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## (54) Novel antifoggant for polyalkylene glycol sensitizers.

(57) Polyalkylene glycol sensitizing agents tend to generate instability towards fogging in silver halide photographic emulsions. The use of certain classes of aromatic hydroxyl compounds reduces this tendency towards fog.

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# NOVEL ANTIFOGGANTS FOR POLYALKYLENE GLYCOL SENSITIZERS

## Background of the Invention

### Field of the Invention

This invention relates to photographic compositions, and more particularly to photographic silver halide enulsions containing addenda that improve stability against fogging in the presence of polyalkylene glycol sensitizing compounds.

### Background of the Invention

It is known that to increase the speed of a light sensitive silver halide emulsion it is quite effective to incorporate a polyalkylene glycol type compound into the material as disclosed in, for example "The Theory of the Photographic Process" by Mees and James, Third edition, 1967, pp. 369-370. However, the amount of polyalkylene glycol which can be used for this purpose is restricted. If the amount used exceeds a definite limit, the fog level of the photographic material is greatly increased. Furthermore, if the photographic material is subjected to rapid drying conditions during its preparation, or is subjected to elevated temperatures during storage or processing, the increase in fog is exacerbated to such an extent that the material can lose its utility. Many different types of antifoggants are known in the art, each having its own particular area of effect or benefit.

It is necessary to find a means to stabilize these high speed photographic materials from the formation of fog due to the use of polyalkylene glycol sensitizers, the use of stabilizing amounts of aryl compounds containing two or more hydroxyl radicals, and at least one sulfo group and or one carboxyl group is made.

### Summary of the Invention

Accordingly it is an aspect of this invention to provide a light sensitive silver halide photographic emulsion sensitized with polyalkylene glycol type compounds that exhibit enhanced speed and are substantially free from fog.

It is another aspect of this invention to provide light sensitive silver halide emulsions containing stabilizing addenda that do not desensitize the emulsion.

Another aspect of this invention is to provide a light sensitive silver halide emulsion which is stable in all of its photographic properties, when manufacturing conditions include high temperatures, or when processed using short development times at elevated temperatures, i.e., in commonly used automatic processing machines.

These and other aspects of the invention are accomplished by incorporating into the silver halide emulsion speed enhancing amounts of polyalkylene glycol type compounds along with fog stabilizing amounts of aryl compounds containing two or more hydroxyl radicals at least one other radical selected from the group consisting of a sulfo radical and a carboxyl group.

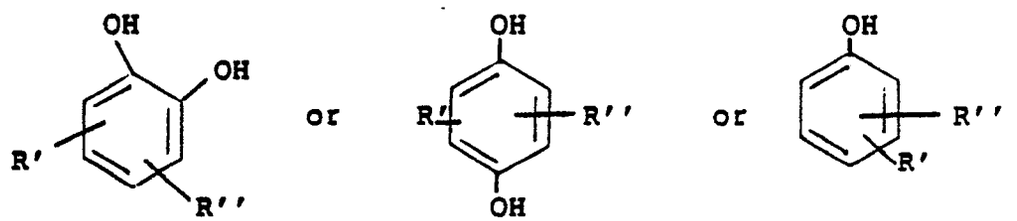
### Detailed Description of the Invention

In accordance with this invention, the above and other objects can be attained with a radiographic element comprising a support having thereon at least one silver halide layer wherein the gelatino silver halide layer comprises either at least 90 mole % bromide the remaining halide being iodide or bromide, or at least 50 mole % chloride the remaining halide being made up of either bromide up to 100 mole % and/or iodide to a maximum of 10 mole %. The emulsion must be in reactive association with a speed enhancing amount of a polylkylene glycol material and an aryl stabilizing compound.

The aryl stabilizing compounds of the invention comprise a phenyl ring containing two or more hydroxyl radicals and at least one other radical selected from the group consisting of sulfo radical and a carboxyl radical. To facilitate the incorporation of these compounds into the silver halide emulsion the water soluble

salts of the compounds, such as the alkali metal salts (Na or K) and ammonium salts can be used in accordance with usual practice.

Typically the stabilizing compounds having the following structures:




I II III

Where R′ represents a sulfo radical or a hydrogen atom, and R″ represents a sulfo radical and/or a carboxyl radical or a hydrogen atom, which describes such compounds as i.e., 4,5-dihydroxy-1,3-benzene sulfonic acid disodium salt, 2,5-dihydroxy benzene-4-sulfonic acid sodium salt, 2,5-dihydroxy-1,4-benzene disulfonic acid disodium salt or 5-sulfosalicylic acid dihydrate.

The polyalkylene glycol compounds used as the sensitizer for the silver halide emulsion according to the present invention includes those with a molecular weight between 1000-5000 more particularly between 1500-4000 and most preferably a molecular weight of between 3000 and 3500.

The sensitizing polyalkylene glycol and aryl stabilizing additions of the invention can be located in any layer of the photographic element which allows the compounds to be in reactive association with the emulsion layer. Reactive association is such a close physical association of the two materials that chemical reaction, physical contact, or electronic contact is effected. For example, the polyalkylene glycol sensitizing compound can be located in a overcoat to the silver halide layer, in an undercoat to the silver halide layer, or virtually any layer adjacent to the silver halide layer. The aryl stabilizing compounds can be located in any layer of the photographic element, for example the aryl stabilizing compound can be located in an overcoat to the silver halide emulsion layer, as an undercoat to the silver halide emulsion layer, or virtually any layer adjacent to the silver halide emulsion layer, either the same or different layer from the sensitizing compound. The polyalkylene glycol, sensitizing, and aryl, stabilizing additions of the invention can be made to the silver halide photographic emulsion utilizing any of the well known techniques in emulsion making. For example they can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a dispersion, similar to the techniques employed to incorporate particular color forming compounds in photographic emulsions. Techniques of such incorporation are described in U.S. Patent Nos. 2,322,027 and 2,801,171. The addenda can be added together or separately. Preferably they should be added to the silver halide emulsion (or any other layer of the element) prior to coating and after chemical sensitization.

The photographic material can comprise a support bearing a silver halide emulsion on one or both sides. In a preferred embodiment of this invention a radiographic material is provided comprising a support bearing on both sides a hydrophilic, preferably a gelatino silver halide emulsion layer wherein the halide comprises at least 90 mole % bromide, the remaining halide being made up of bromide to 100 mole % or a mixture of bromide and iodide to a maximum of 10 mole % iodide. The silver halide grains may be present as any crystal habit, including but not limited to, cubic, tetrahedral, tubular, orthorhombic, spherical, etc.

The compounds used in the present invention may be added together in any effective sensitizing amount (polyalkylene glycol) and any fog stabilizing amount (arylhydroxy compound). The concentration of the addenda can vary significantly in photographic silver halide emulsions such as from 0.25 to 20.0g/mole of silver halide. A generally useful range of the fog stabilizing arylhydroxy compound would be from 0.25 to 20.0g/mole of silver halide. A more preferred range would be from 0.25 to 8.0g/mole of silver halide.

Silver halide emulsions sensitized and stabilized in accordance with this invention can comprise silver chloride, silver bromide, silver bromoiodide, silver chloroiodide, silver chlorobromoiodide or mixtures thereof. Such emulsions can be coarse, medium or fine grain (or mixtures thereof) and can be prepared by any of the well-known procedures, e.g., single jet emulsions or double jet emulsions. Useful emulsions include Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al., U.S. Patent No. 2,222,264, Illingsworth, U.S. Patent No. 3,320,069, and McBride, U.S. Patent No. 3,271,157; or cubic grain emulsions, such as those described by Kline and

Moisar, Journal of Photographic Science, volume 12, page 242 et seq. or Markocki, the Spectral Sensitization of Silver Bromide Emulsions on Different Crystallographic Faces, Journal of Photographic Science, Volume 13, 1965; or Illingsworth, British Pat. No. 1,156,193 published June 25, 1969.

Tabular or lamellar grain emulsions as described in U.S. Patent Nos. 4,425,425, 4,439,520 and 4,425,426 are also equally useful.

The silver halide emulsions sensitized and stabilized with the compounds of this invention can be unwashed or washed to remove soluble salts. In the latter case the soluble salts can be removed by chill-setting and leeching or the emulsion can be coagulation washed e.g., by the procedures described in Hewitson et al., U.S. Pat. No. 2,618,556; Yutzy et al., U.S. Pat. No. 2,614,928; Yackel, U.S. Pat. No. 2,565,418; Hart et al., U.S. Pat. No. 3,241,969; and Waller et al., U.S. Pat. No. 2,489,341.

Photographic emulsions containing sensitizing and stabilizing combinations in accordance with this invention can be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable chemical sensitization procedures are described in Shepard, U.S. Patent No. 1,623,499; Waller, U.S. Patent No. 2,399,083; McVeigh, U.S. Patent No. 3,297,447; and Dunn, U.S. Patent No. 3,297,446.

The sensitized silver halide emulsions of this invention can contain speed increasing compounds such as cationic surface active agents and thioethers or combinations of these as described in Piper, U.S. Patent No. 2,886,437; Chechak, U.S. Patent No. 3,046,134; Carroll et al., U.S. Patent No. 2,944,900; and Goffe, U.S. Patent No. 3,294,540.

Silver halide emulsions containing the sensitizing or stabilising combinations of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers which can be used alone or in combination, include the thiazolium salts described in Staud, U.S. Patent No. 2,131,038 and Allen, U.S. Patent No. 2,694,716; the azaindenes described in Piper, U.S. Patent No. 2,886,437 and Heimbach, U.S. Patent No. 2,444,605; the mercury salts described in Allen, U.S. Patent No. 2,728,663; the urazoles described in Anderson, U.S. Patent No. 3,287,135; the oximes described in Carroll et al., British Patent No. 623,448; nitron; nitroindazoles, the polyvalent metal salts described in Jones, U.S. Patent No. 2,839,405; the thiuronium salts described in Herz, U.S. Patent No. 3,220,839; and the palladium, platinum and gold salts described in Trivelli, U.S. Patent No. 2,566,263 and Damschroder, U.S. Patent No. 2,597,915.

Photographic elements including emulsions sensitized and stabilized in accordance with this invention can contain incorporated developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylenediamines, or combinations of developing agents. The developing agents can be in the silver halide emulsion and/or in another suitable location in the photographic element. The developing agents can be added from suitable solvents or in the form of dispersions as described in Yackel, U.S. Patent No. 2,592,368 and Dunn et al., French Patent No. 1,505,778.

Silver halide sensitized and stabilzied in accordance with the invention can be dispersed in colloids that can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfones, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides, e.g., dialdehyde starch, oxyguargum, etc.

Photographic emulsions sensitized and stabilzied with the materials described herein can contain various colloids alone or in combination as vehicles or binding agents. Suitable hydrophilic materials include both naturally-occurring substances such as proteins, for example, gelatin, gelatin derivatives (e.g., phthalated gelatin), cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds, e.g., poly(vinylpyrrolidone) acrylamide polymers or other synthetic polymeric compounds such as dispersed vinyl compounds in latex form, and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in U.S. Patent Nos. 3,142,568 of Nottorf; 3,193,386 of White; 3,062,674 or Houck, Smith and Yudelson; 3,220,844 of Houck, Smith and Yudelson; Ream and Fowler, 3,287,289; and Dykstra, U.S. Patent No. 3,411,911; particularly effective are those water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross linking sites which facilitate hardening or curing and those having recurring sulfobetaine units as described in Canadian Patent No. 774,054.

Emulsions sensitized and stabilized in accordance with this invention can be used in photographic elements which contain antistatic or conducting layers, such as layers that comprise soluble salts, e.g., chlorides, nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk, U.S.

Patent Nos. 2,861,056 and 3,206,312 or insoluble inorganic salts such as those described in Trevoy, U.S. Patent No. 3,428,451.

Photographic emulsions containing sensitizing and stabilizing combinations of the invention can be coated on a wide variety of supports. Typical supports include polyester film, subbed polyester film, poly(ethylene terephthalate) film, cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible supoprt is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

Sensitized and stabilized emulsions of the invention can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton, U.S. Patent No. 2,960,404; fatty acids or esters such as those described in Robijns, U.S. Patent No. 2,588,765 and Duane, U.S. Patent No. 3,121,060; and silicone resins such as those described in DuPont British Patent No. 955,061.

The photographic emulsions sensitized and stabilized as described herein can contain surfactants such as saponin, anionic, compounds, such as the alkylarylsulfonates described in Baldsiefen, U.S. Patent No. 2,600,831 fluorinated surfactants, and amphoteric compounds such as those described in Ben-Ezra, U.S. Patent No. 3,133,816.

Photographic elements contianing emulsion layers sensitized as described herein can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in Jelley et al., U.S. Patent No. 2,992,101 and Lynn, U.S. Patent No. 2,701,245.

Spectrally sensitized emulsions of the invention can be utilized in photographic elements which contain brightening agents including stilbene, triazine, oxazole and coumarin brightening agents. Water soluble brightening agents can be used such as those described in Albers et al., German Patent No. 972,067 and McFall et al., U.S. Patent No. 2,933,390 or dispersions of brighteners can be used such as those described in Jansen, German Pat. No. 1,150,274 and Oetiker et al., U.S. Patent No. 3,406,070.

Photographic elements containing emulsion layers sensitized and stabilized according to the present invention can be used in photographic elements which contain light absorbing materials and filter dyes such as those described in Sawdey, U.S. Patent No. 3,253,921; Gaspar, U.S. Patent No. 2,274,782; Carroll et al., U.S. Patent No. 2,527,583 and Van Campen, U.S. Patent No. 2,956,879. If desired, the dyes can be mordanted, for example, as described in Milton and Jones, U.S. Patent No. 3,282,699.

The sensitizing dyes and/or supersensitizers (and other emulsion addenda) can be added to the photographic emulsions from water solutions or suitable organic solvent solutions, for example with the procedure described in Collins et al., U.S. Patent No. 2,912,343; Owens et al., U.S. Patent No. 3,342,605; Audran, U.S. Patent No. 2,996,287 or Johnson et al., U.S. Patent No. 3,425,835. The dyes can be dissolved separately or together, and the separate or combined solutions can be added to a silver halide emulsion, or a silver halide emulsion layer can be bathed in the solution of supersensitizers and/or dyes.

Contrast enhancing additives such as hydrazines, rhodium, iridium and combinations thereof are also useful.

Photographic emulsions of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin, U.S. Patent No. 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in Russell, U.S. Patents Nos. 2,761,791 and Wynn, British Patent No. 837,095.

Silver halide emulsions containing sensitizing and stabilizing combinations of this invention can be used in elements designed for color photography, for example, elements containing color-forming couplers such as those described in Frolich et al., U.S. Patent No. 2,376,679; Vittum et al., U.S. Patent No. 2,322,027; Fierke et al., U.S. Patent No. 2,801,171; Godowsky, U.S. Patent No. 2,698,794; Barr et al., U.S. Patent No. 3,227,554 and Graham, U.S. Patent No. 3,046,129; or elements to be developed in solutions containing color-forming couplers such a those described in Mannes and Godowsky, U.S. Patent No. 2,252,718; Carroll et al. U.S. Patent No. 2,592,243 and Schwan, U.S. Patent No. 2,950,970.

Exposed photographic emulsions of this invention can be processed by various methods including processing in alkaline solutions containing conventional developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, phenylenediamines, ascorbic acid deriva tives, hydroxylamines, hydrazines and the like; web processing such as described in Tegillus et al., U.S. Patent No. 3,179,517; stabilization processing as described in Yackel et al. "Stabilization Processing of Films and Papers", PSA Journal, Vol. 16B, Aug. 1950; monobath processing as described in Levy "Combined Development and Fixation of Photographic Images with Monobaths", Phot. Sci. and Eng., Vol. 2, No. 3, Oct. 1958, and Barnes et al., U.S. Patent No. 3,392,019. If desired, the photographic emulsions of this invention can be processed in hardening developers such as those described in Allen et al., U.S. Patent No. 3,232,761; in a roller

transport processor such as those described in Russell, U.S. Patent No. 3,025,779; or by surface application processing as described in Example 3, of Kitze, U.S. Patent No. 3,418,132.

These and other aspects of the invention will be shown by the examples.

## EXAMPLES 1 - 11 Emulsion Preparation

A gelatino silver halide emulsion was prepared by precipitation and ripening steps using 98.0 mole percent silver bromide and 2.00 mole percent silver iodide in the presence of 15.0g of gelatin per mole of silver halide. The precipitated silver halide was freed of unwanted soluble by-product salts by coagulation and washing using the method disclosed in U.S. Pat. No. 2,489,341 wherein the silver halide and most of the gelatin are coagulated by the addition of sodium lauryl sulfate, using an acid coagulation environment. Following the washing step, the solution was reconstituted in water containing about 67.0g of gelatin per mole of silver halide. This emulsion was treated with conventional sulfur and gold sensitizers and was digested at 55° C to increase sensitivity, was cooled to 40° C, and treated with post-sensitization additives and stabilizers, namely tetraazaindines, additional halides, coating aids, and hardening agents, etc. as required and as is known in the art.

Into a gelatino silver bromodiodide emulsion of the type described above was incorporated 5.00g of the polyethylene glycol PEG3350 (Union Carbide) per mole of silver halide followed by the addition of about 0.50-10.0g per mole of silver halide of 4,5-dihydroxy-1,3-benzene-sulfonic acid disodium salt. Two similar emulsions were prepared. One was made without any extra addition, the second with only the addition of 5.00g PEG3350 per mole of silver halide.

The various emulsions were coated double sided on 7.0 mil (0.18 mm) polyester film base in the usual manner. The sensitometric properties of the photographic elements were determined after 7 days storage at 50° C. and 50 % relative humidity, by exposing through a continuous 0-4.0 density photographic wedge with a 1/10 second exposure from 2650° K. The light was filtered with a Corning 5850 blue filter. The exposed films were processed through a 90 second dry-to-dry medical x-ray processor using standard medical x-ray chemistry.

Table 'A' summarizes the results of the sensitometric tests. The speeds indicated are a function of the exposure necessary to yield a density of 0.10 above the background fog. The initial control speed is taken as 100. Substantial reductions in the general overall fog level, as well as the reduction in fog level attributed to the polyethyleneglycol sensitizer alone are achieved.

TABLE A

| Coating Number | PEG3350 g/mole $A_oX$ | Addenda | Conc. of Addenda (g/mole $A_yX$) | 7 days at 50° C 50% RH | | |
|---|---|---|---|---|---|---|
| | | | | Fog | δ | Speed |
| 1 | 0 | control | 0 | 0.13 | 2.52 | 100 |
| 2 | 5.00 | control | 0 | 0.16 | 2.72 | 104 |
| 3 | " | 4,5-dihydroxy 1,3-benzene disulfonate | 0.50 | 0.14 | 2.66 | 104 |
| 4 | " | " | 1.00 | 0.15 | 2.71 | 104 |
| 5 | " | " | 1.50 | 0.14 | 2.75 | 103 |
| 6 | " | " | 2.00 | 0.14 | 2.74 | 104 |
| 7 | " | " | 2.50 | 0.12 | 2.65 | 102 |
| 8 | " | " | 3.00 | 0.13 | 2.66 | 103 |
| 9 | " | " | 4.00 | 0.13 | 2.62 | 102 |
| 10 | " | " | 6.00 | 0.12 | 2.73 | 102 |
| 11 | " | " | 8.00 | 0.11 | 2.79 | 103 |

## EXAMPLES 12-30

A number of other samples of the photographic gelatino silver bromoiodide emulsion were prepared containing other addenda of the invention after the addition of the PEG3350. These samples were prepared coated, exposed and processed in the same manner as those in Examples 1-11. As indicated in Tables 'B' through 'D' the addenda did not adversely affect the sensitometric properties of the silver halide emulsion, but did stabilize the silver halide emulsion in terms of the fog increase imparted by the PEG3350.

TABLE B

| Coating Number | PEG3350 g/mole $A_gX$ | Addenda | Conc. of Addenda (g/mole A.X) | 7 days at 50° C 50% RH | | |
|---|---|---|---|---|---|---|
| | | | | Fog | δ | Speed |
| 12 | 0 | control | 0 | 0.10 | 2.46 | 100 |
| 13 | 5.00 | control | 0 | 0.13 | 2.39 | 106 |
| 14 | " | 4,5-dihydroxy 1,3-benzene disulfonate | 1.00 | 0.11 | 2.49 | 105 |
| 15 | " | 2,5-dihydroxy-4-benzene sulfonic acid | 0.50 | 0.11 | 2.41 | 106 |
| 16 | " | " | 1.00 | 0.12 | 2.36 | 106 |
| 17 | " | " | 1.50 | 0.12 | 2.47 | 106 |
| 18 | " | " | 2.00 | 0.12 | 2.49 | 107 |

TABLE C

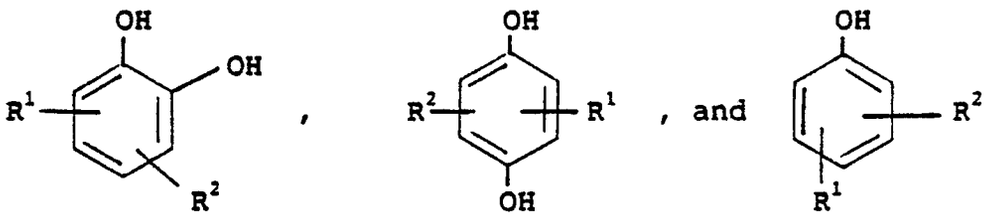
| Coating Number | PEG3350 g/mole $A_gX$ | Addenda | Conc. of Addenda (g/mole $A_gX$) | 7 days at 50° C 50% RH | | |
|---|---|---|---|---|---|---|
| | | | | Fog | δ | Speed |
| 19 | 0 | control | 0 | 0.10 | 2.46 | 100 |
| 20 | 5.00 | control | 0 | 0.13 | 2.39 | 106 |
| 21 | " | 4,5-dihydroxy 1,3-benzene disulfonic acid | 1.00 | 0.11 | 2.49 | 105 |
| 22 | " | 2,5-dihydroxy-1,4-benzene sulfonic acid | 0.50 | 0.11 | 2.41 | 106 |
| 23 | " | " | 1.00 | 0.13 | 2.36 | 106 |
| 24 | " | " | 1.50 | 0.12 | 2.47 | 106 |
| 25 | " | " | 2.00 | 0.11 | 2.49 | 107 |

TABLE D

| Coating Number | PEG3350 g/mole Ag | Addenda COOH OH + $SO_3H$ | Conc. of Addenda (g/mole Ag) | 7 days at 50° C 50% RH | | |
|---|---|---|---|---|---|---|
| | | | | Fog | δ | Speed |
| 26 | 0 | control | 0 | 0.14 | 2.75 | 100 |
| 27 | 5.00 | control | 0 | 0.20 | 2.80 | 107 |
| 28 | " | 5-sulfosalicyclic acid | 2.5 | 0.20 | 3.00 | 107 |
| 29 | " | " | 5.00 | 0.17 | 2.94 | 105 |
| 30 | " | " | 10.0 | 0.18 | 2.98 | 105 |

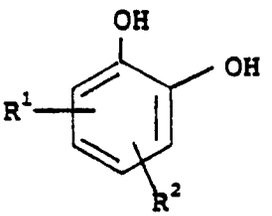
## Claims

1. A silver halide photographic element comprising a substrate having on at least one side thereof a silver halide photographic emulsion, the molar halide content of silver halide grains of said emulsion being selected from the group of silver chloride, silver chlorobromide with at least 50% chloride, silver chloroiodide with less than 10% iodide, silver chlorobromiodide with at least 50% chloride at less than 10% iodide, silver bromide, silver bromoiodide with less than 10% iodide, silver bromochloride with at lesat 90% bromide, and silver bromochloriodide with at lest 90% bromide and less than 10% iodide, said emulsion having in reactive associating therewith a sensitizing amount of polyalkyleneglycol compound and a fog reducing amount of an aryl hydroxy compound having a formula selected form the group consisting of

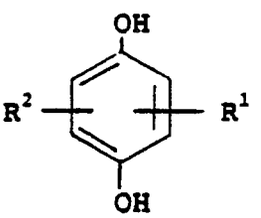


wherein $R^1$ represents a sulfo group or hydrogen, and $R^2$ represents a sulfo group, carboxyl group, or hydrogen, with at least one of $R^1$ and $R^2$ being other than hydrogen.

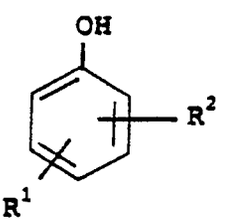
2. The element of claim 1 wherein said aryl hydroxy compound has the formula.



3. The element of claim 1 wherein said aryl hydroxy compound has the formula:



4. The element of claim 1 wherein said aryl hydroxy compound has the formula:



5. The element of claim 1 wherein $R^1$ is sulfo.
6. The element of claim 1 wherein $R^1$ is hydrogen.
7. The element of claims 2, 3 or 4 wherein $R^1$ is sulfo.
8. The element of claims 2, 3 or 4 wherein $R^2$ represents a carboxyl group.
9. The element of claims 2, 3 or 4 wherein $R^2$ represents a sulfo group.

10. The element of claim 8 wherein $R^2$ represents a sulfo group.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 89 30 3934

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
|---|---|---|---|
| Y | DE-A-2 422 772 (KONISHIROKU)<br>* Claims *<br>--- | 1-10 | G 03 C 1/04<br>G 03 C 1/34<br>G 03 C 1/42 |
| Y | GB-A- 981 470 (AGFA)<br>* Claims *<br>--- | 1-4,7 | |
| Y | US-A-3 236 652 (K.C. KENNARD et al.)<br>* Claims; column 2, line 60 *<br>--- | 1 | |
| Y | EP-A-0 209 010 (KODAK)<br>* Claims; page 4, line 31 - page 5, line 16; page 23, line 15 *<br>----- | 1-10 | |

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

G 03 C

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 27-07-1989 | BUSCHA A.J. |

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