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(54) **Silver halide photographic element and process for the formation of high contrast negative images**

(57) High contrast negative images are obtained by developing a silver halide photographic element, in the presence of a hydrazine compound, with an alkali aqueous developing solution which contains a combination of developing agent comprising hydroquinone or substituted hydroquinone and a superadditive developing agent and an antioxidant, wherein the developing solution has a pH lower than about 11, preferably from 9.5 to 11.0 and wherein the silver halide photographic element comprises an emulsion layer including surface latent image negative type silver halide grains in reactive association with a contrast promoting agent, preferably a diarylcarbinol compound, more preferably a diarylmethanol compound in a quantity useful to increase contrast. The aryl hydrazine compound is represented by the following formula:



wherein Ar is an aryl group,

G is CO, SO, SO₂, PO₂, PO₃ or C=NR₂;

X⁺ is a radical containing a cationic group,

R, R₁, R₂, which can be the same or different, are hydrogen, alkyl of 1 to 6 carbon atoms and alkyl sulfinyl of 1 to 6 carbon atoms, and

A⁻ is an anion.

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Description**FIELD OF THE INVENTION**

5 This invention relates to silver halide photographic light-sensitive elements and, more particularly, to silver halide photographic light-sensitive elements which provide high contrast negative images upon processing with a stable developing solution.

BACKGROUND OF THE ART

10 In forming high contrast images necessary for Graphic Arts processes by development of silver halide photographic elements, special developers known in the art as "lith" developers are used. The high contrast is achieved by means of the infectious development as described in *Journal of the Franklin Institute*, vol. 239, 221-230 (1945). These developers exhibit an induction period prior to the development of exposed silver halides, after which the infectious development occurs, which gives rise to the high contrast.

15 The typical "lith" developer contains only a single developing agent of the dihydroxybenzene type, such as hydroquinone. In order to enhance the infectious development, "lith" developers contain a low content of alkali sulfite. This low sulfite content renders the developer more prone to aerial oxidation, especially when it is used in combination with processing machines and, more particularly, with Rapid Access type processing machines, where developer degradation is accelerated.

20 The delay in the start of development caused by the long induction period of hydroquinone developers lengthens the processing time and delays access to the finished material. While the induction period has been eliminated and processing time reduced by using the so called "Rapid Access" developers, which contain both hydroquinone and a superadditive developing agent such as phenidone or metol, these Rapid Access developers are not useful for lithographic purposes because they cannot produce the necessary high contrast. This is because Rapid Access developers have a high sulfite content which prevents infectious development and causes a lower contrast than "lith" developers.

25 Several alternatives to using a hydroquinone developing agent with a low sulfite content of the "lith" processing system to achieve high contrast development are known in the art. They are the so-called "high contrast" processing systems which use a hydrazine compound, either in the photographic element or in the developing solution, to promote high contrast. The use of hydrazine compounds allows the use of auxiliary developing agents in combination with the dihydroxybenzene developing agent in order to increase the developing capacity. It also allows the use of relatively high sulfite concentration to protect the developing agents against oxidation, and thereby increasing the developer stability. The high pH level, about 10.5 to 12.8, necessary to obtain the high contrast from the use of hydrazine compounds makes the life of the developing solution relatively short.

30 Processes which make use of hydrazine are disclosed in US 2,419,975; 4,168,977 and 4,224,401. Modifications and improvements to the hydrazine process are disclosed in US 2,410,690; 2,419,974; 4,166,742; 4,221,857; 4,237,214; 4,241,164; 4,243,739; 4,272,606; 4,272,614; 4,311,871; 4,323,643; 4,332,878 and 4,337,634 and in Research Disclosure No. 235, Nov. 1983, Item 23510 "Development nucleation by hydrazine and hydrazine derivatives". Despite the improvements which have been made in the hydrazine process, a remaining inconvenience was the relatively low stability of the developer to aerial oxidation, which is a consequence of the high pH required to achieve the desired high contrast.

35 Contrast promoting agents have been described in US 4,172,728 and 4,269,929, in EP 155,690 and in the above cited Research Disclosure which, incorporated in the developing solution, allow the photographic element, including the hydrazine compound, to reach the desired high contrast at a lower pH.

40 High contrast developing compositions which contain amino compounds and are intended for carrying out development in the presence of a hydrazine compound are also disclosed in US 4,668,605 and 4,740,452. In fact, US 4,668,605 describes developing compositions containing a dihydroxybenzene, a p-aminophenol, a sulfite, a contrast promoting amount of an alkanolamine comprising a hydroxyalkyl group of 2 to 10 carbon atoms and a mercapto compound. The developing compositions of US 4,740,452 contain a contrast promoting amount of certain trialkyl amines, monoalkyl-dialkanolamines or dialkylmonoalkanol amines. However, the need to use the contrast promoting agent in a large amount and the volatility and odor-generating characteristics of amino compounds that are effective in enhancing contrast represent disadvantageous characteristics of the developer solution therein described.

45 US 4,937,160 and 5,190,847 disclose photographic silver halide elements containing an aryl hydrazide having a cationic group for the production of images with ultrahigh contrast. The photographic elements can be developed at relatively low pH, in the range 10.0-11.5 values, by a developing solution including contrast promoting agents such as alkanolamines or secondary aliphatic or aromatic alcohols. Low fog and low tendency to form black spots in unexposed or slightly exposed areas are obtained.

50 US 4,777,118 discloses a process for forming a high contrast negative photographic image by developing a silver halide photographic element, in the presence of a hydrazine compound as nucleating agent, with an alkali aqueous developing solution which contains a combination of developing agent comprising hydroquinone or substituted hydro-

quinone and a superadditive developing agent and an antioxidant, wherein the developing solution has a pH lower than about 12 and wherein the silver halide photographic element comprises an emulsion layer including surface latent image negative type silver halide grains in reactive association with a contrast promoting agent, preferably a diarylcarbinol compound, in a quantity useful to increase contrast. However, in practice, said photographic elements produce photographic images having high contrasts and adequate image quality only when processed by a developing solution at a pH over 11.5. In addition, at lower pH values, in the range from 9.0 to 11.0, the developer solutions are not stable enough. In particular they are very sensitive to atmospheric oxygen, despite their high sulfite content.

US 4,914,003 describes a photographic material containing a generic hydrazine compound as nucleating agent and a specified amine compound as contrast promoting agent to obtain a superhigh contrast negative image when processed by a developing solution having a pH value of 10.5 to 12.0.

Recently, it has been found that well defined photographic elements can be developed in developing solutions having pH below 11.0. For example, US 4,975,354 discloses photographic elements, particularly useful in the field of graphic arts, which are capable of high contrast development, when processed in the presence of a hydrazine compound that functions as a nucleating agent. The elements include certain amino compounds which function as incorporated booster. The characteristics of the compounds contained in the photographic element allow the photographic element to be processed in a developer solution having a pH value in the range of 9 to 10.8.

It would be still desirable to obtain a photographic element providing a very high contrast and good dot quality upon development, in the presence of a hydrazine compound and of a contrast promoting agent, with a conventional Rapid Access type developer solution at a pH value lower than 11.0, without the necessary addition to said solution of ingredients of uncommon use such as the above mentioned contrast promoting agents.

SUMMARY OF THE INVENTION

This invention refers to a silver halide photographic element to be used with a high speed, Rapid Access developer formulation producing a very high contrast negative image suitable for lithographic purposes. Advantages such as reduced dwell time in developer baths, reduced concentrations of ingredients in baths, reduced developer bath costs, and reduced concentrations of environmentally sensitive materials in wastes may be achievable by using a silver halide photographic element comprising at least one silver halide emulsion layer including negative acting surface latent image-type silver halide grains in reactive association (prior to image-wise exposure) of the grains with a useful amount of a diarylcarbinol contrast promoting agent, preferably a diarylmethanol compound, said photographic element containing an aryl hydrazine compound represented by the following formula (I):



wherein Ar is substituted or unsubstituted aryl group, G is CO, SO, SO₂, PO₂, PO₃ or C=NR₂;

X⁺ is a radical containing a cationic group,

R, R₁, R₂, which can be the same or different, are hydrogen, alkyl of 1 to 6 carbon atoms and alkyl sulfinyl of 1 to 6 carbon atoms, and

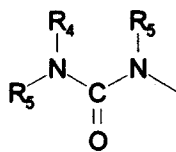
A⁻ is an anion.

This silver halide photographic element can be developed with an aqueous alkaline developing solution which contains a combination of developing agents comprising hydroquinone or substituted hydroquinone and at least one auxiliary developing agent and a useful amount of an antioxidant (such as a sulfite compound), wherein the developing solution has a pH value in the range of 9 to 11.

DETAILED DESCRIPTION OF THE INVENTION

The group Ar in the formula (I) is represented by a substituted or unsubstituted aromatic group, e.g. a substituted or unsubstituted phenyl group, a substituted or unsubstituted naphthyl group. Such aromatic groups may be substituted with one or more substituents, such as straight or branched-chain alkyl groups preferably having from 1 to 20 carbon atoms (e.g. methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, n-octyl, n-hexyl, tert.-octyl, n-decyl, n-dodecyl, etc.), aralkyl groups having from 6 to 20 carbon atoms (e.g. benzyl, phenethyl, etc.), alkoxy groups having from 1 to 20 carbon atoms (e.g. methoxy, ethoxy, 2-methyl-propyloxy, etc.), amino groups which are mono- or disubstituted with alkyl groups, acylaminoaliphatic groups (e.g. acetylamino, benzoylamino, etc.), etc., as disclosed in US 4,168,977 and 4,937,160 and

in CA 1,146,001. Such aromatic groups may also be substituted with a ureido group of formula:



wherein R_3 and R_4 (which may be same or different) each represents hydrogen, an aliphatic group (such as a straight or branched-chain alkyl group, a cycloalkyl group, a substituted cycloalkyl group, an alkenyl group and an alkynyl group), an aromatic group (such as a phenyl group and a naphthyl group) or a heterocyclic group; R_5 represents hydrogen or an aliphatic group (such as those listed above) as described in US 4,323,643.

Although many aryl groups may be considered for the group Ar, substituted phenyl groups are preferred because of easier availability.

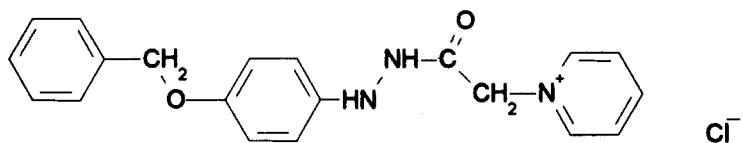
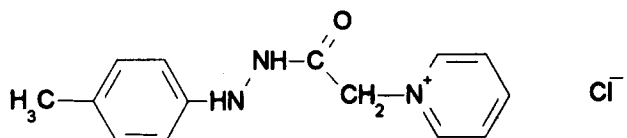
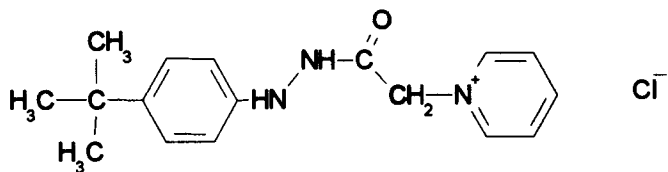
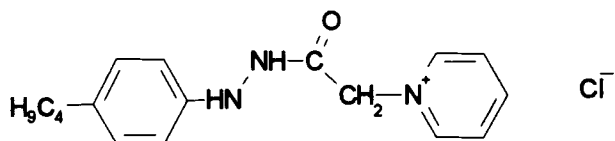
The radical X^+ contains a group with a permanent positive charge, such as is present, for example, in onium compounds, such as ammonium, phosphonium and oxonium compounds. Among the radicals X^+ which contain a cationic group, those radicals, Y^+ , in which the positive charge is introduced by a quaternated nitrogen atom are preferred, e.g., in an aliphatic or aromatic bond. In particular, the radical Y^+ may represent quaternary ammonium radicals which are bound to G via a straight-chained or possibly branched hydrocarbon chain with 1 to 4 carbon atoms, which may also contain an ether-like bound oxygen atom or also by heterocyclic radicals with quaternary nitrogen. In the latter case, the bond of the quaternary nitrogen to G can be achieved both by carbon atoms of the heterocyclic ring system and also by side chain carbon or oxygen atoms. A direct bond of the quaternary nitrogen to G is excluded. Examples of such radicals are trialkylammonium methyl, 2-trialkylammonium ethyl, pyridinium 1-yl-methyl, 1-alkyl-pyridinium-2-yl, 1-alkyl-pyridinium-3-yl, 1-alkyl-pyridinium-4-yl, hydroxyethyl-di-methylammonium methyl, 4-sulfoethyl-pyridinium-1-yl-methyl, N-dodecylmethyl-ammonium methyl-2-methyl-thiazolinium-3-yl-methyl, N-ethylpyridinium-3-oxy-methyl.

The anion A^- may be a halide anion, such as chloride, bromide or iodide or also a complex inorganic ion such as sulfate or perchlorate or also a common organic anion such as toluene sulfonate or trichloroacetate. Anions of strong acids are preferred. If the hydrazine compound is substituted on a radical with an anionic group, the anion may drop off due to the formation of an internal salt.

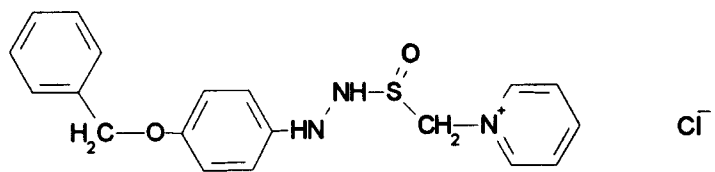
G is represented by the groups CO, SO, SO_2 , PO_2 , PO_3 or $C=NR_2$, preferably G is represented by a carbonyl group.

R , R_1 , R_2 , which can be the same or different, are hydrogen, alkyl of 1 to 6 carbon atoms (e.g. methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl) and alkyl sulfinyl of 1 to 6 carbon atoms (e.g. methylsulfinyl, ethylsulfinyl, propylsulfinyl, isopropylsulfinyl, n-butylsulfinyl, isobutylsulfinyl).

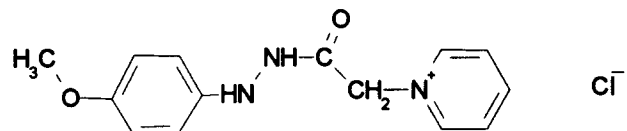
Specific examples of hydrazine compounds represented by the formula above are disclosed in US 4,937,160. In the following, some examples of the aryl hydrazine of formula (I) according to the invention are listed.

H1**H2****H3****H4**

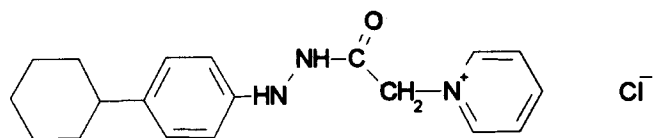
H5



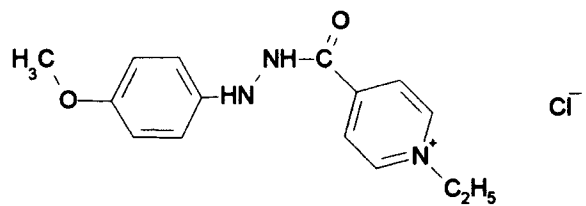
H6



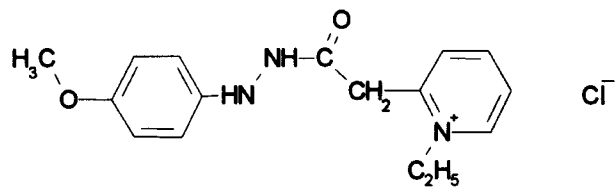
H7



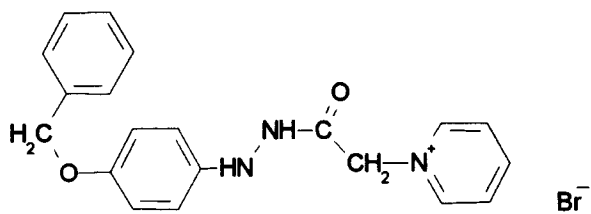
H8



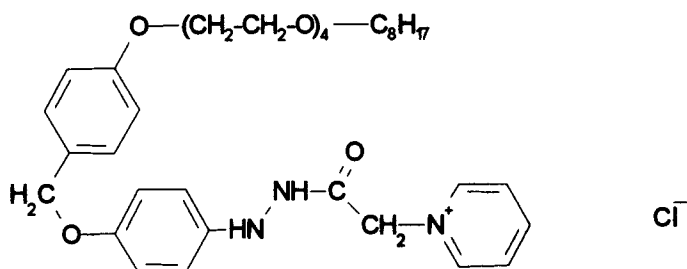
H9



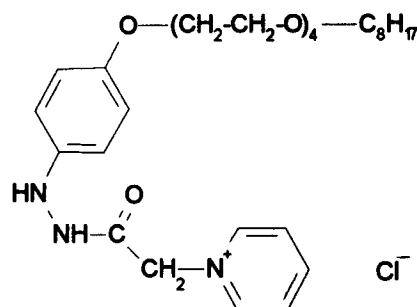
H10



H11



H12



The aryl hydrazine according to this invention can be synthesized by various processes in a simple way, as described in US 4,937,160, e.g. from equimolar quantities of the aryl hydrazine, with the corresponding carboxylic acid and dicyclohexylcarbodiimide (cfr. *Methoden der Organische Chemie* (Houben-Weyl), 4th edition, Vol. X/2 page 355). Another way of incorporating the aryl radical into the hydrazine is by way of quinone monoacyl hydrazones and quinone oxime monoacyl hydrazones (cf. Houben-Weyl, same volume, page 233). A third possibility consists in the hydrazinolysis of carboxylic acid esters (cf. Houben-Weyl, same volume, page 360 f.). Other possibilities of synthesis are known to the experts.

The hydrazine compound of formula (I) is incorporated in the photographic element, for example in a silver halide emulsion layer or in a hydrophilic colloidal layer, preferably a hydrophilic colloidal layer adjacent to the emulsion layer in which the effects of the hydrazine compound are desired. It can, of course, be present in the photographic element distributed between the emulsion and the hydrophilic colloidal layers, such as a subbing layer, interlayers and protective layers.

The hydrazine compound of formula (I) to be incorporated in the photographic element can be substituted with ballasting groups, such as the ballasting groups of incorporated color couplers and other non-diffusing photographic emulsion addenda. Said ballasting groups contain at least 8 carbon atoms and can be selected from the relatively non-reactive aliphatic and aromatic groups, such as alkyl, alkoxy, alkylphenyl, phenoxy, alkylphenoxy groups.

Such hydrazine compounds of formula (I) can be incorporated in the photographic element using various methods well-known in the photographic art. If containing a ballasting group, the most common method is that of dissolving the hydrazine derivatives in a high boiling crystalloidal solvent and dispersing the mixture in the emulsion, as described for example in US 2,322,027.

Hydrazine compounds of formula (I) incorporated in the photographic element are effective at very low levels of concentration. For example, hydrazine compounds incorporated in the photographic element are typically employed in a concentration ranging from 10^{-4} to 5×10^{-2} moles per mole of silver and preferably in a quantity from 8×10^{-4} to 5×10^{-3} moles per mole of silver.

In accordance with this invention, a silver halide photographic element is described for use in a process for forming a high contrast negative photographic image by development of said photographic element, including at least a negative acting surface latent image-type silver halide emulsion layer, with an aqueous alkaline developing solution containing a dihydroxybenzene developing agent, a superadditive developing agent and an antioxidant at a pH lower than 11, in the presence of an aryl hydrazine compound of formula (I) as above, wherein at least one layer of said silver halide photographic element comprises, prior to being contacted with said developing solution, a useful contrast promoting amount of a diarylcarbinol contrast promoting agent. A "contrast promoting agent" (hereinafter "CPA") is defined according to

the present invention as a compound which when added to test developer (A) at a quantity of 10 grams per liter (or in an amount sufficient to give a saturated solution if this is less than 10 grams per liter) results in an increase in contrast of at least 20% (preferably 30%, more preferably at least 50%) when test film (B) is processed in test developer (A) for 80 seconds at 30°C, compared with the contrast when test developer (A) is used under the same conditions without any further additions. The contrast is measured between densities of 0.5 and 1.5.

Test Developer (A)

Water	750 ml
Potassium Hydroxide	32 g
Sodium Sulfite	92 g
Ortho Phosphoric Acid 85%	1.5 ml
Ethylene Diamine Tetracetic Acid Disodium Salt	1.0 g
Sodium Bromide	3 g
Hydroquinone	30 g
1-Phenyl-4-Methyl-3-Pyrazolidone	0.4 g
5-Methylbenzotriazole	0.8 g
Water to make	1,000 ml
Finally and after any addition of CPA, adjust pH to	11.6

Test Film (B)

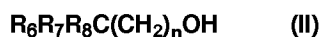
Test film (B) comprises a silver halide coating of the "hydrazine infectious development" type (described for example in U.S. 4,168,977) prepared as follows:

A cubic monodisperse emulsion of average grain size between 0.2 µm and 0.3 µm is precipitated by the conventional double jet procedure. The halide composition is Br 70%, Cl 28% and I 2%. The emulsion is desalted and coated at 3.5 g of silver per square meter and 3.0 g gelatin/m² on polyester base with the following additions.

- Sensitizing dye: Anhydro-5,5'-dichloro-9-ethyl-3, 3'-bis-(3-sulfopropyl)-oxacarbocyanine hydroxide sodium salt	200 mg/mole silver
- Hydrazine derivative: 1-phenyl-2-formylhydrazine	3.0 g/mole silver
- Wetting agent: polyoxyethylene(20)cetyl ether	1 g/mole silver
- Hardener: 2-hydroxy-4,6-dichlorotriazine	0.4 g/mole silver
pH adjusted to 5.0.	

Unique properties and capabilities are achieved in the film and processes of the present invention when the contrast promoting agent comprises a diarylcarbinol compound, preferably a diarylmethanol compound, in a quantity useful to increase contrast, as described in US 4,777,118.

Preferably, according to the present invention, the silver halide emulsion layer is reactively associated with a diarylcarbinol compound of formula (II):



wherein R_6 and R_7 represent a substituted or unsubstituted aromatic group, R_8 represents a hydrogen atom, a substituted or unsubstituted alkyl group or a substituted or unsubstituted aromatic group and n represents a positive integer from 0 to 4 wherein R_6 , R_7 and R_8 are bonded to the carbon atom in the formula.

More preferably, the silver halide emulsion layer is reactively associated with a diarylmethanol compound of formula (III):



wherein R_6 and R_7 represent a substituted or unsubstituted aromatic group bonded to the carbon atom in formula (III).

The diarylcarbinol compounds, preferably the diarylmethanol compounds above, are incorporated into the photographic element prior to the contact with the whole developer solution and preferably prior to the exposure of the photographic element itself, such as for example when the diarylcarbinol compound is introduced into the element prior to the coating of the emulsion layer. For example they can be incorporated in the silver halide emulsion layer of the element or in a hydrophilic colloidal layer of the element, particularly a hydrophilic colloidal layer adjacent to the emulsion layer in which the effects of the diarylcarbinol compounds are desired. They can, for instance, be present in the photographic element distributed between the emulsion and the hydrophilic colloidal layers, such as for instance a subbing layer, interlayers and protective layers.

The aromatic groups represented by R_6 , R_7 and R_8 of formulae (II) and (III) above include a naphthyl group and, preferably, a phenyl group. The alkyl groups represented by R_8 of formula (II) above include branched or straight-chain alkyl groups, preferably alkyl groups having from 1 to 5 carbon atoms. Such groups may contain substituents, such substituents being chosen in nature and size as not to negatively affect their behaviour. Such substituents include, for example, an alkyl group, an alkoxy group, a cyano group, a dialkylamino group, an alkoxy carbonyl group, a carboxy group, a nitro group, an alkylthio group, a hydroxy group, a sulfoxyl group, a carbamoyl group, a sulfamoyl group, a halogen atom. Regarding their size, such substituents are preferred to have from 1 to 10 carbon atoms, more preferably from 1 to 5 carbon atoms.

Parameters to take into proper account are solubility and boiling point of the diarylcarbinol compounds of the present invention. These compounds are to be substantially soluble in water or soluble in water miscible solvents (by "substantially soluble" in water it is meant that they are to be soluble in water in a quantity of at least 1% by weight and by "soluble" in water-miscible solvents it is meant that they are to be soluble in water miscible solvents in a quantity of at least 5% by weight) in order to introduce them into the aqueous coating compositions used to form the layers of the photographic elements according to the present invention. Said diarylcarbinol compounds are required to have a sufficiently high boiling point so as not to evaporate during drying of the layer forming coating composition. Said boiling points are preferably higher than 150°C, more preferably higher than 200°C.

Specific examples of diarylcarbinol contrast promoting agent include the following:

- CP1) diphenylmethanol (benzhydrol)
- CP2) 4,4'-dimethoxydiphenylmethanol
- CP3) 4,4'-dimethyldiphenylmethanol
- CP4) 2,2'-dibromodiphenylmethanol
- CP5) 4,4'-dibromodiphenylmethanol
- CP6) 2,2'-dinitrodiphenylmethanol
- CP7) 4,4'-dinitrodiphenylmethanol
- CP8) 2,3'-dimethoxydiphenylmethanol
- CP9) 2,4'-dihydroxydiphenylmethanol
- CP10) 4-methyldiphenylmethanol
- CP11) 4-ethyldiphenylmethanol
- CP12) 2,2',4,4'-tetramethyldiphenylmethanol.

The diarylcarbinol compounds are incorporated into the photographic element in amount of from 10^{-4} to 10^{-1} mole per mole of silver, more preferably in an amount of from 10^{-3} to 5×10^{-2} mole per mole of silver.

The addition of the contrast promoting agents directly to the emulsion may enable reduction of the concentration of conventionally known contrast promoting agents, such as those described in US 4,269,929 and EP 155,690, in the developing solutions with attendant reductions in cost and environmental impact. The use of the unique class of diarylcarbinols and diarylmethanols can even eliminate the need for additional contrast promoting agents in the developer solutions, as described in US 4,777,118. These carbinol classes of compounds can also reduce the dwell time necessary in developer baths and enable the film to perform well at lower pH levels than films without these contrast promoting agents present in the film prior to contact with the developer solutions. The addition of the contrast promoting agents directly to the film has surprisingly not been found to adversely affect the sensitometry or characteristics of the film (e.g., graininess, sharpness, speed, D_{min}).

The silver halide emulsions for use in the present invention may be silver chloride, silver chloro-bromide, silver iodo-bromide, silver iodo-chloride, silver iodo-chloro-bromide or any mixture of thereof. Generally, the iodide content of the silver halide emulsions is less than about 10% silver iodide moles, said content being based on the total silver halide. The silver halide emulsions are usually monodispersed or narrow grain size distribution emulsions, as described for example in US 4,166,742; 4,168,977; 4,224,401; 4,237,214; 4,241,164; 4,272,614 and 4,311,871. The silver halide emulsions may comprise a mixtures of emulsions having different grain combinations, for example a combination of an emulsion having a mean grain size below 0.4 μm with an emulsion having a mean grain size above 0.7 μm , as described in Japanese Patent Application S.N. 57-58137 or a combination of two emulsions, both having a grain size below 0.4 μm , such as for example a first silver halide emulsion having a mean grain size from 0.1 to 0.4 μm and a second silver halide emulsion with particles having a mean grain volume lower than one half the particles of the first emulsion.

The silver halide grains of the emulsions of the present invention are capable of forming a surface latent image, as opposed to those emulsions forming an internal latent image. Surface latent image-forming silver halide grains are most employed in negative type silver halide emulsions, while internal latent image-forming silver halide grains, though capable of forming a negative image when developed in an internal developer, are usually employed with surface developers to form direct-positive images. The distinction between surface latent image and internal latent image-forming silver halide grains is well-known in the art. Generally, some additional ingredients or steps are required in the preparation of silver halide grains capable of preferentially forming an internal latent image instead of a surface latent image.

In the silver halide emulsions of the present invention, the precipitation or the growth of the silver halide grains may be carried out in the presence of metal salts or complex salts thereof, such as rhodium and iridium salts or complex salts thereof. According to the present invention, it has been found, anyhow, that the presence of rhodium or iridium is not necessary for obtaining the high contrasts. Silver halide grains free of rhodium or iridium, as well as those formed or ripened in the presence of rhodium or iridium may be used to the purposes of the present invention.

The silver halide emulsions of the present invention may not be chemically sensitized, but are preferably chemically sensitized. As chemical sensitization methods for silver halide emulsions, the known sulfur sensitization employing sulfur compounds, the reduction sensitization employing mild reducing agents and the noble metal sensitization can be used, either alone or in combination.

The silver halide emulsions can be spectrally sensitized with dyes from a variety of classes, including the polymethine dye class, such as cyanines, merocyanines, complex cyanines and merocyanines (i.e., tri-, tetra- and poly-nuclear cyanines and merocyanines), oxonols, hemioxonols, styryls, merostyryls and streptocyanines. The silver halide emulsions can be spectrally sensitized at different wavelengths to be exposed to all the laser exposures, i.e. at 488, 633 and 670 nm.

The binder or protective colloid for the silver halide layer and the layers of the photographic element is preferably gelatin, but other hydrophilic colloids or synthetic water insoluble polymers in the form of latexes can be used to partially or completely replace gelatin.

In addition, the photographic elements of the present invention may also contain any photographic additives known in the art, such as for example stabilizers, antifoggants, hardeners, plasticizers, development accelerators, gelatin extenders, matting agents.

According to the process of the present invention, the image-wise exposed silver halide photographic element can be processed with a stable aqueous alkaline developing solution to produce high contrasts negative images. These contrasts are the Toe contrast, named in this invention TetaA and TetaB, and respectively being the absolute value of the slope of the line joining the density points of 0.07 and 0.17 above D_{min} and the absolute value of the slope of the line joining the density points of 0.17 and 0.37 above D_{min} , and the Shoulder contrast, C1, that is the absolute value of the slope of the line joining the density points of 0.10 and 2.50 above D_{min} . Very high Toe and Shoulder contrasts and very good dot quality can be obtained by developing an image-wise exposed element comprising the diarylcarbinol compound, in the presence of a hydrazine compound of formula (I), the contrast and the dot quality being much better with reference to those obtained by developing an image-wise exposed element comprising the same diarylcarbinol compound, in the presence of a hydrazine compound not belonging to formula (I) of the present invention. In addition, the developing solution used to develop the photographic element of the present invention can be useful also at a low pH level, in the range from 9.0 to 11.0, while, in practice, the developing solution used to develop a photographic element containing a diarylcarbinol compound and a hydrazine compound not belonging to formula (I) of the present invention is useful only at a higher pH level, in the range from 11.0 to 12.0. As a consequence of the lower pH in the developer bath and the presence of the diarylcarbinol compound and of aryl hydrazine compound of formula (I) in the element, the process can be carried out to obtain the desired high contrast and dot quality characteristics by using a conventional Rapid Access type developing solution stable during the time to the aerial oxidation (the higher the pH the lower being the stability of the developing solution, as known to the skilled in the art).

The dihydroxybenzene developing agents employed in the aqueous alkaline developing solution for use in the practice of this invention are well-known and widely used in photographic processings. The preferred developing agent of this class is hydroquinone. Other useful dihydroxybenzene developing agents include chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, tolylhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, 2,5-dimethylhy-

droquinone, 2,3-dibromohydroquinone, 1,4-dihydroxy-2-acetophenone-2,5-dimethylhydroquinone, 2,5-diethylhydroquinone, 2,5-di-p-phenethylhydroquinone, 2,5-di-benzoylhydroquinone, 2,5-diacetaminohydroquinone.

The preferred auxiliary developing agents are those described in US 5,236,816; particularly useful are the auxiliary developing agents such as aminophenol and substituted aminophenol (e.g., N-methyl-p-aminophenol, also known as Metol and 2,4-diaminophenol) and the 3-pyrazolidone developing agents (e.g. 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone and 1-phenyl-4,4-dihydroxymethyl-3-pyrazolidone. Other useful 3-pyrazolidone developing agents include: 1-phenyl-5-methyl-3-pyrazolidone, 1-p-aminophenyl-4-methyl-4-propyl-3-pyrazolidone, 1-p-chlorophenyl-4-methyl-4-ethyl-3-pyrazolidone, 1-p-acet-amido-phenyl-4,4-di-ethyl-3-pyrazolidone, 1-p-β-hydroxyethylphenyl-4,4-dimethyl-3-pyrazolidone, 1-p-hydroxyphenyl-4,4-dimethyl-3-pyrazolidone, 1-p-methoxyphenyl-4,4-diethyl-3-pyrazolidone, 1-p-tolyl-4,4-dimethyl-3-pyrazolidone).

The aqueous alkaline photographic developing solution for use in the practice of this invention contains a sulfite preservative at a level sufficient to protect the developing agents against the aerial oxidation and thereby assure good stability characteristics. Useful sulfite preservatives include sulfites, bisulfites, metabisulfites and carbonyl bisulfite adducts. Typical examples of sulfite preservatives include sodium sulfite, potassium sulfite, lithium sulfite, ammonium sulfite, sodium bisulfite, potassium metabisulfite, sodium formaldehyde bisulfite salt. Also ascorbic acid is a known preservative agent against aerial oxidation of the developer for use in the bath.

The aqueous alkaline developing solutions for use in the practice of this invention can vary widely with respect to the concentration of the various ingredients included therein. Typically, the dihydroxybenzene developing agent is used in an amount of from 0.040 to 0.70 moles per liter, more preferably in an amount of from 0.08 to about 0.40 moles per liter; the 3-pyrazolidone developing agent is used in an amount of from 0.001 to 0.05 moles per liter, more preferably in an amount of from 0.005 to 0.01 moles per liter; the sulfite preservative is used in an amount of from 0.03 to 1.0 moles per liter, more preferably in an amount of from 0.10 to 0.70 moles per liter.

In carrying out the method of this invention, it is preferred to use an organic antifogging agent to minimize fog formation in the processed element. The organic antifogging agent can be incorporated in the photographic element or can be added to the developing solution or can be both incorporated in the photographic element and added to the developing solution. According to the present invention, it has been found that more preferred organic antifogging agents for specific use in the developing solutions are benzotriazole and/or a benzimidazole antifogging agents, which proved to have beneficial effects on increasing contrast. Useful compounds are both substituted and unsubstituted benzotriazole and benzimidazole compounds, with the proviso that electron withdrawing substituents at least as strong as nitro groups are excluded. As a matter of fact, nitro substituted benzotriazole and benzimidazole compounds, although good to prevent fog, do not provide beneficial effects with reference to contrast increase. Benzimidazoles and benzotriazoles, as a class, are believed to be useful in the practice of this invention. Anyhow, as indicated, difficulties in obtaining significantly improved performance with benzotriazoles and benzimidazoles having strong electron withdrawing groups have been encountered. Benzotriazoles and benzimidazoles are therefore preferred not to have any substituents on the aromatic rings which are electron attracting groups as strong as or stronger than a nitro group. Other substituents known in the art such as lower alkyl groups (having 1 to 5 carbon atoms) and halogen substituents (chlorine) proved to be substituents good to the purposes of the invention. Said benzotriazole and benzimidazole antifogging and contrast promoting agents are normally used in amounts effective to prevent fog, although quantity can be optimized to get the best results from the contrast point of view. Useful quantities, when they are included in the emulsion, may vary from 1 to 100 milligrams per 100 grams of emulsion and, when included in the developing bath, as preferred, may vary from 0.01 to 5 grams per liter.

In addition to the essential components specified hereinabove, the developing solutions can optionally contain any of a wide variety of addenda, as known, useful in photographic developing solutions. For example, they can contain solvents, buffers, sequestering agents, development accelerators, agents to reduce swelling of the emulsion layers, and the like.

The invention is further illustrated by the following examples.

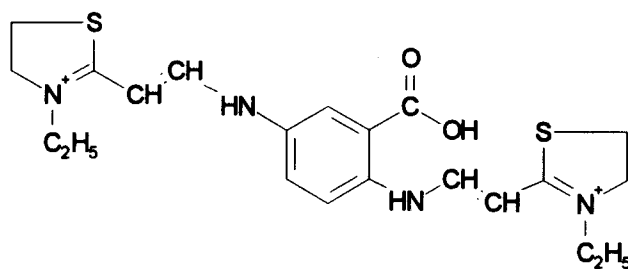
EXAMPLE

Emulsion

A cubic $\text{AgBr}_{0.30}\text{Cl}_{0.70}$ emulsion of narrow grain size distribution and mean grain size of $0.28\ \mu\text{m}$ was prepared by the conventional double jet procedure. The emulsion was then coagulated and washed in the conventional manner and reconstituted to give a final gelatin to silver ratio of 100 g gelatin/silver mole. The emulsion was then doped with ruthenium and iridium and was sulfur and gold chemically sensitized. A coating composition was prepared by mixing this emulsion with:

- an anionic surfactant of the alkylphenyloxyethylene sulfonate type as wetting agent,
- formaldehyde as hardener (0.8 g/mole Ag),

- sensitizing dye (0.62 g/mole Ag), sensitive to 488 nm., of formula:



Sample 1 (Comparison)

Reference hydrazide compound A (2.08 g/mole Ag) and contrast promoting agent CP1 (2.06 g/mole Ag) were added to the emulsion.

A coating was then prepared by the application of the described mixture onto a subbed polyester base at a silver coverage of 3.2 g/m².

The obtained coating was exposed in a sensitometer consisting of a 500 watt tungsten filament light source attenuated by a 0-4 continuous neutral density wedge in contact with the film sample. The film was then developed for 30 seconds at 32°C in the developer composition A having the following composition at a pH of 11.5:

Deionized water	780 g
KOH 35%	85 g
Sodium metabisulfite 98%	18.04g
DTPA . 5 Na 40%	3.8 g
Potassium bromide	3.3 g
Hydroquinone	15 g
1-Phenyl-3-pyrazolidone	0.38g
Benzotriazole	0.29g
1-Phenyl-1H-tetrazole-5-thiol	0.03g
Ethylene glycol	2 g
KHCO ₃ 92%	10 g
Potassium metabisulfite 96%	20.48g
Diethanolamine	8 g
Water to make	1 l
pH at 20°C adjusted at 11.50 with KOH	

The strips were then fixed, washed and dried.

Sample 2 (Comparison)

The same coating of sample 1 was developed for 30 seconds at 32°C through the Rapid Access developing solution B having the following formula at a pH equal to 10.5:

Deionized water	780 g
KOH 35%	85 g
Sodium metabisulfite 98%	18.04 g
DTPA . 5 Na 40%	3.8 g
Potassium bromide	3.3 g
Hydroquinone	15 g
1-Phenyl-3-pyrazolidone	0.38 g
Benzotriazole	0.29 g
1-Phenyl-1H-tetrazole-5-thiol	0.03 g
Ethylene glycol	2 g
KHCO ₃ 92%	10 g
Potassium metabisulfite 96%	20.48 g
Diethanolamine	8 g
Water to make	1 l
pH at 20°C	10.50

The strips were then fixed, washed and dried.

Sample 3 (Comparison)

The aryl hydrazine H1 was added (0.24 g/mole Ag) to the emulsion without any addition of contrast promoting agents. A coating was then prepared by the application of the described mixture onto a subbed polyester base at a silver coverage of 3.6 g/m².

The obtained coating was developed for 30 seconds at 32°C through the developing solution B, at a pH of 10.5.

Sample 4 (Comparison)

The same coating of sample 3 was developed for 30 seconds at 32°C through the DuPont "QUANTAONE" developing solution containing reference contrast promoting agent B, at a pH of 10.5.

Sample 5 (Comparison)

As sample 3, but the reference contrast promoting agent B was added to the emulsion (2.90 g/mole Ag).

Sample 6 (Invention)

As sample 3, but the aryl hydrazine H2 (0.694 g/mole Ag) replaced the aryl hydrazine H1 and the contrast promoting agent CP1 was added to the emulsion (5.52 g/mole Ag).

Sample 7 (Invention)

As sample 6, but the aryl hydrazine H3 (0.305 g/mole Ag) replaced the aryl hydrazine H2.

Sample 8 (Invention)

As sample 6, but the aryl hydrazine H4 (0.160 g/mole Ag) replaced the aryl hydrazine H2.

Sample 9 (Invention)

As sample 3, but the contrast promoting agent CP1 was added to the emulsion (3.68 g/mole Ag).

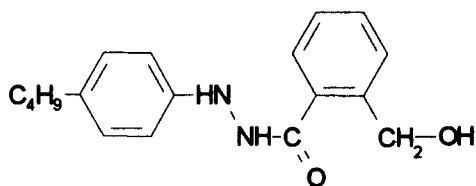
Table 1 shows the sensitometric values in terms of Toe contrast TetaA and TetaB, respectively being the absolute value of the slope of the line joining the density points of 0.07 and 0.17 above Dmin and the absolute value of the slope of the line joining the density points of 0.17 and 0.37 above Dmin, in terms of shoulder contrast C1, that means the absolute value of the slope of the line joining the density points of 0.10 and 2.50 above Dmin. The dot quality results are also reported, the score going from 1 (best) to 5 (worst).

Table 1

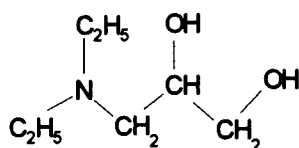
Sample	pH Dev.	Hydr.	Contr. Prom.	Teta A	Teta B	C1	Dot
1 (comp.)	11.5	A	CP1	4	6	15	1-2
2 (comp.)	10.5	A	CP1	1.7	3	6	5
3 (comp.)	10.5	H1	none	2.5	4	7	4
4 (comp.)	10.8	H1	none	3.5	8	12	2
5 (comp.)	10.5	H1	N	2.4	4	8	4
6 (inv.)	10.5	H2	CP1	4.5	8	20	3
7 (inv.)	10.5	H3	CP1	4	9	20	3
8 (inv.)	10.5	H4	CP1	4	8	20	2
9 (inv.)	10.5	H1	CP1	4	10	20	1

Table 1 shows the improvements obtained by the combination of aryl hydrazine of formula (I) and diarylcarbinol contrast promoting agent of formula (II) according to the present invention. In fact, sample 1, containing a contrast promoting agent of formula (II) and a hydrazine compound not of formula (I), gives good results in terms of contrast and dot quality, but only when developed with a developing solution at a high pH level (about 11.5). In fact, at lower pH level (about 10.5), the contrast and the dot quality are very bad (sample 2). Similar bad results are obtained when a hydrazine of formula (I) is used alone (comparison sample 3) or in combination with a contrast promoting agent not of formula (II) (comparison sample 5). On the contrary, samples 6-9 comprising the combination of the aryl hydrazine compounds and the diarylcarbinol contrast promoting agents according to the present invention give photographic images with very high contrasts and good dot quality, when developed with a developing solution at a low pH value (about 10.5). The obtained results are in fact even better than the results obtained by comparison sample 4, in which the same hydrazine of formula (I) has been used, but in absence of any contrast promoting agent incorporated in the film, a contrast promoting agent different from the ones of formula (II) being incorporated in the developing solution, at a higher pH value, about 10.8.

Reference hydrazide compound A:



Reference contrast promoting agent B:



Claims

1. A silver halide photographic element, free of photolytically generated latent images, comprising at least one silver halide emulsion layer including negative acting surface latent image-type silver halide grains in reactive association with a diarylcarbinol contrast promoting agent, said photographic element containing an aryl hydrazine compound represented by the following formula (I):



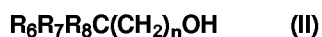
wherein Ar is an aryl group, G is CO, SO, SO₂, PO₂, PO₃ or C=NR₂;

X⁺ is a radical containing a cationic group,

R, R₁, R₂, which can be the same or different, are hydrogen, alkyl of 1 to 6 carbon atoms and alkyl sulfinyl of 1 to 6 carbon atoms, and

A⁻ is an anion.

2. The element of claim 1, characterized in that said diarylcarbinol contrast promoting agent comprises a diarylmethanol compound.
3. The silver halide photographic element of claim 1, characterized in that the diarylcarbinol compound has the formula (II):



wherein R₆ and R₇ each represent an aromatic group, R₈ represents a hydrogen atom, an alkyl group or an aromatic group and n represents a positive integer from 0 to 4.

4. The silver halide photographic element of claim 1, characterized in that the diarylcarbinol compound has the formula (III):

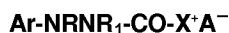


wherein R₆ and R₇ each represent an aromatic group.

5. The silver halide photographic element of claim 1, characterized in that said diarylcarbinol contrast promoting agent is incorporated in the silver halide emulsion layer.

6. The silver halide photographic element of claim 1, characterized in that said diarylcarbinol contrast promoting agent is incorporated in the silver halide emulsion layer in an amount from 10^{-4} to 10^{-1} mole per mole of silver halide.

7. The silver halide photographic element of claim 1, characterized in that the aryl hydrazine compound corresponds to the formula:



wherein Ar is a phenyl group,

X^+ is a radical containing a cationic group,

R and R_1 , which can be the same or different, are hydrogen, alkyl of 1 to 6 carbon atoms and alkyl sulfinyl of 1 to 6 carbon atoms, and A^- is an anion.

8. The silver halide photographic element of claim 1, characterized in that the aryl hydrazine compound corresponds to the formula:



wherein Ar is a phenyl group.

G is CO, SO, SO_2 , PO_2 , PO_3 or C=NR_2 ;

Y^+ is a radical containing a cationic group with at least one quaternated nitrogen atom,

R, R_1 and R_2 , which can be the same or different, are hydrogen, alkyl of 1 to 6 carbon atoms and alkyl sulfinyl of 1 to 6 carbon atoms, and A^- is an anion.

9. The silver halide photographic element of claim 1, characterized in that the aryl hydrazine compound is in an amount from 10^{-4} to 5×10^{-2} mole per mole of silver halide.

10. A process for forming a high contrast negative photographic image by development of a silver halide photographic element, including at least a negative acting surface latent image-type silver halide emulsion layer, with an aqueous alkaline developing solution containing a dihydroxybenzene developing agent, a superadditive developing agent and an antioxidant at a pH lower than 11 in the presence of an aryl hydrazine compound of formula (I), characterized in that at least one layer of said silver halide photographic element comprises, prior to being contacted with said developing solution, a diarylcarbinol contrast promoting agent,



wherein Ar is an aryl group,

G is CO, SO, SO_2 , PO_2 , PO_3 or C=NR_2 ;

X^+ is a radical containing a cationic group,

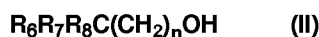
R, R_1 , R_2 , which can be the same or different, are hydrogen, alkyl of 1 to 6 carbon atoms and alkyl sulfinyl of 1 to 6 carbon atoms, and

A^- is an anion.

11. The process of claim 10 characterized in that said diarylcarbinol contrast promoting agent is present in said at least one layer of said silver halide photographic element prior to image-wise exposure of said silver halide emulsion layer.

12. The process of claim 10, characterized in that the diarylcarbinol compound is a diarylmethanol compound.

13. The process of claim 10, characterized in that the diarylcarbinol compound has the formula (II):



wherein R_6 and R_7 each represent an aromatic group, R_8 represents a hydrogen atom, an alkyl group or an aromatic group and n represents a positive integer from 0 to 4.

14. The process of claim 10, characterized in that the diarylcarbinol compound has the formula (III):



wherein R₆ and R₇ each represent an aromatic group.

15. The process of claim 10, characterized in that the aryl hydrazine compound is included in the silver halide emulsion layer.

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16. The process of claim 10, characterized in that the hydroxybenzene developing agent is hydroquinone.

17. The process of claim 10, characterized in that the superadditive developing agent is a 3-pyrazolidone compound.

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18. The process of claim 10, characterized in that the antioxidant is a sulfite compound.

19. The process of claim 10, characterized in that said developing solution comprises an organic antifogging agent selected within the class including a benzotriazole compound and a benzimidazole compound.

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20. The process of claim 19, characterized in that said benzotriazole compound and said benzimidazole compound are without electron-attracting substituents as strong as or stronger than a nitro group.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 11 1357

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	EP-A-0 231 850 (MINNESOTA MINING AND MANUFACTURING COMPANY) * the whole document *	1-20	G03C1/06
D	& US-A-4 777 118 ---		
Y	EP-A-0 356 898 (DU PONT DE NEMOURS (DEUTSCHLAND) GMBH) * the whole document *	1-20	
D	& US-A-4 937 160 ---		
Y	EP-A-0 444 506 (DU PONT DE NEMOURS (DEUTSCHLAND) GMBH) * the whole document *	1-20	
D	& US-A-5 190 847 -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C
Place of search		Date of completion of the search	Examiner
THE HAGUE		25 April 1995	Buscha, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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