(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 745 577 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.12.1996 Bulletin 1996/49

(21) Application number: **96302867.5**

(22) Date of filing: **24.04.1996**

(51) Int Cl.^{6}: **C07C 43/23**, C07C 323/19, C07C 235/16, C07C 217/08, G03C 1/06

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **26.05.1995 GB 9510741**

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(54) Boosters for high contrast silver halide imaging elements

(57) Boosters for high contrast negative-acting silver halide emulsions comprising hydrazine derivatives. The boosters comprise a polyoxyethylene chain terminated at one or both ends by a group comprising a benzyl alcohol or a diaylcarbinol functionality. Compounds having at least 8 carbon atoms in the polyoxyethylene chain are novel.

Printed by Jouve, 75001 PARIS (FR)

Description

The invention relates to compounds which act as boosters in high contrast negative-acting silver halide emulsions comprising hydrazine derivatives. The compounds comprise a polyethyleneglycol chain terminated at one, and preferably at both ends, by a primary benzyl alcohol group or a diarylcarbinol group.

In the graphic arts field it is desirable to provide ultra-high contrast ("hard dot") films from which contact masks are prepared for the imaging of printing plates and colour proofs. Such films (known as "lith films") generally show a shoulder contrast of at least 10, and frequently of 20 or more. Shoulder contrast (θ_c) is defined as the average contrast between density 0.5+fog and density 2.5+fog.

Historically, these high contrasts were obtained by an auto-accelerated development process, as described in "The Theory of the Photographic Process" (Mees and James), 3rd edition, page 366. This process involved the use of a special "lith" developer, characterised by a very high pH and a low sulphite concentration. Such solutions are extremely unstable, they are prone to oxidation, and hence have a very short usable lifetime.

More recently, the high contrast has been obtained by incorporation in the developer, or more commonly in the film, of a hydrazine derivative, as described for example, in patents such as US 2,419,974; 2,419,975; 2,4410,690; 4,168,977; 4,224,401; 4,221,857; 4,237,214; 4,241,164; 4,311,871; 4,243,739; 4,272,614; and 4,798,780; and in Research Disclosure No..235, Nov. 1983, Item 23510, "Development nucleation by hydrazine and hydrazine derivatives".

Hydrazine derivatives are believed to react with oxidised developer to form species capable of fogging unexposed silver halide grains, and hence rendering the grains developable by conventional developing agents. The net effect is that development of a particular grain in the conventional manner triggers development of adjacent grains in an infectious process, thus providing an extremely high contrast. The presence of hydrazine compounds enables the use of more stable developer solutions of lower pH and higher sulphite content than traditional lith developers, but there is a continuing need to lower the developer pH still further, and in particular lower the pH to the levels used in conventional (non-infectious) processing, while maintaining the same standards of dot quality, speed, Dmax, Dmin etc. There is also a continuing need to increase the contrast of the lith film, particularly the toe contrast (θ_A), which is defined as the average contrast between density 0.07+fog and density 0.17+fog.

Various additives (sometimes known as "boosters") have been proposed for use in conjunction with hydrazines and hydrazides to enhance their activity, particularly at lower pH. For example, US 4,619,886 discloses the addition of a range of compounds, including primary and secondary benzyl alcohols, to the developer solution, and US 4,221,857 discloses the addition of polyalkyleneoxides to either the developer or the film. EP0364166 discloses boosters for incorporation in the film comprising amino groups and poly(oxyethylene) chains. EP0231850 discloses the use of diarylcarbinols such as benzhydrol as boosters incorporated in the film. This patent also teaches that primary benzyl alcohols and arylalkylcarbinols are ineffective for this purpose.

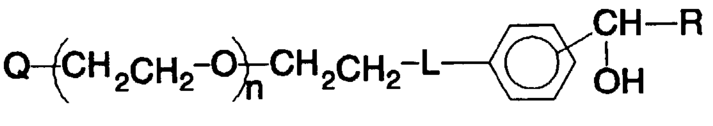
Japanese Patent Publication 05-232615 discloses the incorporation, in high contrast emulsions comprising hydrazine derivatives, of a wide variety of primary and secondary alcohols. Primary benzyl alcohols and diarylcarbinols are not included although heteroarylcarbinols are taught. Some of the compounds disclosed in this publication possess poly(oxyethylene chains), but no particular advantage is associated with such chains.

US-A-5091274 discloses ionic polymer electrolytes which are complex compounds prepared from an alkali metal salt and a side-chain liquid crystalline polysiloxane. Intermediate materials disclosed in the preparation of such compounds include 4-(2-allyloxyethoxy)benzyl alcohol, 4-[2-(2-allyloxyethoxy) ethoxy]benzyl alcohol and 4-{2-[2-(2-allyloxyethoxy)ethoxy] ethoxy}benzyl alcohol.

The present invention provides an imaging element comprising a high contrast negative-acting silver halide emulsion comprising a hydrazine derivative in said emulsion or in a layer adjacent thereto and a compound comprising a polyoxyethylene chain terminated at one or both ends by a group comprising a benzyl alcohol or diarylcarbinol functionality.

The present invention further provides novel compounds comprising a poly(oxyethylene) chain having at least 8 carbon atoms terminated at one or both ends by a group comprising a primary benzyl alcohol or a diarylcarbinol functionality.

The compounds in accordance with the invention have a nucleus represented by the following general formula:-



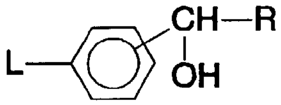
(I)

in which n is an integer of at least 3;

R represents H or phenyl;

L represents a covalent bond or a divalent linking group; and Q represents H, OH or any organic group.

Q is preferably selected from H, alkyl, alkoxy, alkylthio, aryl, aryloxy, arylthio, and hydroxy, but most preferably Q represents:-



in which L and R are defined above.

L is preferably a divalent linking group comprising up to 10, preferably up to 5, skeletal atoms selected from C, N, O and S. Examples of such divalent linking groups include -O-, -S-,-OCH$_2$CONH-, and -N$^+$R$_1$R$_2$X$^-$, where R$_1$ and R$_2$ represent alkyl groups such as methyl, ethyl etc and X$^-$ is an anion, such as chloride, bromide, p-toluenesulphonate etc.

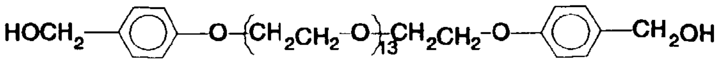
n is preferably in the range 3 to 50, more preferably 5 to 40.

R represents H or phenyl, but compounds in which R is H are most preferred.

In the above formula, any phenyl ring may bear one or more additional substituents, preferably comprising up to 10, more preferably up to 5, skeletal atoms selected from C, N, O and S. Examples of such substituents include alkyl, alkoxy, alkylthio, or hydroxy groups, halogen atoms etc.

Examples of compounds in accordance with the invention include the following:-

(1)



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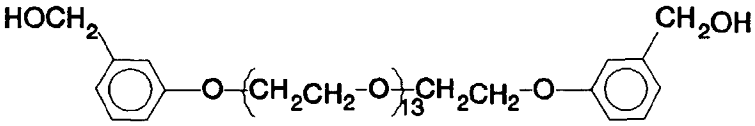

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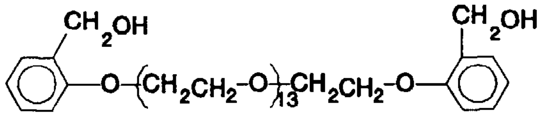

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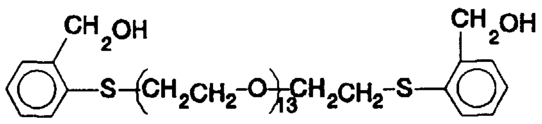

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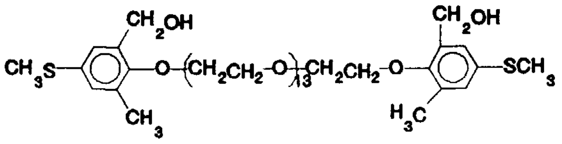

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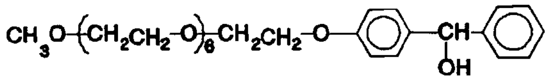
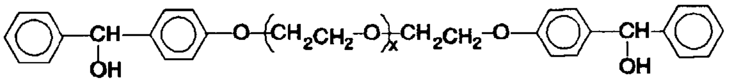


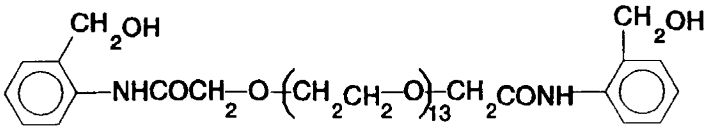


(7)x = 13

(8)x = 19

(9)x = 33

(10)



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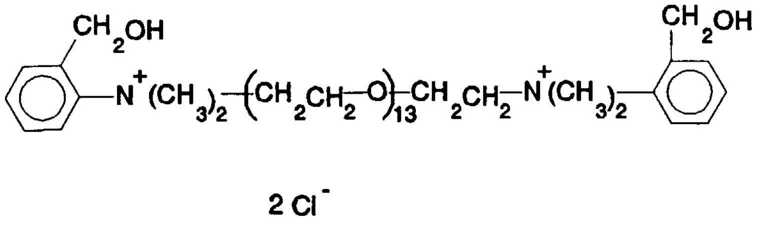


The compounds of the invention may be prepared by standard synthetic techniques. For example, a poly(ethylene glycol) of the desired chain length may be reacted with p-toluenesulphonyl chloride, and the resulting tosylate groups subjected to nucleophilic displacement by the sodium salt of a hydroxy- or mercapto-substituted benzaldehyde or benzophenone. Thereafter, reduction of the benzaldehyde or benzophenone functionality (e.g. by metal hydrides) gives the desired compound.

The compounds of the invention find use in high contrast silver halide imaging elements comprising one or more hydrazine derivatives, and may be added directly to the silver halide emulsion or coated in a separate layer adjacent to the emulsion layer(s), the former being preferred. The compounds may be added to the emulsion at any stage after completion of the grain growth, but are typically added (as a solution in water or a water-miscible solvent) immediately prior to coating. The concentration of the compounds is generally in the range 0.01 to 10.0 mmol/mol Ag, preferably 0.10 to 7.5 mmol/molAg. This is considerably less than the typical loading level of analogous booster compounds of the prior art, such as benzhydrol, which requires a loading of about 30 mmol/mol Ag to achieve a comparable effect.

The compounds of the invention enable a higher contrast to be obtained and in particular a higher toe contrast, even when the developer pH is relatively low e.g. in the region 10.5. They show a higher activity than analogous compounds of the prior art, and have beneficial solubility properties in that they dissolve readily in the coating solutions, and show no tendency to crystallise in the coatings. The reason for the high activity shown by the compounds of the invention is not clear, and the fact that the highest activity is shown by the primary benzyl alcohols (R = H in Formula I) is particularly surprising, since the analogous compounds lacking a poly(oxyethylene) chain were previously shown to be inactive (EP0231850). Furthermore, compounds in which a benzyl alcohol or diarylcarbinol group is attached to the middle of a poly(oxyethylene) chain are found to be much less active.

The preparation of the photographic silver halide emulsions and other ingredients in the emulsions are known in the art and are disclosed, for example, in EP 0285308 and EP 0253665.

It is preferred that silver halide grains used for the silver halide emulsion layer in this invention be of the substantially surface latent image type.

Any light sensitive silver halide may be used in this invention e.g., silver chloride, silver chlorobromide, silver iodochlorobromide, silver bromide, silver iodochloride and silver iodobromide can be used. In the case of using silver iodobromide or silver iodochlorobromide, it is preferred that the content of silver iodide not be more than 10 mole percent. Since in the material of this invention a wide range of silver halides can be used, it is possible to obtain a very high sensitivity as compared with a process using a conventional "lith" type development. The preferred silver halide for use in the invention is silver chlorobromide.

The silver halide photographic emulsions used in this invention can be prepared by the processes described in, for example, P. Glafkides, Chimie et Physique Photographique (published 1967) by Paul Montel); G.F. Duffin, Photographic Emulsion Chemistry, (published 1966), by the Focal Press; and V.L. Zelikman et al., Making and coating Photographic Emulsions (published 1964 by The Focal Press). That is, the silver halide emulsions may be prepared by an acid process, a neutral process, an ammonia process, etc.. The silver halide may be precipitated by a single jet mixing process, a simultaneous mixing process (double jet), or a combination thereof. Also, a so-called reverse mixing method, wherein silver halide grains are formed in the presence of silver ion can be employed. In an embodiment of the simultaneous mixing method, a method of maintaining the pAg of the liquid phase wherein silver halide is formed at a constant value, that is, a so-called controlled double jet method, can be employed. According to the method, a silver halide emulsion having regular crystal form and almost uniform grain size is obtained.

Silver halide grains in the silver halide photographic emulsion used in this invention may have a relatively broad grain size distribution, but it is preferred that the emulsion has a narrow grain size distribution. Alternatively, a mixture of two emulsions may be employed as described in British Patent Application No. 8516935, e.g. a first silver halide emulsion having an average grain size of from 0.1 to 0.4 microns and a second silver halide emulsion having an average grain volume of less than one half that of the first emulsion.

Silver halide grains used in this invention are preferably fine grains (e.g. less than 0.7 microns) but since the hydrazines will provide a high contrast image even if the mean grain size is large and sufficiently improves the dot qualities, silver halide emulsions having large grains (e.g., larger than 0.7 microns) can be used.

The silver halide grains in the silver halide photographic emulsions may be regular crystals such as cubic or octahedral crystals, or irregular crystals such as spherical or plate-like (tabular or laminar) crystals, as well as composite forms of fixed crystals thereof. They may be mixture of various crystal form grains.

The silver halide grain may have a uniform phase throughout the inside and surface layer thereof or may be different in phase between the inside and the surface layer (e.g., a shell-core structure). Moreover, two or more sorts of silver halide emulsions prepared separately may be mixed.

Preferred emulsions comprise cubic silver chlorobromide (chloride content 50 to 90 mole%) of narrow size distribution, with an average grain size in the range 0.1 to 0.4μm.

As the binder or protective colloid for the silver halide emulsions, gelatin is advantageously used, but other hydrophilic colloids can be also used. For example, gelatin derivatives, graft polymers of gelatin and other polymers, albumin, casein, etc., cellulose derivatives such as hydroxyethyl cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulphate ester, etc., sugar derivatives such as sodium alginate, a starch derivative, etc., and various sorts of synthetic hydrophilic polymers as homopolymers or copolymers, such as polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole, polyvinyl pyrazole, etc., can be used.

As the gelatin, limed gelatin and acid-processed gelatin may be used, as well as a gelatin hydrolyzed product and gelatin enzyme-decomposition product may be also used. Examples of the gelatin derivatives used in this invention are the products obtained by reacting gelatin and various compounds such as acid halide, acid anhydride, isocyanate, bromoacetic acid, alkanesultones, vinylsulphonimides, maleimide compounds, polyalkylene oxides, epoxy compounds, etc. Practical examples of these materials are described in U.S. Patents 2614928, 3134945, 3186646, 3312553, British Patents 861414, 1033189 and 1005784 and Japanese Patent Publication No. 26845/67.

Examples of gelatin graft polymers include those prepared by grafting to gelatin a homopolymer or copolymer of a vinylic monomer such as acrylic acid, methacrylic acid, the derivative thereof such as the ester or amide, acrylonitrile, styrene, etc. In particular, a graft polymer of gelatin and a polymer having a compatibility with gelatin to some extent, such as acrylic acid, methacrylic acid, acrylamide, methacrylamide, hydroxyalkylmethacrylate, etc., is preferred. Such graft polymers are described in U.S. Patents 2763625, 2831767 and 2956884. Typical examples of the synthetic hydrophilic polymer are described in West German Patent Application (OLS) No. 2312708, U.S. Patents 3620751 and 3879205 and Japanese Patent Publication No. 7561/68.

It is preferred that the silver halide emulsion used in this invention does not contain more than 250g of binder per mol of silver halide. When the silver halide emulsion contains a binder in an amount not over 250g per mol of silver halide, extremely high contrast photographic characteristics which are the object of this invention can be more easily obtained.

After forming a precipitate or after physical ripening, soluble salts formed are usually removed from the silver halide emulsion. For this purpose, the well known noodle washing method, or a flocculation method utilizing an inorganic salt composed of a polyvalent anion, such as sodium sulphate, an anionic surface active agent, an anionic polymer (e.g. polystyrenesulphonic acid), or a gelatin derivative (e.g. aliphatic-acylated gelatin, aromatic-acylated gelatin, aromatic-carbamolyated gelatin etc.) may be used. The step of removing soluble salts may be omitted.

The silver halide emulsions used in this invention need not be chemically sensitized, but preferably are chemically sensitized. As methods for chemically sensitizing silver halide emulsions, known sulphur sensitization, reduction sensitization, and noble metal sensitization methods can be used, either solely or in combination. These sensitization methods are described in the aforesaid books by Glafkides and Zelikman et al as well as Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden, edited by H. Freiser (Akademische Verlagsgesellschaft, 1968).

Of the noble metal sensitization methods, a gold sensitization method is typical and uses gold compounds, in particular gold complexes. Complexes of noble metals other than gold, such a platinum, palladium, iridium etc., may be also used. Preferred examples thereof as described in U.S. Patent 2448060 and British Patent 618061.

Examples of sulphur sensitizers useful for sulphur sensitization include sulphur compounds contained in gelatin as well as various sulphur compounds such as thiosulphates, thioureas, thiazoles, rhodanines, etc. Preferred examples of sulphur sensitizers are described in U.S. Patents 1574944, 2278947, 2410689, 2728668, 3501313 and 3656955.

Examples of reduction sensitizers useful in this invention include stannous salts, amines, formamidinesulphinic acid, silane compounds, etc. Practical examples of them are described in U.S. Patents 2487850, 2518698, 2983609, 2983610 and 2694637.

The silver halide emulsions used in the invention comprise a hydrazine derivative. Suitable hydrazines are disclosed in the literature referred to above. The preferred hydrazine derivatives are the cyclisable compounds of U.S. 4925832 and pyridinium acetylhydrazides as disclosed in U.S. 4937160.

The hydrazines may be added to the silver halide photographic emulsion at any desired period from the initiation of chemical ripening to before coating, but it is preferred to add the compound after finishing chemical ripening. It is particularly preferred to add the compound to a coating composition prepared for coating.

It is preferred that the hydrazine employed in the invention be incorporated in an amount of from 10^{-6} mol to 10^{-1} mol, and preferably from 10^{-5} mol to 2 x 10^{-2} mol per mol of silver halide, but it is desirable to select the optimum amount of the compound according to the grain size of silver halide emulsion, the halogen composition the matter and extent of chemical sensitization, and the kind of antifoggant compounds. The most appropriate compound and amount thereof for a particular use can be easily selected by general tests well known to persons skilled in the art.

The light-sensitive materials of this invention may contain various other additives known in the art e.g., spectral sensitizers, hardeners, stabilizers etc.

The emulsions may be sensitized throughout the near infrared visible and near UV, but the 480-500 nm, 620-640 nm, and 650-680 nm regions are particularly important (for Ar ion laser, HeNe laser, and red laser diode address, respectively). Broad band sensitisation by combinations of dyes may also be employed e.g., covering the range 620-680 nm, thus enabling exposure by more than one type of exposure source.

In the process of this invention, the image-exposed silver halide photographic light-sensitive materials can be processed by using a stable developing solution to obtain a high-contrast image and it is unnecessary to process said photographic light-sensitive materials by unstable lithographic developers.

Suitable black-and-white developing agents for use in the invention include 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone) aminophenols (e.g., N-methyl-p-aminophenol), ascorbic acid, 1-phenyl-3-pyrazolines and dihydroxybenzenes (e.g., hydroquinone) . It is most preferred that a dihydroxybenzene e.g., hydroquinone, is used as the developer, optionally in the presence of one or more other developing agents.

The developer used in this invention generally contains preservatives, alkaline agents, pH buffers, anti-foggants (such as, in particular, nitroindazoles, benzotriazoles, etc.) and further may contain, if necessary, dissolution aids, toning agents, development accelerators, surface active agents (e.g., polyalkylene glycols), defoaming agents, water softeners, hardening agents and viscosity-imparting agents.

According to the process of this invention, a gamma higher than 10 can be obtained even when the light-sensitive materials are developed in a developer containing not less than about 0.15 mol/liter of sulphite ion. In the process of this invention the pH of the developer may be above about 9 but it is preferably from about 9.5 to 12.3, most preferably 10.0 - 11.5. If the pH of the developer is over 12.3, the developer is unstable even when the concentration of sulphite ion is high and hence it is difficult to maintain stable photographic characteristics for more than three days using such a developer. With preferred embodiments of the invention, it is possible to use a conventional "Rapid Access" graphic arts developer of the type normally used for non-infectious development.

A fix solution having a conventional composition may be used. Fixing agents such as thiosulphates, thiocyanates, as well as organic sulphur compounds may be employed.

The invention will be illustrated by the following Examples.

Example 1

Synthesis of Compound 7

Poly(ethylene glycol) (M.W. 600) (91g), toluene sulfonyl chloride (59.45g) and dichloromethane (300 mL) were stirred together under nitrogen with ice cooling. Powdered potassium hydroxide (68g) was added portionwise keeping the temperature below 10°C. The mixture was allowed to warm to room temperature and stirred overnight. Ice water (600g) was added, the organic layer and one dichloromethane extract of the aqueous layer were separated, dried over MgSO4 and evaporated to yield 122g of an oil - PEG-600 ditosylate.

Sodium (3.7g) was dissolved in ethanol (350 mL) and 4-hydroxy benzophenone (31.9g) was added. The solution was evaporated to dryness and THF (1 L) was added. PEG-600 ditosylate (69.5g) was added and the mixture refluxed overnight. The resulting mixture was filtered and washed with 5% aqueous sodium carbonate and water. The solution was dried over MgSO4 and evaporated to yield 68.2g of an oil - PEG-600 bis(4-benzoylphenyl ether).

A solution of the above ketone (59.9g) in anhydrous THF (500 mL) was added dropwise to a suspension of $LiA1H_4$ (6.0g) in anhydrous THF (500 mL) maintaining a temperature of 0°C. After the addition was complete, the mixture was allowed to warm to room temperature. A 5% solution of ammonium chloride was added cautiously until no further effervescence occurred. The organic layer was separated, combined with a dichloromethane extract of the aqueous layer, dried over MgSO4 and evaporated to yield 53.3 of Compound 7.

Compounds 1 to 6, 8 and 9 of the invention were prepared by analogous procedures.

Example 2

Preparation and Evaluation of Photographic Element

Emulsion Preparation

Emulsion E-1 was a cubic silver chlorobromide emulsion (64:36 molar ratio of Cl:Br) of mean grain edge 0.28µm prepared by double jet precipitation. Thus, silver nitrate (5.85M) and a mixture of potassium chloride (2.52M) and potassium bromide (1.42M) were jetted into a solution of gelatin (11 wt%) containing adenine (0.02 wt%) held at 54%C. The silver and halide solutions were added at a quadratically increasing rate such that 10.0 mol silver chlorobromide was precipitated over 62 minutes. Potassium aquachloropentaruthenate (III) and potassium hexachloroiridate (III) were dissolved in the halide solution such that the final emulsion contained a uniform distribution of both compounds at 0.3µmol/mol silver. The emulsion was acid precipitated, washed, chemically sensitised with sulphur and gold, and spectrally sensitised to 670 nm by conventional methods.

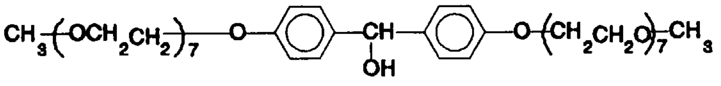
Emulsion E-2 was prepared by an analogous method, and comprised cubic silver chlorobromide grains (70:30) molar ration of Cl:Br) of mean grain edge 0.30µm.

Prior to coating on polyester film base, hydrazides and test compounds were added (as solutions in methanol or methanol/dimethylformamide mixture) to portions of these emulsions in the quantities indicated below.

In addition to Compounds 1 - 10 of the invention, the following comparison compounds A - D were tested:-

A -Benzhydrol

B



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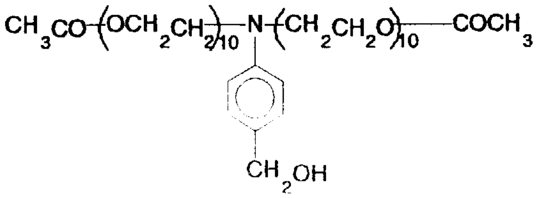
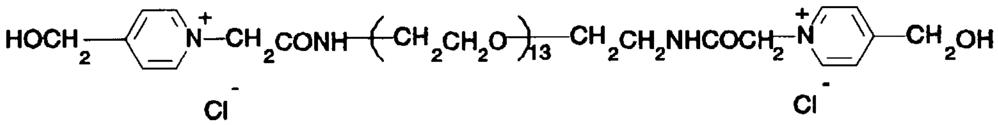
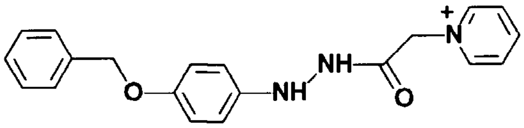


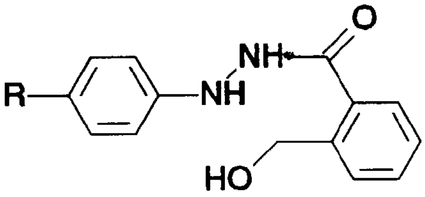
D



The following hydrazine derivatives H1 - H3 were tested:-

H1





H2 R = n-C_4H_9-

H3 R = $(CH_3)_2CHO$-

Evaluation

Samples of the resulting coatings were exposed by Xe flash through a narrow cut filter, a neutral density filter (1.0) and a 0 - 2 continuous density wedge, then processed for 30 seconds at 35°C in one of the developer solutions listed below, with washing and fixing by normal methods.

The following developers were used:-

Developer A - 3M "RDC V Rapid Access" developer, used at 1 + 2 dilution, with a pH of 10.6

Developer B - 3M "Excelerate" developer, used at the standard dilution, with a pH of 11.0

Sensitometric evaluation was carried out by standard procedures, and contrast values recorded for the density ranges 0.07+fog - 0.17+fog (toe contrast) and 0.50+fog - 2.5+fog (average contrast), giving the following results:-

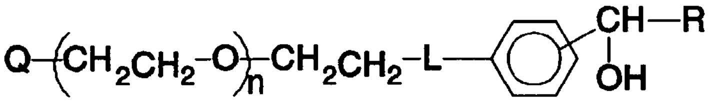
Emulsion	Compound (mmol/molAg)	Hydrazide (mmol/molAg)	Developer	Toe Contrast	Average Contrast
E-1	1 (5.0)	H1 (0.65)	A	2.0	20
E-1	1 (2.0)	H1 (0.65)	A	3.5	20
E-1	1 (5.0)	H1 (0.80)	A	3.6	20
E-1	1 (1.4)	H2 (1.7)	B	2.8	22
E-2	1 (5.0)	H3 (0.5)	A	2.3	23
E-1	2 (5.0)	H1 (0.80)	A	4.0	15
E-2	3 (2.0)	H3 (0.5)	A	2.5	24.5
E-2	4 (5.0)	H3 (0.5)	A	3.1	26.5
E-2	6 (5.0)	H3 (0.5)	A	2.3	20.2
E-1	7 (3.0)	H1 (0.65)	A	3.8	20
E-1	7 (1.4)	H2 (1.7)	B	1.6	22
E-1	8 (5.0)	H1 (0.80)	A	3.8	10
E-1	9 (5.0)	H1 (0.80)	A	4.1	20
E-1	A (30.0)	H1 (0.80)	A	3.8	15
E-2	B (5.0)	H3 (0.5)	A	1.0	14.5
E-1	C (1.4)	H2 (1.7)	B	1.6	13
E-1	D (1.0)	H3 (0.5)	A	0.7	6.7
E-1	D (5.0)	H3 (0.5)	A	0.7	5.8
E-1	none	H3 (0.5)	A	0.9	7.0

The results show that the compounds of the invention promote a high contrast at relatively low developer pH, and do so at low levels of incorporation (5 mmol/mol Ag or less). The analogous compounds of the prior art either require much higher levels of incorporation (so that crystallisation in the coating becomes a problem) (Compound A), or are found to be totally ineffective (Compound D). Compounds in which the benzyl alcohol or diarylcarbinol group is situated at the middle of a poly(oxyethylene) chain are at best only marginally effective (Compounds B and C).

Claims

1. A compound comprising a polyoxyethylene chain having at least 8 carbon atoms terminated at one or both ends by a group comprising a benzyl alcohol or diarylcarbinol functionality.

2. A compound as claimed in Claim 1 having a nucleus of the general formula:



(I)

in which:

n is an integer of at least 3;

R represents H or a phenyl;

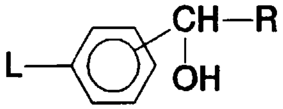
L represents a covalent bond or a divalent linking group; and

Q represents H, OH or any organic group.

3. A compound as claimed in Claim 2 in which n is from 3 to 50.

4. A compound as claimed in any one of Claims 2 to 4 in which

Q is selected from H, alkyl, alkoxy, alkylthio, aryl, aryloxy, arylthio, hydroxy and



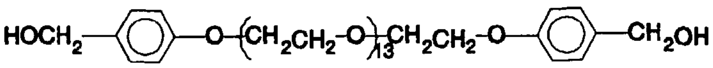
and

L is a divalent linking group comprising up to 10 skeletal atoms selected from C, N, O and S.

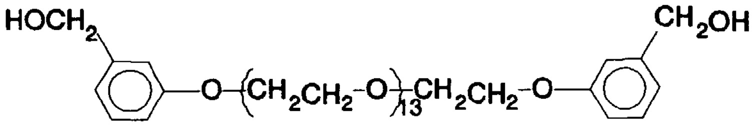
5. A compound as claimed in any one of Claims 2 to 4 in which L is selected from -0-, -S-, $-OCH_2CONH-$ and $N^+R_1R_2X^-$ in which R_1 and R_2 independently represent alkyl groups and X^- is an anion.

6. A compound as claimed in Claim 1 selected from:

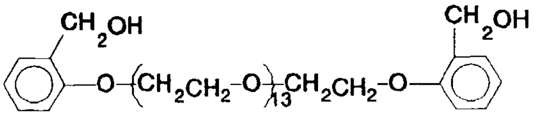
(1)



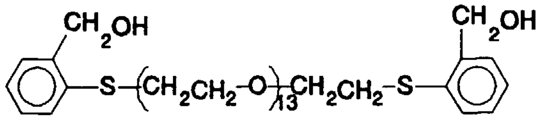
(2)



(3)



(4)



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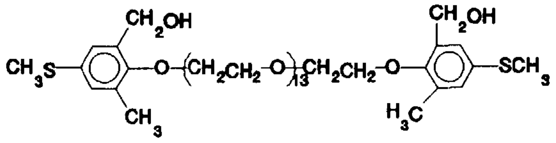
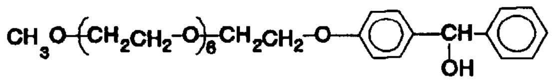
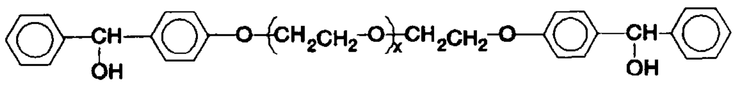


(6)



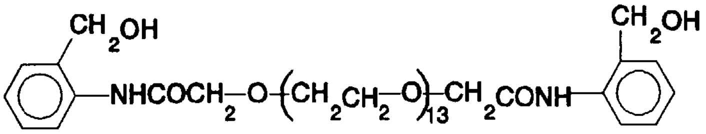


(7)x = 13

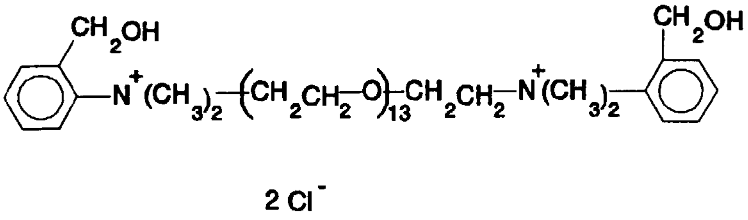
(8)x = 19

(9)x = 33

(10)



(11)



7. An imaging element comprising a high contrast negative-acting silver halide emulsion comprising a hydrazine derivative in said emulsion or in a layer adjacent thereto and a compound comprising a polyoxyethylene chain terminated at one or both ends by a group comprising a benzyl alcohol or diarylcarbinol functionality.

8. An imaging element as claimed in Claim 7 in which said compound is as defined in any one of Claims 1 to 6.

9. An imaging element as claimed in Claim 7 or Claim 8 in which said compound is present in an amount in the range from 0.01 to 10.0 mmol/mol Ag.

10. An imaging element as claimed in any one of Claims 7 to 9 in which the emulsion comprises cubic silver chlorobromide grains having a chloride content in the range 50 to 95% and an average grain size of from 0.1 to 0.4/μm.

11. A photographic process which comprises image-wise exposing an element as claimed in any one of Claims 7 to 10 and thereafter developing the exposed element.

12. A photographic process as claimed in Claim 11 in which the developer has a pH in the range 9.5 to 12.3 and comprises a dihydroxybenzene.