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N. HEIMBACH

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PHOTOGRAPHIC FILTER AND ANTIHALATION LAYER

Filed April 19, 1944

FIG. 1

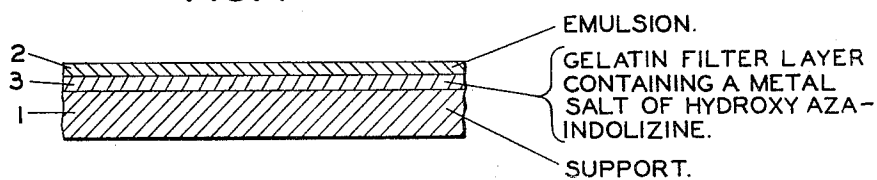
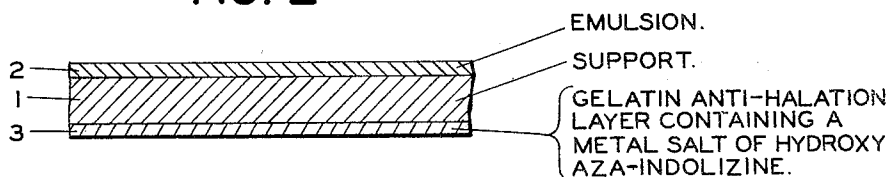


FIG. 2



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## UNITED STATES PATENT OFFICE

2,390,707

## PHOTOGRAPHIC FILTER AND ANTI-HALATION LAYERS

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Application April 19, 1944, Serial No. 531,770

11 Claims. (Cl. 95—8)

This invention relates to filter and anti-halation layers for photographic materials, and particularly to hydroxy aza-indolizine dyes as photographic filter and anti-halation agents.

It is known in the art of making photographic materials such as multilayer color films, that color separation by the various layers is facilitated by the use of filters either incorporated directly into the emulsion layers or added as adjacent layers in the appropriate sequence. For example, blue light passing through the non-sensitized blue sensitive layer must be absorbed by a minus blue (i. e., yellow) filter before it reaches the green sensitive and red sensitive layers, which are likewise sensitive to blue light. Similarly, green absorbing filters are frequently desirable in order to obtain a better separation between the green and the red sensitive layers. Other filters with special characteristics are occasionally used, depending upon the absorption desired.

In a similar manner, colored light-absorbing layers are frequently used adjacent to a photographic support in order to prevent light scattering or halation effects caused by reflection of light rays from the support onto the sensitive layer. Such layers are commonly known as anti-halation layers.

In order to perform their desired functions, filter and anti-halation materials must be reasonably stable in a colloid carrier. They must be non-diffusing and readily removable in the customary processing baths. Moreover, it is essential that they have no injurious effects, such as fogging action, on the emulsion layers. Many materials suggested in the art as suitable for filter layers fail to fulfill completely all of the above requirements.

Colored organic compounds having free imino (>NH) or mercapto (—SH) groups have been applied in the form of their silver salts as filter and anti-halation layers. The silver salt forming capacity of imino or mercapto groups is well known and utilized in many photographic applications. Moreover, these silver salts are generally insoluble, thereby imparting the necessary non-diffusing properties in the use of such compounds in light absorbing filters. Unfortunately imino and mercapto silver salts frequently have severe desensitizing properties, especially in concentrations required for adequate light absorption, and consequently their desirability is considerably limited by this deficiency. On the other hand, compounds with other suitable salt forming groups are rarely encountered, since their

silver salts are usually not sufficiently insoluble to prevent diffusion. For example, silver salts of carboxyl or sulfonic acid groups generally have appreciable water solubility.

The primary object of the present invention is to provide a new class of silver salts suitable as filter layers and anti-halation layers for photographic materials.

Another object is to provide colored compounds which form non-diffusing silver salts readily dischargeable in the usual processing baths.

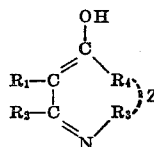
A further object is to provide filter and anti-halation layers which have no deleterious effect on the photographic properties of the film.

A still further object is to provide hydroxy azaindolizine dyes as filter and anti-halation layers in the form of their heavy metal salts, and preferably in the form of their silver salts.

Other objects and advantages of this invention will be apparent by reference to the following specification in which its preferred details and embodiments are described.

I have discovered that hydroxy aza-indolizines containing in addition to one or more chromophoric groups, one or more water solubilizing groups, are capable of forming insoluble stable silver salts particularly adaptable as filter and anti-halation layers in photographic materials.

According to the present invention analogues of hydroxy aza-indolizines are incorporated in a layer or applied to the film in the form of their silver salts. These hydroxy aza-indolizines are characterized by a structure corresponding to the following general formula:



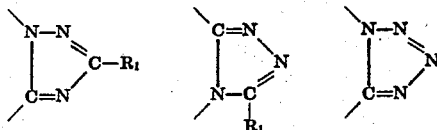
wherein R<sub>1</sub> and R<sub>2</sub> may be hydrogen, alkyl, e. g. methyl, ethyl, propyl, butyl, amyl and the like, aryl, e. g. phenyl, naphthyl, etc., aralkyl, e. g. benzyl, methyl naphthyl, etc., and either R<sub>1</sub> or R<sub>2</sub> or both containing at least one chromophore group such as azo, nitro, or nitroso, as well as one or more water solubilizing groups such as arsonic, carboxylic or sulfonic acid groups, R<sub>3</sub> always being aryl or aralkyl when R<sub>1</sub> is hydrogen, or alkyl and vice versa. Thus, specific R<sub>1</sub> and R<sub>2</sub> groups containing suitable chromophoric and solubilizing substituents may be, for example, nitrophenyl-, sulfophenylazo-, sulfonaphthaleneazo-, dicarboxy-phenylazo, hydroxy aza-indolizine-azosulfo-

tolylazo-, sulfonaphthaleneazo-sulfophenylazo-, etc.  $R_3$  and  $R_4$  are either nitrogen or carbon, and  $Z$  represents the atoms necessary to complete an aza-indolizine ring.

The indolizine portion of the formula represented by:

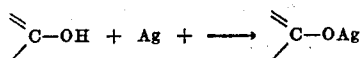


may, for example, contain the following general configurations:



wherein  $R_1$  has the same values as above.

The hydroxy group on the carbon atom adjacent to  $R_4$  in the above general configurations is capable of forming insoluble stable silver salts in the presence of silver ions,



This insoluble silver salt formation is wholly unexpected and surprising among hydroxy compounds containing water solubilizing substituents, such as arsonic, carboxyl, or sulfonic acid groups.

The insoluble silver salts formed by the hydroxy aza-indolizine dyes are non-diffusing and

readily adaptable as filter and anti-halation agents. Moreover, their usefulness is not dependent upon the nature of the  $R_1$  and  $R_2$  substituents so long as the desired chromophore groups are contained therein as well as suitable water solubilizing groups, the latter facilitating complete removal of the residual aza-indolizine dye after the silver of its silver salt is removed in the processing baths. Furthermore, they are prepared in good yield from readily available intermediates by the reactions hereinafter described.

In the accompanying drawing, the two figures are enlarged section views of photographic elements having filter layers and anti-halation layers made according to the present invention.

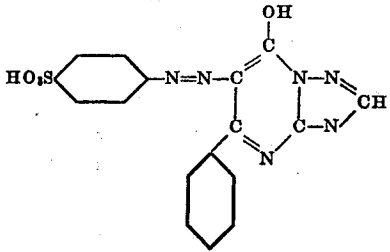
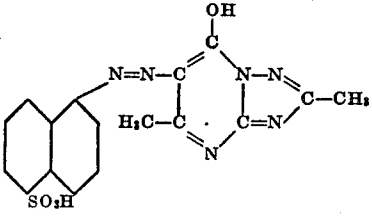
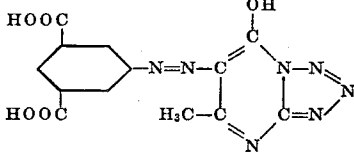
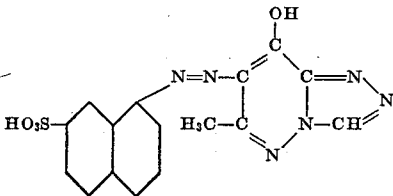
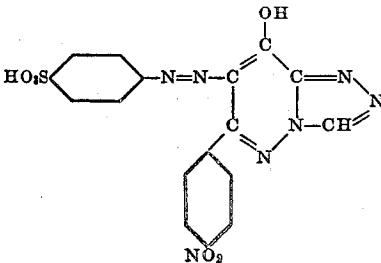
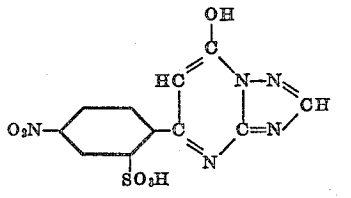
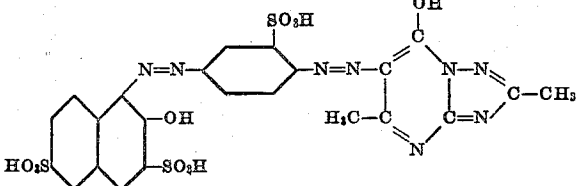
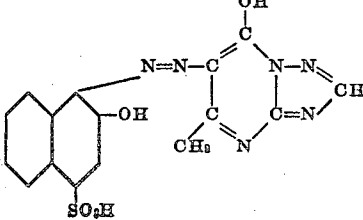
Figure 1 represents an embodiment of the invention in which the filter layer is interposed between the emulsion and the support.

Figure 2 represents an embodiment in which the anti-halation layer is in the form of a backing.

In Figures 1 and 2, 1 is the support, 2 the light-sensitive silver-halide emulsion layer and 3 the gelatin filter or anti-halation layer.

Specific hydroxy aza-indolizine dyes useful in the present invention in the form of their silver salts are the following, it being understood that these are exemplary only, and that they may contain other substituent groups as well as those included in these formulae. It will also be understood that more complex dyes containing, for example, two or more azo groups of the bis-hydroxy aza-indolizine type, as illustrated in Formula 3, or of the naphthyl disazo phenyl hydroxy aza-indolizines as illustrated in Formulae 4 and 11, are within the scope of the present invention.

| Formula of hydroxy aza-indolizine |  | Color of Ag salt |
|-----------------------------------|--|------------------|
| (1)                               |  | Yellow.          |
| (2)                               |  | Do.              |
| (3)                               |  | Orange.          |
| (4)                               |  | Magenta.         |

| Formula of hydroxy aza-indolizine                                                        | Color of Ag salt |
|------------------------------------------------------------------------------------------|------------------|
| (5)     | Yellow.          |
| (6)     | Do.              |
| (7)     | Do.              |
| (8)    | Do.              |
| (9)   | Do.              |
| (10)  | Light yellow.    |
| (11)  | Magenta-red.     |
| (12)  | Yellow.          |

|      | Formula of hydroxy aza-indolizine | Color of Ag salt |
|------|-----------------------------------|------------------|
| (13) |                                   | Yellow.          |
| (14) |                                   | Do.              |

The hydroxy aza-indolizine dyes containing azo groups, may be prepared by first diazotizing a suitable amine, coupling the diazonium salt with a  $\beta$ -keto ester, and then condensing the resulting azo- $\beta$ -keto ester with an amino triazole or tetrazole.

The preparation of the azo- $\beta$ -keto esters is further described in the chemical literature. For example, carboxy benzolazo-acetoacetic ester and its preparation are disclosed in Ber. 41, 2365. In general, the various desired azo- $\beta$ -keto esters can be prepared in a similar manner as outlined in this reference.

As typical illustrations of primary amines usable for the preparation of the azo- $\beta$ -keto esters, may be mentioned, sulfanilic acid, 1-naphthylamine-5-sulfonic acid, diaminotoluene sulfonic acid, nitroaniline sulfonic acid, 1-amino-2-naphthol-4-sulfonic acid, 1-naphthylamine-5,7-disulfonic acid, 1-naphthylamine-4-sulfonic acid, 1-naphthylamine-3,6,8-trisulfonic acid, 2-naphthylamine-6-sulfonic acid and arsanilic acid.

As suitable  $\beta$ -keto esters may be mentioned, acetoacetic ester, benzoylacetic ester and p-nitrobenzoylacetic ester.

Suitable amino-azoles that can be condensed with the azo-ester intermediates are 4-amino-1,2,4-triazole, 3-amino-1,2,4-triazole, 5-amino-tetrazole and 3-amino-5 methyl-1,2,4-triazole. The indolizine condensation is conveniently carried out in a solvent such as glacial acetic acid.

The preparation of hydroxy aza-indolizine dyes containing other chromophore groups such as nitro or nitroso groups may be accomplished by the same condensation of aminotriazoles or aminotetrazoles with the appropriate nitro or nitroso substituted benzoylacetic ester. Formula 10 of the preceding compounds illustrates a typical hydroxy aza-indolizine containing a nitro chromophore group.

The following examples are illustrative of methods which I have found suitable for preparing various colored hydroxy aza-indolizines which I disclose herein and their use as filter layers in the form of their silver salts.

#### EXAMPLE I

One-tenth (0.1) mol (30.3 grams) of  $\alpha$ -naphthylamine-5,7 disulfonic acid was diazotized with 0.11 mol (7.7 grams) sodium nitrite and 0.3 mol (11.0 grams) of hydrochloric acid at 0-5° C. The diazonium salt was coupled with a solution of 0.1 mol (13.0 grams) acetoacetic ester and 0.2 mol

(8.0 grams) sodium hydroxide at 0° C. After allowing to stand for 15 minutes, the yellow sodium salt of the azo-keto ester intermediate was precipitated in 90% yield by the addition of sodium acetate. The crude ester intermediate was dried in vacuum at room temperature and then refluxed in glacial acetic acid (150 cc.) with 0.1 mol (8.4 grams) 3-amino-1,2,4 triazole for 6 hours. The sodium salt of the hydroxy azaindolizine corresponding to Formula 1 precipitated during the course of the reaction. Purification was accomplished by recrystallization from water in the presence of sodium acetate. Total overall yield of pure dye was 75%. The dye is water soluble and forms a deep yellow insoluble silver salt.

#### EXAMPLE II

The azo ester intermediate of Formula 2 was prepared in the same manner as in Example I, except that the compound precipitated from the cold solution as the free acid without the addition of sodium acetate. The azo ester intermediate was condensed as in Example I, using in this case 8.4 grams 4-amino-1,2,4-triazole. The sodium salt dissolves to a yellow solution and forms a yellow silver salt.

#### EXAMPLE III

The hydroxy aza-indolizine dye corresponding to Formula 3 was prepared in a similar manner as in Example I. Twenty (20) grams 2,6-diaminotoluene-4-sulfonic acid was diazotized with 15 grams sodium nitrite in the presence of hydrochloric acid. The diazonium salt was coupled with 26 grams of acetoacetic ester in alkaline solution at 0° C. The resulting orange-red azo ester intermediate was refluxed with 16.8 grams 4-amino-1,2,4-triazole in 150 cc. glacial acetic acid for 8 to 10 hours. The dye was precipitated by the addition of ether and recrystallized from a small volume of water. The dye had a red color, dissolved to an orange solution, and formed an orange silver salt.

#### EXAMPLE IV

The hydroxy aza-indolizine dye corresponding to Formula 4 was prepared in the following manner:

p-Nitro aniline-o-sulfonic acid (21.8 grams) was diazotized with one equivalent (7.5 grams) of sodium nitrite and hydrochloric acid. The diazonium salt thus formed was then coupled with

acetoacetic ester as in the previous examples. The sodium salt of the azo-ester intermediate precipitated as deep yellow crystals upon the addition of sodium acetate. The azo ester intermediate was coupled with 8.4 grams of 3-amino-1,2,4-triazole in 150 cc. glacial acetic acid by refluxing for 6 to 8 hours. The product was recovered as the sodium salt and recrystallized from water in the presence of sodium acetate.

The sodium salt of the nitrophenylazo hydroxy aza-indolizine compound was dissolved in excess aqueous ammonia and saturated with hydrogen sulfide at 30-40° C. The mixture was allowed to digest for 2 hours at 40° C., and allowed to stand overnight at room temperature.

During this period a color change from deep red to yellow occurred. Excess ammonia and hydrogen sulfide were then removed by evaporation on a steam bath. Upon addition of sodium acetate, the reduced yellow amino phenylazo hydroxy aza-indolizine precipitated from solution.

The dried crude amino compound was diazotized with one equivalent of sodium nitrite in hydrochloric acid solution and coupled directly with an alkaline solution of  $\alpha$ -naphthol-4,8-disulfonic acid to a deep magenta solution. The dye was precipitated with sodium acetate and recrystallized from water. It had a dark green color, dissolved in water to a brilliant magenta solution and formed a magenta silver salt.

#### EXAMPLE V

A photographic filter layer was prepared by mixing the following ingredients to form a colored silver salt dispersion in gelatin:

##### Solution A

|                                                                                                              |         |     |
|--------------------------------------------------------------------------------------------------------------|---------|-----|
| 6-[5,7-disulfonaphthalene - 1 - azo] - 7 - hydroxy - 5 - methyl 1,3,4 - triaza - indolizine (Formula 1)----- | grams-- | 4.7 |
| Water -----                                                                                                  | cc--    | 100 |
| Sodium carbonate (anhydrous)-----                                                                            | grams-- | 2.1 |
| Gelatin (10% solution)-----                                                                                  | cc--    | 25  |

##### Solution B

|                      |         |     |
|----------------------|---------|-----|
| Water -----          | cc--    | 100 |
| Silver nitrate ----- | grams-- | 1.7 |

##### Solution C

|                             |      |     |
|-----------------------------|------|-----|
| Gelatin (10% solution)----- | cc-- | 100 |
|-----------------------------|------|-----|

Solution B was added to Solution A with rapid stirring. After several minutes, Solution C was added. The silver of the silver nitrate formed a silver salt with the hydroxy group of the dye in the gelatin solution. The final gelatin suspension thus obtained was then coated on a photographic film in the customary manner to serve as a yellow filter layer for blue light absorption. The silver salt of the dye is non-diffusing.

The amount of hydroxy aza-indolizine dye used according to the present invention will vary somewhat depending upon the color desired. In general an amount more or less than that given in Example V may be used for satisfactory results.

For the production of anti-halation coatings, the hydroxy aza-indolizines of the present invention are incorporated into gelatin, treated with silver nitrate, and the dispersions thus obtained are cast in a known manner as coatings underneath the emulsion layer, intermediate layer between the support and the emulsion or as a backing layer on the rear surface of the emulsion support, or as a super coat on the emulsion when the material is intended to be exposed through

the support. Similarly, the dispersions may be coated on one of multilayer elements employed for color photography, which usually comprise a base coated with two or three light sensitive emulsions, each of which records one of the desired spectral regions.

#### EXAMPLE VI

A photographic anti-halation layer was prepared by mixing the following ingredients to form a colored silver salt dispersion in gelatin:

##### Solution A

|                                                                                            |         |     |
|--------------------------------------------------------------------------------------------|---------|-----|
| 5-[3,5-dicarboxy phenyl-1-azo]-4-hydroxy-6-methyl-2,3,7-triaza-indolizine (Formula 2)----- | grams-- | 7.0 |
| Water -----                                                                                | cc--    | 200 |
| Sodium hydroxide (4%)-----                                                                 | cc--    | 7.5 |
| Gelatin (10% solution)-----                                                                | cc--    | 100 |

##### Solution B

|                      |         |     |
|----------------------|---------|-----|
| Water -----          | cc--    | 100 |
| Silver nitrate ----- | grams-- | 3.4 |

##### Solution C

|                             |      |     |
|-----------------------------|------|-----|
| Gelatin (10% solution)----- | cc-- | 300 |
|-----------------------------|------|-----|

Solution B was added to Solution A with rapid stirring. After several minutes, solution C was added. The final gelatin suspension of the silver salt thus obtained was coated on a support in the customary manner as an anti-halation layer.

The filter and anti-halo coatings prepared as described above have been found to have particularly good filter and anti-halant properties and to have no effect on the normal keeping properties of the light-sensitive layer.

It will be understood that where in the claims appended hereto the term filter layer is used, that such is intended to include anti-halation layer.

While the present invention has been described in considerable detail with reference to certain preferred procedures, materials and uses, it is understood that the new class of hydroxy aza-indolizines and their use as filter and anti-halation materials is not limited thereto and that numerous variations and modifications described in the foregoing specification may be made. All such modifications and variations are within the scope of the invention as defined by the appended claims.

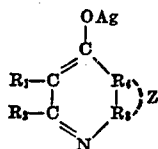
#### What I claim is:

1. A photographic material which comprises a support, a light-sensitive gelatino-silver halide emulsion and a filter layer containing a silver salt of a hydroxy aza-indolizine in which the nuclear carbon atom adjacent to the five-membered heterocyclic ring of the aza-indolizine nucleus is substituted by a hydroxy group, the hydrogen atom of which is replaced by silver and which compound contains at least one chromophoric group and at least one water solubilizing group.

2. A photographic material which comprises a support, a light-sensitive gelatino-silver-halide emulsion and a filter layer containing a silver salt of a disazo bis-hydroxy aza-indolizine in which the nuclear carbon atoms adjacent to the five-membered heterocyclic rings of the aza-indolizine nuclei are each substituted by a hydroxy group, the hydrogen atoms of which are replaced by silver, and which compound contains at least one water solubilizing group.

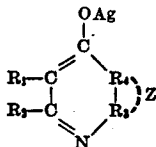
3. A photographic material which comprises a support, a light-sensitive gelatino-silver-halide

emulsion and a filter layer containing a silver salt having the general formula:



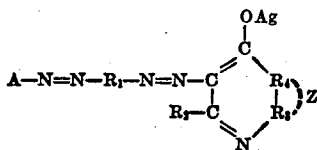
wherein R<sub>1</sub> and R<sub>2</sub> represent members selected from the class consisting of hydrogen, alkyl, aryl and aralkyl groups containing at least one chromophoric group and at least one water solubilizing group, R<sub>1</sub> always being a member selected from the class consisting of aryl and aralkyl groups when R<sub>2</sub> is a member selected from the class consisting of hydrogen and alkyl, and R<sub>2</sub> always being a member selected from the class consisting of aryl and aralkyl groups when R<sub>1</sub> is a member selected from the class consisting of hydrogen and alkyl, R<sub>3</sub> and R<sub>4</sub> are members selected from the group consisting of carbon and nitrogen, and Z represents the atoms necessary to complete an aza-indolizine ring.

4. A photographic emulsion comprising gelatin having a light sensitive silver salt dispersed therein and containing as a filter layer a silver salt of a hydroxy aza-indolizine of the following formula:



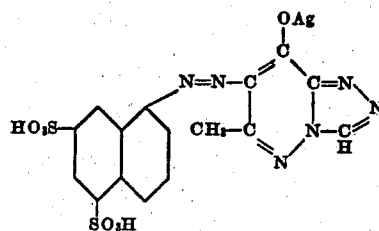
wherein R<sub>1</sub> and R<sub>2</sub> represent members selected from the group consisting of hydrogen, alkyl, aryl and aralkyl groups containing at least one chromophoric group selected from the class consisting of azo, nitro and nitroso groups, and at least one solubilizing group selected from the class consisting of arsonic, carboxylic or sulfonic acid groups, R<sub>1</sub> always being a member selected from the class consisting of aryl and aralkyl groups when R<sub>2</sub> is a member selected from the class consisting of hydrogen and alkyl, and R<sub>2</sub> always being a member selected from the class consisting of aryl and aralkyl groups when R<sub>1</sub> is a member selected from the class consisting of hydrogen and alkyl, R<sub>3</sub> and R<sub>4</sub> are selected from the group consisting of carbon and nitrogen and Z represents the atoms necessary to complete an aza-indolizine ring.

5. A photographic material which comprises a support, a light-sensitive gelatino-silver-halide emulsion and a filter layer containing a silver salt having the general formula:

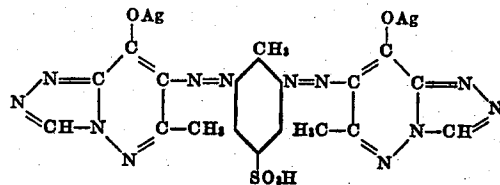


wherein A is a radicle of the aryl and hydroxy aza-indolizine series, R<sub>1</sub> is a radicle of the benzene series and R<sub>2</sub> is a member selected from the class consisting of hydrogen, alkyl and aryl groups, R<sub>3</sub> and R<sub>4</sub> are members selected from the group consisting of carbon and nitrogen, and Z represents the atoms necessary to complete an aza-indolizine ring.

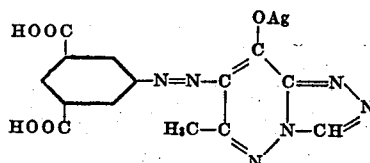
6. A photographic material which comprises a support, a light-sensitive gelatino-silver-halide emulsion and a filter layer containing a silver salt having the formula:



7. A photographic material which comprises a support, a light-sensitive gelatino-silver-halide emulsion and a filter layer containing a silver salt having the formula:



8. A photographic material which comprises a support, a light-sensitive gelatino-silver-halide emulsion and a filter layer containing a silver salt having the formula:



9. A photographic element having at least one silver-halide emulsion layer and at least one filter layer containing the silver salt defined in claim 1.

10. A photographic element having at least one silver-halide emulsion layer and at least one filter layer containing the silver salt defined in claim 3.

11. A photographic element having at least one silver-halide emulsion layer and at least one filter layer containing the silver salt defined in claim 5.

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