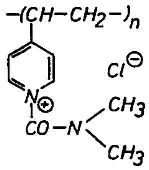
melting point 95—96°C

14.



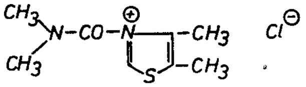
melting point 106°C

15.



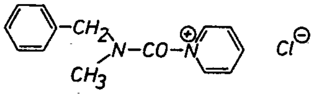
molecular weight higher than 10,000

16.

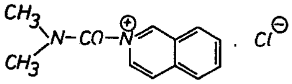


melting point 66—68°C

17.

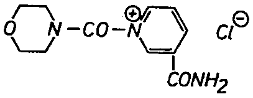


18.



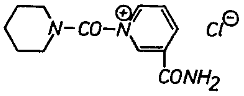
oil

19.



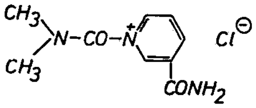
melting point 103—105°C

20.



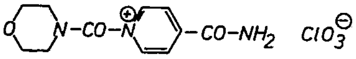
oil

21.

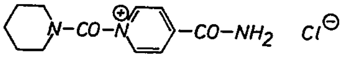


melting point 109°C

22.

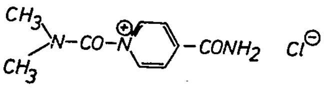


23.



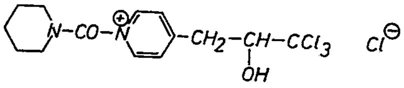
oil

24.



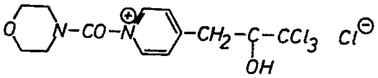
melting point 115°C

25.



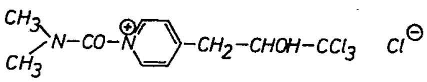
melting point 154°C

26.



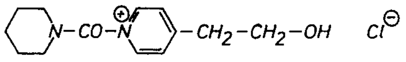
melting point 140°C

27.



melting point 115°C

28.



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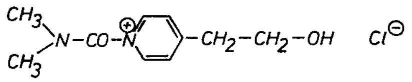
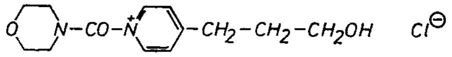
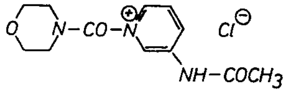


melting point 140—145°C

30.

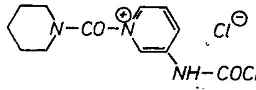


31.



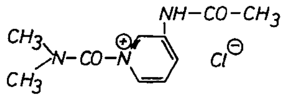
melting point 118—120°C

32.



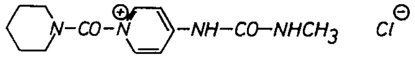
melting point 90°C

33.



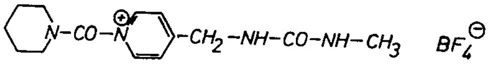
melting point 210°C

34.



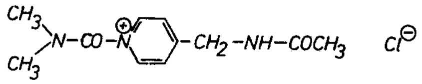
oil

35.



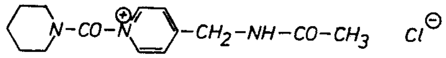
oil

36.



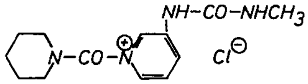
oil

37.



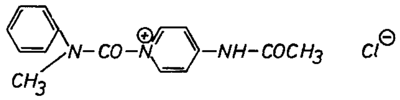
oil

38.

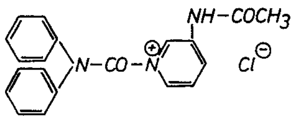


melting point 60—65°C

39.



40.



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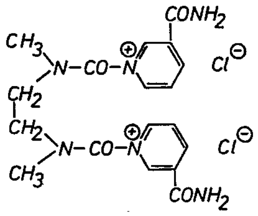

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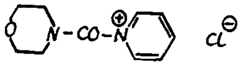
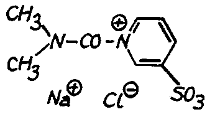
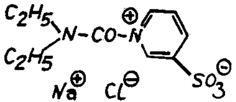


Compounds according to formula (B):

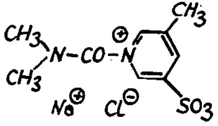
1.



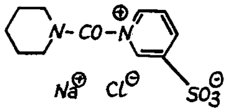
2.



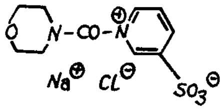
3.



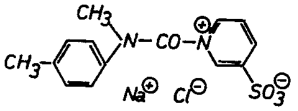
4.



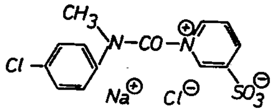
5.



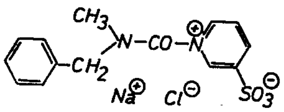
6.



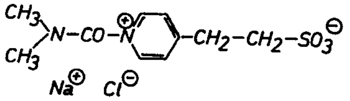
7.



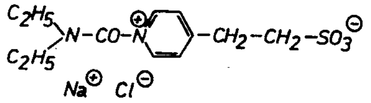
8.



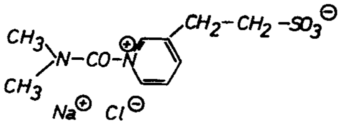
9.



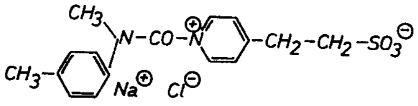
10.



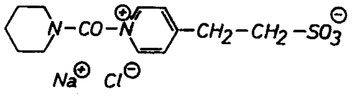
11.



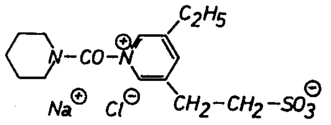
12.



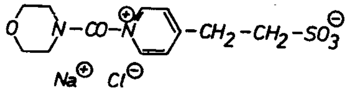
13.



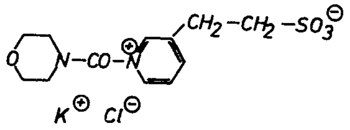
14.



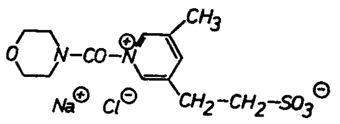
15.



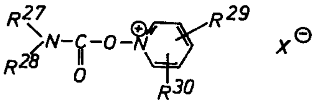
16.

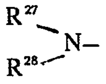
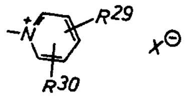
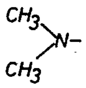
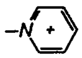
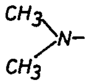
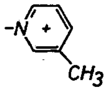
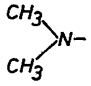
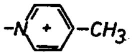
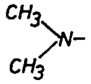
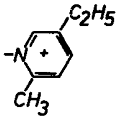
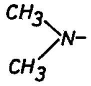
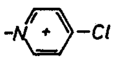
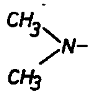
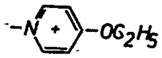
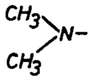
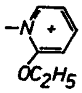
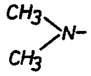
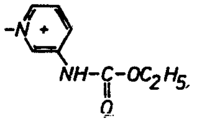
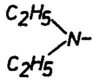
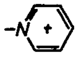
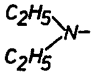
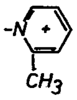
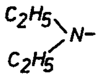
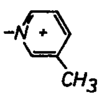
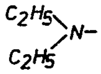
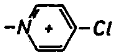
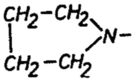
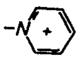


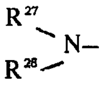
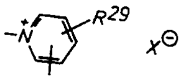
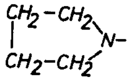
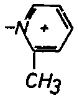
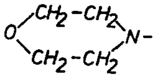
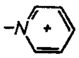
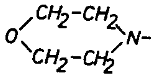
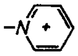
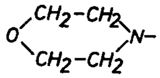
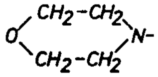
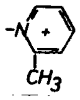
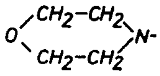
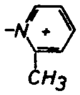
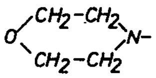
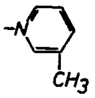
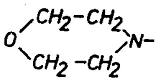
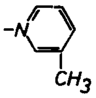
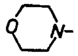
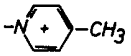
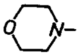
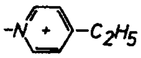
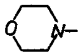
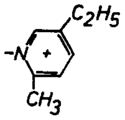
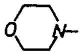
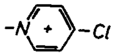
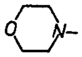
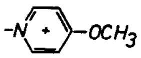
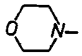
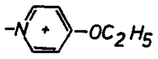
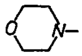
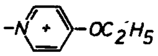
17.

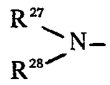
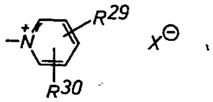
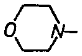
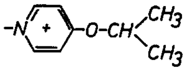
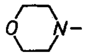
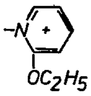
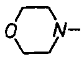
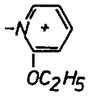
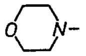
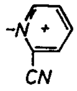
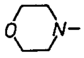
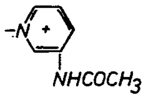
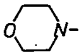
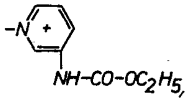
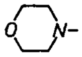
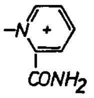
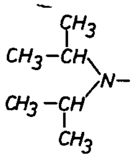
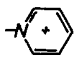
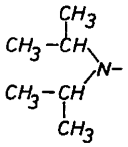
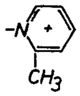
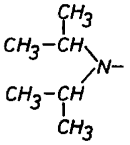
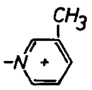
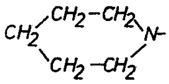
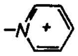
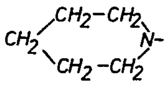
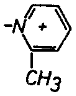
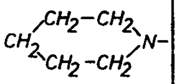
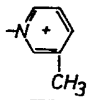
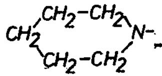
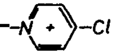


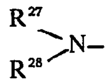
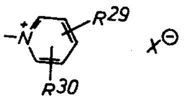
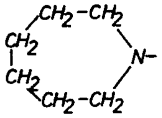
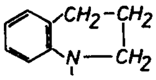
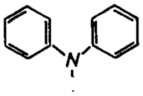
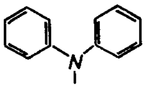
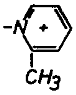
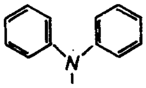
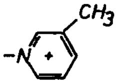
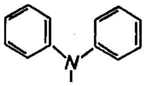
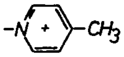
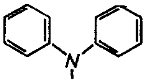
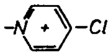
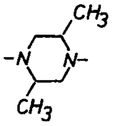
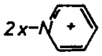
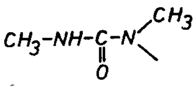
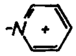
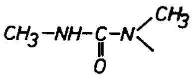
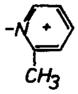
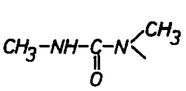
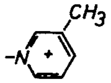
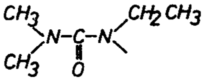
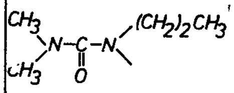
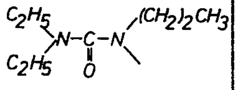
Compounds according to formula (C):

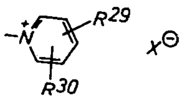
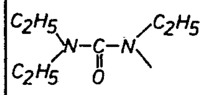
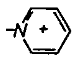
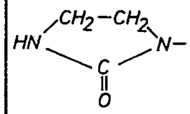
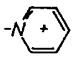
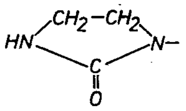
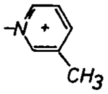


| Subst. No. |  |  | $X^{(-)}$ | melting point °C (decomp.) |
|---|---|---|---|---|
| 1 |  |  | $Cl^{\ominus}$ | 163–67° |
| 2 |  |  | $Cl^{\ominus}$ | 168–70° |
| 3 |  |  | $Cl^{\ominus}$ | 86° |
| 4 |  |  | $Cl^{\ominus}$ | 90° |
| 5 |  |  | $ClO_4^{\ominus}$ | 100–102° |
| 6 |  |  | $ClO_4^{\ominus}$ | 95–100° |
| 7 |  |  | $ClO_4^{\ominus}$ | 100–102° |
| 8 |  |  | $ClO_4^{\ominus}$ | 150° |
| 9 |  |  | $Cl^{\ominus}$ | 108–110° |
| 10 |  |  | $ClO_4^{\ominus}$ | 64–65° |
| 11 |  |  | $ClO_4^{\ominus}$ | 130–32° |
| 12 |  |  | $Cl^{\ominus}$ | 95–100° |
| 13 |  |  | $Cl^{\ominus}$ | 114–115° |

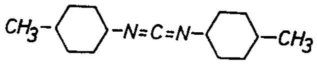
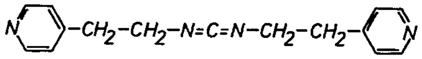
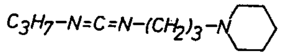
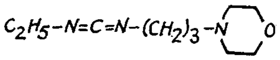
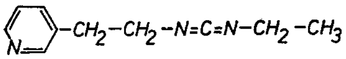
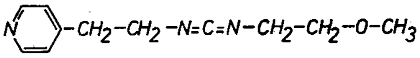
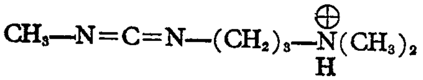
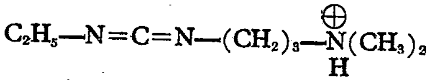
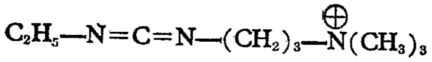
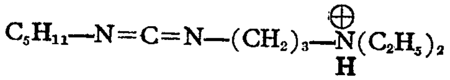
| Subst. No. |  |  | $X^{(-)}$ | melting point °C (decomp.) |
|---|---|---|---|---|
| 14 |  |  | $Cl^{\ominus}$ | 90–92° |
| 15 |  |  | $Cl^{\ominus}$ | 132° |
| 16 |  |  | $BF_4^{\ominus}$ | 138–140° |
| 17 |  |  | $ClO_4^{\ominus}$ | 150–152° |
| 18 |  |  | $Cl^{\ominus}$ | 110–13° |
| 19 |  |  | $ClO_4^{\ominus}$ | 140–42° |
| 20 |  |  | $Cl^{\ominus}$ | 130–32° |
| 21 |  |  | $ClO_4^{\ominus}$ | 144–46° |
| 22 |  |  | $Cl^{\ominus}$ | >90° |
| 23 |  |  | $Cl^{\ominus}$ | 100–102° |
| 24 |  |  | $Cl^{\ominus}$ | 102–104° |
| 25 |  |  | $Cl^{\ominus}$ | 100–102° |
| 26 |  |  | $Cl^{\ominus}$ | 113–115° |
| 27 |  |  | $Cl^{\ominus}$ | >115° |
| 28 |  |  | $ClO_4^{\ominus}$ | 112–14° |

| Subst. No. |  |  | $X^{(-)}$ | melting point °C (decomp.) |
|---|---|---|---|---|
| 29 |  |  | $Cl^{\ominus}$ | 93–95° |
| 30 |  |  | $Cl^{\ominus}$ | 65–70° |
| 31 |  |  | $Cl^{\ominus}$ | 65–70° |
| 32 |  |  | $Cl^{\ominus}$ | 80–82° |
| 33 |  |  | $ClO_4^{\ominus}$ | 150° |
| 34 |  |  | $ClO_4^{\ominus}$ | 162–63° |
| 35 |  |  | $ClO_4^{\ominus}$ | 200° |
| 36 |  |  | $Cl^{\ominus}$ | 158° |
| 37 |  |  | $Cl^{\ominus}$ | 138° |
| 38 |  |  | $Cl^{\ominus}$ | 152–154° |
| 39 |  |  | $Cl^{\ominus}$ | 85–86° |
| 40 |  |  | $ClO_4^{\ominus}$ | 100° |
| 41 |  |  | $ClO_4^{\ominus}$ | 80° |
| 42 |  |  | $Cl^{\ominus}$ | 104–106° |

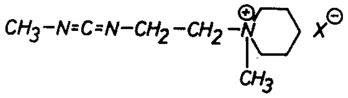
| Subst. No. |  |  | $X^{(-)}$ | melting point °C (decomp.) |
|---|---|---|---|---|
| 43 |  |  | $Cl^{\ominus}$ | 76–78° |
| 44 |  |  | $Cl^{\ominus}$ | 140–144° |
| 45 |  |  | $Cl^{\ominus}$ | 160–162° |
| 46 |  |  | $Cl^{\ominus}$ | 98–100° |
| 47 |  |  | $Cl^{\ominus}$ | 218–220° |
| 48 |  |  | $Cl^{\ominus}$ | 116° |
| 49 |  |  | $Cl^{\ominus}$ | 125–128° |
| 50 |  |  | $2Cl^{\ominus}$ | 109–112° |
| 51 | <br>$CH_3-NH-C(=O)-N(CH_3)-$ |  | $Cl^{\ominus}$ | 87–89° |
| 52 | <br>$CH_3-NH-C(=O)-N(CH_3)-$ |  | $Cl^{\ominus}$ | 105° |
| 53 | <br>$CH_3-NH-C(=O)-N(CH_3)-$ |  | $Cl^{\ominus}$ | 88–89° |
| 54 | <br>$(CH_3)_2N-C(=O)-N(CH_2CH_3)-$ |  | $Cl^{\ominus}$ | 168–170° |
| 55 | <br>$(CH_3)_2N-C(=O)-N((CH_2)_2CH_3)-$ |  | $Cl^{\ominus}$ | 169–173° |
| 56 | <br>$(C_2H_5)_2N-C(=O)-N((CH_2)_2CH_3)-$ |  | $Cl^{\ominus}$ | 173–180° |

| Subst. No. | $R^{37}R^{28}N-$ |  | $X^{(-)}$ | melting point °C (decomp.) |
|---|---|---|---|---|
| 57 |  |  | $Cl^{\ominus}$ | 173–183° |
| 58 |  |  | $Cl^{\ominus}$ | 221–223° |
| 59 |  |  | $Cl^{\ominus}$ | 180–185° |

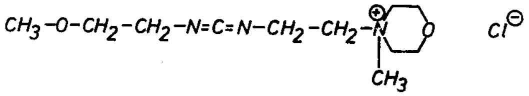
Compounds according to formula (D):

1. $C_2H_5-N=C=N-C_2H_5$
2. $CH_2=CH-CH_2-N=C=N-CH_2-CH=CH_2$
3. $CH_3O-CH_2-CH_2-N=C=N-CH_2-CH_2-OCH_3$
4. 
5. $C_2H_5-(CH_3)CH-N=C=N-CH(CH_3)-C_2H_5$
6. $(C_2H_5)_2N-CH_2-CH_2-N=C=N-CH_2-CH_2-N(C_2H_5)_2$
7. 
8. $CH_3-N=C=N-CH(CH_3)_2$
9. $C_2H_5-N=C=N-(CH_2)_2-OCH_3$
10. 
11. 
12. 
13. 
14.  $CH_3-N=C=N-(CH_2)_3-\overset{\oplus}{\underset{H}{N}}(CH_3)_2$ $Cl^{\ominus}$
15.  $C_2H_5-N=C=N-(CH_2)_3-\overset{\oplus}{\underset{H}{N}}(CH_3)_2$ $Cl^{\ominus}$
16.  $C_2H_5-N=C=N-(CH_2)_3-\overset{\oplus}{N}(CH_3)_3$ $Cl^{\ominus}$
17.  $C_5H_{11}-N=C=N-(CH_2)_3-\overset{\oplus}{\underset{H}{N}}(C_2H_5)_2$ $Cl^{\ominus}$

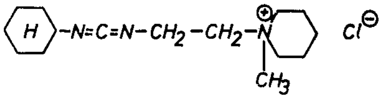
18.



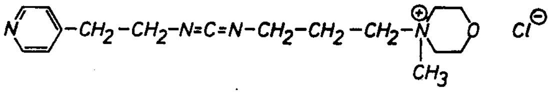
19.



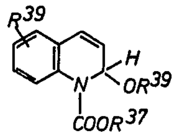
20.



21.



Compounds according to formula (E)



| No. | $R^{37}$ | $R^{38}$ | $R^{39}$ | Boiling point (°C) | Melting point (°C) |
|---|---|---|---|---|---|
| 1 | $CH_3$ | $CH_3$ | H | 130° | |
| 2 | $C_2H_5$ | $C_2H_5$ | H | | 64–66° |
| 3 | $CH_3$ | $C_2H_5$ | H | | 75–76° |
| 4 | $C_2H_5$ | $CH_3$ | H | 135–140° | |
| 5 | $CH_3$ | $(CH_2)_2.CH_3$ | H | 135–140° | |
| 6 | $CH_3$ | $CH.(CH_3)_2$ | H | 180–185° | |
| 7 | $CH_3$ | $(CH_2)_2.OCH_3$ | H | 180–168° | |
| 9 | $CH_3$ | $(CH_2)_2.SO_2.CH_3$ | H | non-distillable oil | |
| 10 | $CH_3$ | $(CH_2)_2.SO_2.C_2H_5$ | H | ,, | |
| 11 | $CH_3$ | $(CH_2)_2.Cl$ | H | 135–150° | |
| 12 | $CH_3$ | $(CH_2)_2.\overset{\oplus}{N}(CH_3)_3\ Cl^{\ominus}$ | H | | |
| 13 | $C_2H_5$ | $(CH_2)_2.CH_3$ | H | 140–145° | |
| 14 | $C_2H_5$ | $CH.(CH_3)_2$ | H | 130–134° | |
| 15 | $C_2H_5$ | $(CH_2)_2.OCH_3$ | H | 160–165° | |

| No. | $R^{37}$ | $R^{38}$ | $R^{39}$ | Boiling point (°C) | Melting point (°C) |
|---|---|---|---|---|---|
| 16 | $C_2H_5$ | $(CH_2)_2.OC_2H_5$ | H | 175–180° | |
| 17 | $C_2H_5$ | $CH_2.C_6H_5$ | H | 180–185° | |
| 18 | $C_2H_5$ | $(CH_2)_2.C_6H_5$ | H | 180–190° | |
| 19 | $C_2H_5$ | $(CH_2)_2.SO_2.CH_2.CH_3$ | H | non-distillable oil | |
| 20 | $C_2H_5$ | $(CH_2)_2.Cl$ | H | 135–145° | |
| 21 | $C_2H_5$ | $(CH_2)_2.\overset{\oplus}{N}(CH_3)_3Cl^{\ominus}$ | H | | 140° (decomp.) |
| 22 | $C_2H_5$ | $(CH_2)_3.CH_3$ | H | 137–139° | |
| 23 | $(CH_2)_2.OCH_3$ | $CH_3$ | H | 175–180° | |
| 24 | $(CH_2)_2.OCH_3$ | $(CH_2)_2.OCH_3$ | H | 180–185° | |
| 25 | $C_2H_5$ | $C_2H_5$ | (5) $SO_3Na$ | syrup | |
| 26 | $C_2H_5$ | $C_2H_5$ | (8) $OCH_3$ | 160 | |

The fast-acting hardeners can be added in aqueous or alcoholic solution to the hydrophilic protein colloid used as the vehicle for the silver halide in the photographic material according to the invention prior to the coating thereof.

The hardeners have to be added immediately before the coating since they enter into reaction very quickly with the hydrophilic colloid e.g. gelatin or the other proteins commonly used in photography. After the hardeners had been added, the coating solutions have to be coated within a few minutes. The speed, at which the hardening reaction takes place, depends mainly upon the concentrations of the proteins in the coating solution.

The concentrations at which the hardeners according to the invention are used in the coating solution may vary within wide limits and depend mainly upon the particular compound used as hardener.

Satisfactory results are obtained with quantities of 0.1 to 10% by weight and preferably 0.2 to 5% by weight based on the dry weight of binder.

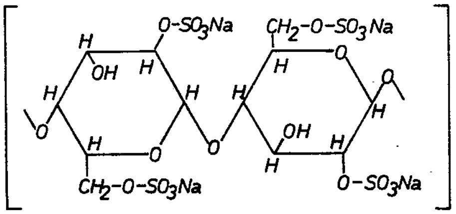
It is also possible to coat non-hardening coating solutions first and then to cover the thus obtained layers with a solution of the hardening compounds. It is advantageous to use in this solution a high molecular compound as film forming colloid, which does not enter into reaction with the hardener and has good film forming properties. Polysaccharides described in the published German Patent Application 2,417,779 have proved to be very appropriate for this purpose. Suitable polysaccharides are straight-chain polymers, in which either

(A) at least one third of the monosaccharide units are linked in the 1-2-position and the remaining monosaccharide units are linked in the 1-4-position, or

(B) substantially all the monosaccharide units are linked in the 1-4-position and at least 50% of the hydroxyl groups of the monosaccharide units are acetylated or replaced by an $OSO_3Me$ group in which Me represents an alkali metal.

Examples of such polysaccharides include the polymers, which can be synthetized by biosynthesis from special strains of bacteria and which are named after the bacteria that bring about this biosynthesis, e.g. B—1459 and B—1973. This nomenclature is conventionally used in literature and makes it possible for the polysaccharides to be identified unequivocally. Further information on the two above-mentioned polysaccharides B—1459 and B—1973 can be found in the papers by D. G. Orentas et al, Can. J. Microbiol., 9, 427 (1963); J. H. Sloneker et al, Can. J. Chem., 46, 3, 353 (1968); L. L. Wallen et al, Appl. Microbiol., 13, 272 (1965); M. E. Slodke, Biochem. Biophys. Acta 69; and in the U.S. Patent Specifications 3,000,790; 3,383,307; 3,391,061 and 3,516,983.

A further example of a polysaccharide suitable for the process of the invention is the cellulosesulphate obtained under the Trade Mark KELCO SCS, to which the following formula is attributed:



Another product suitable for the process of the invention is the polysaccharide B—1459, obtained under the Trade Mark KELZAN.

The quantities of polysaccharide and hardener to be employed depend mainly upon the nature of the material to be hardened, the number and the thickness of the layers to be hardened, the quantity of composition to be applied, and the polysaccharide used. The commercial polysaccharides, e.g. those obtained under the Trade Mark KELZAN and graded HV (High-Viscosity), MV (Medium-Viscosity), and LV (Low-Viscosity) allow for wide variations in the quantity applied wet or in the resulting thickness of the layer. Satisfactory results are generally obtained with coating solutions containing 1 to 20 g of polysaccharide and 5 to 50 g of hardener per 1000 ml of water applied in a quantity corresponding to 20 to 100 g/sq.m when wet if the solutions are required for hardening a photographic three-colour-negative material of conventional structure. A photographic material treated in this way will in any case be capable of withstanding the mechanical stress produced by machine processing at 30 to 40°C after it has been dried and stored for one day. Without regard to the structure of the photographic material it can be said that 0.1 to 10% by weight of hardener according to the invention, based on the dry weight of the binder to be hardened, suffices to produce a photographic material that can be processed at 30 to 40°C.

The fast-acting hardeners can be used either alone or combined. Furthermore the compounds can be combined with any compounds from the classes of hardeners previously known, e.g. formaldehyde, mucochloric acid, triacrylformal, bisvinylsulphones, bisvinylsulphonamides, dialdehydes, or bischloroacetamides, or inorganic salts, e.g. chromium(III), aluminium(III), and zirconium salts.

The colloid layers to be hardened of the colour material acording to the invention may contain, in addition to gelatin, water-soluble high polymeric compounds, in particular polyvinyl alcohol, the sodium salt of polyacrylic acid, and other copolymers containing carboxyl groups, polyvinyl pyrrolidone, polyacrylamide or high molecular weight natural substances such as dextranes, dextrines, starch ether, alginic acid, or derivatives of alginic acid.

The 2-pyrazolin-5-one coupler precursors according to formulae I and II having a ballasting group in the 1- or 3-position can be incorporated into the photographic silver halide material according to any suitable known process. The coupler precursors are incorporated preferably into photographic hydrophilic colloid media from solutions in high boiling sparingly water-miscible solvents such as di-n-butyl phthalate and tricresyl phosphate or in low boiling sparingly water-miscible solvents e.g. ethyl acetate, methylene chloride, diethyl carbonate and chloroform, or mixtures of two or more thereof.

For this purpose these solutions can be dispersed in extremely fine droplets, preferably in the presence of one or more wetting or dispersing agents, into the hydrophilic colloid medium e.g. aqueous gelatin, or into water, the low boiling sparingly water-miscible solvent being removed then by evaporation. The stable dispersions of the colour coupler precursors can be stored as such and then admixed whenever desired with the very coating composition of the hydrophilic colloid layer such as a silver halide emulsion layer, in which the coupler precursors have to be present.

If desired the coupler precursors can be incorporated in another way into the hydrophilic colloid medium.

More details about particularly suitable techniques that may be employed for incorporating the coupler precursors into a hydrophilic colloid layer of a photographic material can be found in the United States Patent Specifications 2,269,158; 2,284,887; 2,304,939; 2,304,940 and 2,322,027, the United Kingdom Patent Specifications 791,219; 1,098,594; 1,099,414; 1,099,415; 1,099,416; 1,099,417; 1,218,190; 1,272,561; 1,297,347 and 1,297,947, the French Patent Specification 1,555,663, the Belgian Patent Specification 722,026 and the German Patent Specification 1,127,714.

The silver halide — the photographic materials according to the invention may be silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide, silver bromoiodide, and silver chlorobromoiodide .The coupler precursors can be used in emulsions of the mixed packet type as described in the U.S. Patent Specification 2,698,794 or emulsions of the mixed grain type as described in the U.S. Patent Specification 2,592,243. The coupler precursors can be used with emulsions in which latent images are formed predominantly at the surface of the silver halide crystals, or with emulsions in which latent images are formed predominantly inside the silver halide crystals.

The hydrophilic colloid used as the vehicle for the silver halide is usually gelatin, but other proteinaceous colloids can be used, possibly in addition to gelatin.

The light-sensitive silver halide emulsions for use in the preparation of a photographic material according to the present invention can be sensitized chemically as well as optically. They can be sensitized chemically by effecting the ripening in the presence of small amounts of sulphur-containing compounds such as allyl thiocyanate, allyl thiourea or sodium thiosulphate. The emulsions can also be sensitized by means of reductors, e.g. tin compounds as described in the French Patent Specification 1,146,955 and in the Belgian Patent Specification 568,687, imino-aminomethanesulphinic acid compounds as described in the United Kingdom Patent Specification 789,823 and small amounts of noble metal compounds such as gold, platinum, palladium, iridium, ruthenium, and rhodium compounds. They can be sensitized optically by means of cyanine and merocyanine dyes.

The emulsions can also comprise compounds that sensitize by development acceleration e.g. compounds of the polyoxyalkylene type such as alkylene oxide condensation products as described i.e. in the U.S. Patent Specifications 2,531,832;

2,533,990; 3,158,484 and 3,210,191, in the United Kingdom Patent Specifications 920,637 and 991,608, and in the Belgian Patent Specification 648,710, and onium derivatives of amine oxides, as described in the United Kingdom Patent Specification 1,121,696.

The emulsions may comprise stabilizers e.g. heterocyclic nitrogen-containing thioxo compounds such as benzothiazoline 2-thione and 1-phenyl-2-tetrazolin-5-thione and compounds of the hydroxytriazolopyrimidine type. They can also be stabilized with mercury compounds such as the mercury compounds described in the Belgian Patent Specifications 524,121; 677,337, and 707,386, and in the U.S. Patent Specification 3,179,520.

The light-sensitive emulsions may comprise any other type of ingredients such as plasticizers, hardeners or wetting agents.

The non-diffusing magenta coupler precursors described in the present invention are incorporated usually into the green-sensitized silver halide emulsion for forming one of the differently sensitized silver halide emulsion layers of a photographic multilayer colour material. Such photographic multilayer colour material usually comprises a support, a red-sensitized silver halide emulsion layer with a cyan colour coupler, a green-sensitized silver halide emulsion layer with a magenta colour coupler, and a blue-sensitive silver halide emulsion layer with a yellow colour coupler.

The emulsions can be coated on a wide variety of photographic emulsion supports. Typical supports include cellulose ester film, polyvinylacetal film, polystyrene film, polyethylene terephthalate film, and related films or resinous materials, as well as paper and glass. It is also possible to employ paper coated with $\alpha$-olefin polymers e.g. paper coated with polyethylene, polypropylene or ethylene butylene copolymers.

The colour photographic materials according to the invention can be developed with any of the known aromatic primary amino colour developing substances e.g. p-phenylenediamine and derivatives thereof such as N,N - diethyl - p - phenylenediamine, N - butyl - N - sulphobutyl - p - phenylenediamine, 2 - amino - 5 - diethylaminotoluene, 4 - amino - N - ethyl - N - ($\beta$ - methanesulphonamidoethyl) - m-toluidine, N - hydroxyethyl - N - ethyl - p - phenylenediamine or 4 - amino - 3-methyl - N - ethyl - N - ($\beta$ - hydroxyethyl)aniline.

It may be advisable to accelerate the setting free of the 2-pyrazolin-5-one coupler from the coupler precursor during the development. For this purpose organic amines can be added to the developer or the material to be developed can be treated before the development with an alkaline solution containing an organic amine, as described in the U.S. Defensive Publication T 887007.

Suitable organic amines are primary, secondary, and tertiary amines as well as saturated and unsaturated cyclic amines. Representative examples of amines are alkyl-, dialkyl-, and trialkylamines, in which the alkyl group may be substituted and have an aliphatic chain length of 1 to 10 carbon atoms, preferably of 1 to 4 carbon atoms, e.g. methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl and t-butyl, e.g. methylamine, ethylamine, allylamine, trimethylamine, triethylamine, 2-aminoethanol; arylamine such as aniline or dimethylaniline; alkyldiamines, the alkyl group of which may be substituted and have an aliphatic chain length of 2 to 10 carbon atoms, preferably of 2 to 4 carbon atoms, e.g. ethyl, propyl or butyl, such as ethylenediamine or propylenediamine; unsaturated cyclic amines e.g. pyridine or imidazole; saturated cyclic amines, wherein the amine-nitrogen atom is a part of a 4- to 6-membered ring, e.g. piperidine, indoline or 1,4-ethylenepiperidine; hydrazines including alkyl- and arylhydrazines, wherein the alkyl group contains 1 to 4 carbon atoms, e.g. methyl, ethyl, propyl or butyl, such as hydrazine, 1,1-dimethylhydrazine, phenylhydrazine, nitrophenylhydrazine or dinitrophenylhydrazine.

The following examples illustrate the invention.

### Example 1.

117 g of silver bromoiodide emulsion (2—3 mole % of iodide) containing per kg an amount of silver halide equivalent to 47 g of silver nitrate as well as 73.4 g of gelatin were diluted with 192.5 g of a 7.5% aqueous gelatin solution and 200 g of distilled water. The resulting emulsion was admixed with an emulgate obtained by dissolving 0.006 mole of colour coupler precursor 22 in 18 ml of ethyl acetate, dispersing the solution in 100 ml of a 5% aqueous gelatin solution in the presence of a dispersing agent by means of an ultrasonic wave generator, and eliminating the ethyl acetate by evaporation under reduced pressure. After neutralization of the emulsion and addition of the usual ingredients distilled water was added to make 720 g.

In the same way an emulsion was prepared, which instead of the acylated colour coupler contained the non-acylated one.

The emulsions obtained were coated on a cellulose triacetate support in a ratio of 125 g per m$^2$ and then covered with an aqueous gelatin solution of hardener C 15 in an amount of 2.6% by weight based on the dry weight of gelatin of the emulsion layer.

The dried materials were exposed for 1/20 s through a continuous wedge having a constant of 0.3 and developed subsequently for 10 minutes at 22°C in a developing bath having the following composition:

| | |
|---|---|
| 2-amino-5-diethylaminotoluenehydrochloride | 3 g |
| sodium hexametaphosphate | 2 g |
| anhydrous sodium sulphite | 4 g |
| anhydrous sodium carbonate | 17 g |
| potassium bromide | 2 g |
| water to make | 1 litre |

The developed materials were treated for 5 minutes at 24°C in an intermediate bath containing 200 g of sodium thiosulphate per litre of water, rinsed for 10 min. in water, and treated in a potassium bichromate bleaching bath.

The bleached materials were rinsed for 5 min in water and fixed in an aqueous solution of 200 g of sodium thiosulphate per litre.

After a final rinsing in water of 10 min the materials were dried. Magenta wedges having the following photographic characteristics were obtained:

| Colour coupler Precursor | Relative sensitivity | Gamma | $D_{max}$ |
|---|---|---|---|
| non-acylated | 100 | 1.20 | 1.85 |
| acylated | 98 | 1.21 | 2.07 |

## Example 2.

Example 1 was repeated with the difference that instead of the acylated coupler precursor 22 the acylated coupler precursor 9 was used.

The materials were exposed for 1/20 s to a continuous wedge having a constant of 0.3 and developed subsequently for 8 min and 20°C in a developing bath having the following composition:

| | |
|---|---|
| N,N-diethyl-p-phenylenediamine sulphate | 2.75 g |
| hydroxylaminesulphate | 1.2 g |
| sodium hexametaphosphate | 4 g |
| anhydrous sodium sulphite | 2 g |
| anhydrous potassium carbonate | 75 g |
| potassium bromide | 2.5 g |
| water to make | 1 litre |

The developed materials were treated for 2 min at 18—20°C in an intermediate bath containing 30 g of sodium thiosulphate in 1 litre of water.

The materials were rinsed for 15 min and then treated in a bleaching bath having the following position:

| | |
|---|---|
| borax | 20 g |
| anhydrous potassium bromide | 15 g |
| anhydrous sodium hydrogensulphite | 4.2 g |
| potassium cyanoferrate(III) | 100 g |
| water to make | 1 litre |

The bleached materials were rinsed for 5 min and fixed in an aqueous solution of 200 g of sodium thiosulphate per litre.

After a final rinsing in water of 15 min the materials were dried.

Magenta wedges and the following photographic characteristics were obtained:

| Colour coupler Precursor | Relative sensitivity | Gamma | $D_{max}$ |
|---|---|---|---|
| non-acylated | 100 | 0.60 | 1.04 |
| acylated | 100 | 0.88 | 2.22 |

When the emulsion layers had not been coated with a solution of hardener C 15, but with a conventional gelatin antistress layer, a maximum density of 2.20 was obtained for the material containing the non-acylated colour coupler precursor and of 2.46 for the material containing the acylated colour coupler precursor.

### Example 3.

Example 2 was repeated with the difference that the materials now contain the acylated coupler precursor 3 and the corresponding non-acylated coupler precursor.

Magenta wedges having the following photographic characteristics were obtained:

| Colour coupler Precursor | Relative sensitivity | Gamma | $D_{max}$ |
|---|---|---|---|
| non-acylated | 100 | 1.00 | 1.66 |
| acylated | 98 | 0.85 | 2.00 |

### Example 4.

Strips of a photographic material consisting of a film support and two green-sensitized silver bromoiodide emulsion layers coated with a gelatin antistress layer contain 14 g of gelatin and an amount of silver halide equivalent to 1.4 g of silver nitrate, and 1.3 mmole of colour coupler or precursor per sq.m. The colour couplers or precursor were incorporated into the emulsion from a solution in ethyl acetate and tricresyl phosphate, whereupon the ethyl acetate was removed by evaporation.

The gelatin antistress layers were coated with an aqueous solution of hardener C 15 in an amount of 7% by weight calculated on the dry weight of gelatin of the strips.

The strips were then exposed to a continuous wedge, developed for 4 min 30 s at 25°C in a common developing bath containing N,N - diethyl - p - phenylene-diamine sulphate, and further treated in the usual way in a bleaching bath and a fixing bath.

In the accompanying Table the maximum density values ($D_{max}$) of the magenta wedges obtained as well as the scratch resistance values of the strips of photographic material are given. The values of scratch resistance constittute the weight (in gram) applied to a steel ball having a diameter of 6.4 mm, required to make this ball penetrate into the wet photographic layers down to the very support, when the ball is passed over the material.

TABLE

| Strip | Magenta coupler or Precursor | $D_{max}$ | Scratch resistance |
|---|---|---|---|
| 1 | 1 | 1.66 | 1300 |
| 2 | 3 | 1.66 | 1300 |
| 3 | non-acylated form of coupler precursor 1 and 3 | 1.35 | 700 |

### Example 5.

Strips were made as described in Example 4 with the difference that hardener A 30 was used now.

The strips were exposed to a continuous wedge, developed for 4 min 30 s at 25°C in a common colour develeping bath containing 4 - amino - 3 - methyl - N-ethyl - N - ($\beta$ - hydroxyethyl)aniline - sulphate, and treated in the usual way in a bleaching bath and a fixing bath.

In the accompanying Table the maximum density values ($D_{max}$) of the magenta wedges obtained as well as the values of the scratch resistance as defined in Example 4 are given.

TABLE

| Strip | Magenta coupler or Precursor | Scratch resistance | $D_{max}$ |
|---|---|---|---|
| 1 | 1 | 1450 | 1.65 |
| 2 | 3 | 1450 | 1.44 |
| 3 | non-acylated form of coupler precursor 1 and 3 | 800 | 1.08 |

### Example 6.

Example 5 is repeated with the difference that hardener B 5 was used and that the treatment of the exposed strips occurred at increased temperature (38°C, developing time: 3 min).

TABLE

| Strip | Colour coupler or Precursor | $D_{max}$ | Scratch resistance |
|---|---|---|---|
| 1 | 1 | 2.23 | 1200 |
| 2 | 3 | 1.96 | 1400 |
| 3 | non-acylated form of coupler precursor 1 and 3 | 1.78 | 1400 |

### Example 7.

Strips of material as described in Example 1 and containing coupler precursors 3, 9, 16, and 30 were prepared. The strips were developed as described in Example 2 and the colour strips obtained in this way were exposed in a xenon illuminating device $2.4 \times 10^6$ lux-hours and to a light table lit by fluorescent lamps for $4.10^6$ lux-hours. For comparison analogous strips were prepared, exposed, developed, and irradiated, which strips instead of the acylated coupler precursors 3, 9, 16, and 30 contained corresponding non-acylated couplers.

The decrease in colour densities of the irradiated samples, as compared with non-irradiated samples, measured at density 1.05 is given in % of the following table. The colour density at D=1.05 decreases far less in the case of acylated coupler precursors than in the case of non-acylated couplers. Indeed, the acylated component brings about the stabilization of the dye.

| Coupler or Precursor | xenon test | projection screen |
|---|---|---|
| 3 (acylated) | 18 | 28 |
| non-acylated | 28 | 42 |
| 9 (acylated) | 12 | 8 |
| non-acylated | 35 | 30 |
| 16 (acylated) | 8 | 4 |
| non-acylated | not determined | 17 |
| 30 (acylated) | 8 | 14 |
| non-acylated | 24 | 32 |

### Example 8.

Emulsions were prepared as described in Example 1 containing one of the colour coupler precursors 25, 26 and the parent non-acylated coupler.

All emulsions were coated on a cellulose triacetate support in a ratio of 125 g per sq.m and then covered with an aqueous gelatin solution of hardener C 15 in an amount of 5% by weight based on the dry weight of gelatin of the emulsion layer.

The materials were exposed and processed as described in Example 1.

Magenta wedges with the max.density values listed in the table were obtained.

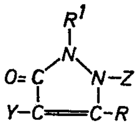
| Coupler or Precursor | $D_{max}$ |
|---|---|
| 25 | 2.53 |
| 26 | 2.81 |
| non-acylated | 1.26 |

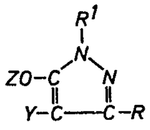
When the emulsion with non-acylated coupler was not used with a fast-acting hardener but with a conventional antistress layer max.density was 2.65.

WHAT WE CLAIM IS:—

1. Colour photographic silver halide material containing a proteinaceous emulsion and a fast-acting hardener, as hereinbefore defined, wherein said material contains a 2-pyrazolin-5-one coupler precursor corresponding to one of the following general formulae I or II:

I.





II.

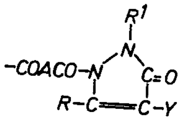
in which

$R^1$ represents an alkyl, substituted alkyl, aryl, substituted aryl or a heterocyclic group,

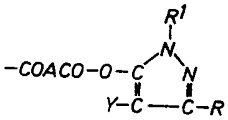
R represents an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, an anilino group, a substituted anilino group, an acylamino group derived from a carboxylic or sulphonic acid or such an acylamino group which is substituted,

Y represents hydrogen, a group or atom that is capable of being split off during colour development in which instance the colour precursor is a colour-forming coloured or colourless 2-pyrazolin-5-one coupler precursor, or a group that cannot be so split off in which instance the coupler precursor is a pyrazolin-5-one competing coupler precursor, and

Z represents an acyl group deriving from an organic carboxylic acid, an alkoxy-carbonyl group, a substituted alkoxy-carbonyl group, an aryloxy-carbonyl group, a substituted aryloxy-carbonyl group, or the group



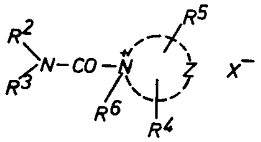
or



in which $R^1$, R, and Y have the above-defined significance, and A represents an alkylene group or an arylene group.

2. A colour photographic material according to claim 1, wherein the 2-pyrazolin-5-one coupler precursor corresponds to formulae I or II, in which $R^1$ represents an alkyl group, a substituted alkyl group, an aryl group or a substituted aryl group.

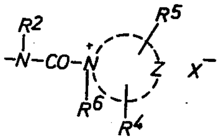
3. Colour photographic material according to claim 1 or 2, wherein the fast-acting hardener corresponds to the following formula:



in which:

$R^2$ represents an alkyl group, substituted alkyl group, aryl group or aryl group substituted with $C_1$—$C_3$ alkyl or halogen,

$R^3$ may have one of the significances given for $R^2$ or an alkyl, aryl, aralkyl, or alkylarylalkyl group substituted with a further carbamoylammonium group of the following formula:



or $R^2$ and $R^3$ together represent the atoms required to complete a substituted or unsubstituted heterocyclic ring,

$R^4$ represents hydrogen, a $C_1$—$C_3$ alkyl group or the group $-[-A-]_{\alpha}-$, in which A represents a vinyl group of a polymerized vinyl compound or of a copolymer with other copolymerizable monomers and $\alpha$ represents a number such that the molecular weight of the compound is greater than 1000,

$R^5$ hydrogen or a $C_1$—$C_3$ alkyl group, or when Z denotes the atomic group required for completing a pyridinium ring and $R^4$ is hydrogen, $R^5$ may represent one of the following groups:

—$NR^7$—CO—$R^8$ wherein

$R^7$=H, alkyl ($C_1$—$C_4$)
$R^8$=H, alkyl ($C_1$—$C_4$), $NR^9R^{10}$
$R^9$, $R^{10}$ (similar or different) H, alkyl ($C_1$—$C_4$)

—$(CH_2)_m$—$NR^{11}R^{12}$ wherein

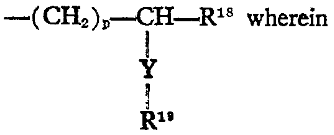
$R^{11}$=—CO—$R^{13}$
$R^{12}$=H, alkyl ($C_1$—$C_4$)
$R^{13}$=H, alkyl ($C_1$—$C_4$), $NR^{14}R^{15}$
$R^{14}$=alkyl ($C_1$—$C_4$), aryl
$R^{15}$=H, alkyl, aryl
m=1—3

—$(CH_2)_n$—$CONR^{16}R^{17}$ wherein

$R^{16}$=H, alkyl ($C_1$—$C_4$), aryl
$R^{17}$=H, alkyl ($C_1$—$C_4$) or

$R^{16}$ and $R^{17}$ together represent the atoms required to complete a 5-membered or 6-membered aliphatic ring

$n=0$—3



$$-(CH_2)_p-\underset{\underset{R^{19}}{|}}{\underset{Y}{\underset{|}{CH}}}-R^{18}$$ wherein

$R^{18}=H$, alkyl ($C_1$—$C_4$), which may be substituted by halogen

$Y=$—O—, —$NR^{20}$—

$R^{19}=H$, alkyl, —CO—$R^{21}$, —CO—$NHR^{22}$

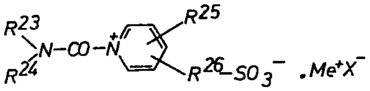
$R^{20}$, $R^{21}$, $R^{22}$ (similar or different) H, alkyl ($C_1$—$C_4$)

$p=2$—3

$R^6$ represents alkyl, aryl, aralkyl, but $R^6$ is absent, if the nitrogen atom, to which $R^6$ is attached, carries a double bond in the heterocyclic aromatic ring formed by Z,

Z represents the group of atoms required for completing a 5-membered or 6-membered substituted or unsubstituted heterocyclic aromatic ring, including a condensed ring system, which group may include 1 or more additional heteroatoms, and $X^-$ represents an anion.

4. Colour photographic material according to any of claims 1 and 2, wherein the hardener corresponds to the following general formula:



in which

$R^{23}$ and $R^{24}$ have one of the meanings given for $R^2$ and $R^3$ in claim 3,

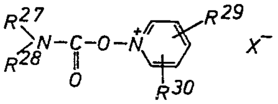
$R^{25}$ represents hydrogen, methyl, or ethyl,

$R^{26}$ represents methylene, ethylene, propylene, or a single chemical bond,

$Me^+$ represents an alkali metal cation,

$X^-$ represents an anion.

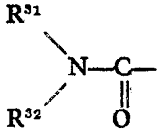
5. Colour photographic material according to any of claims 1 and 2, wherein the hardener corresponds to the following general formula:



in which:

$R^{27}$ represents $C_1$—$C_3$ alkyl or aryl,

$R^{28}$ represents $C_1$—$C_3$ alkyl or the group



$$\begin{matrix} R^{31} & & \\ & \diagdown & \\ & & N-\underset{\underset{O}{\|}}{C}- \\ & \diagup & \\ R^{32} & & \end{matrix}$$

$R^{31}$ represents hydrogen or alkyl, and

$R^{32}$ represents alkyl, or

$R^{27}$ and $R^{28}$ together represent the atoms required to complete a heterocyclic ring system,

$R^{29}$ represents hydrogen, halogen, $C_1$—$C_3$ alkyl, $C_1$—$C_3$ alkoxy, cyano, —$CONH_2$, or —NH—CO—O-alkyl,

$R^{30}$ represents hydrogen or alkyl,

$X^-$ represents an anion.

6. Colour photographic material according to any of claims 1 and 2, wherein the hardener corresponds to the following general formula:

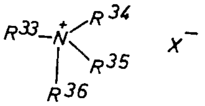
$$R^{31}—N=C=N—R^{32}$$

in which:

$R^{31}$ and $R^{32}$ represent (similar or different) alkyl, alkoxyalkyl, benzyl, $\beta$-phenylethyl, diethylaminoethyl, cyclohexyl, methylcyclohexyl, allyl, morpholinylethyl, morpholinylpropyl, pyridylmethyl or pyridylethyl, aryl or substituted aryl, or

$R^{31}$ represents alkyl having 1 to 5 carbon atoms, and

$R^{32}$ represents the group



in which:

$R^{33}$ represents alkylene having 1 to 5 carbon atoms,

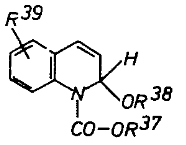
$R^{34}$ and $R^{35}$ represent alkyl having 1 to 3 carbon atoms, or

$R^{34}$ and $R^{35}$ together represent a 6-membered heterocyclic ring having 1 or 2 hetero atoms,

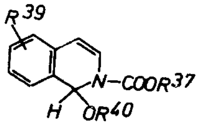
$R^{36}$ represents hydrogen or $C_1$—$C_5$ alkyl, and

$X^-$ represents an anion.

7. Colour photographic material according to any of claims 1 and 2, wherein the hardener corresponds to one of the following general formulae:



and

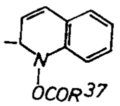


I II

in which:

$R^{37}$ represents $C_1$—$C_4$ alkyl which may be substituted with alkoxy or halogen,

$R^{38}$ represents $C_1$—$C_4$ alkyl which may be substituted with alkoxy, halogen, dialkylamino, trialkylammonium, aryl, alkylsulphonyl, or if $R^{39}$ represents hydrogen, the group



$R^{39}$ represents hydrogen, halogen, alkyl, alkoxy, or sulpho and

$R^{40}$ represents alkyl or substituted alkyl.

8. Colour photographic material according to claim 1 and substantially as described herein.

9. Colour photographic material according to claim 1 and substantially as described in the Examples herein.

HYDE, HEIDE & O'DONNELL,
2 Serjeants' Inn,
London EC4Y 1LL,
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Agents for the Applicants.

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