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2,238,632

YELLOW FOG INHIBITOR FOR PHOTOGRAPHIC MATERIALS

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11 Claims. (Cl. 95—7)

Our invention relates to yellow fog inhibitors for photographic materials, and more particularly to the use of phosphonium, arsonium, and antimonium iodides as such inhibitors.

It is well known that there are two general types of fog to which certain light sensitive gelatino-silver halide and other emulsions are susceptible. The more common type is known as grey fog and may be caused by premature exposure of the emulsion to light, by over-ripening of the emulsion during manufacture and handling, or by the normal aging of the emulsion over a period of time. The second type of fog, and the one with which this application is concerned, is variously referred to as yellow fog, color fog, or dichroic fog. This yellow fog essentially comprises a colloidal deposit of silver, the color intensity and appearance of which are chiefly determined by the great degree of subdivision and minute particle size involved. This colloidal silver deposit is usually yellow and is most discernible in the lighter portions of a negative. The silver particles may, however, appear green by reflected light and yellow or red by transmitted light, in which case the effect is often spoken of as color fog or dichroic fog.

The occurrence of yellow fog may be traced to the particular emulsion involved or to one of its constituents, or to some element in the preparation of the emulsion. Unfavorable conditions during the processing of the film may also cause such fog. Thus the use of nearly exhausted developing or fixing solutions, or the use of a developer which contains small amounts of fixing solution or an excess of silver halide solvent such as sulfite will tend to favor the formation of these minute colloidal silver particles. In the handling of X-ray films in particular, the formation of yellow fog is quite common because of the thickness of the emulsions and the repeated use of partly exhausted fixing solutions.

The literature references in this field suggest other possible causes of dichroic fog, as well as various remedies for the problem. United States Patent No. 2,059,642, for instance, discloses the use of a mixture of soluble gold and mercury salts to prevent the formation of both grey and yellow fog. Similarly, in German Patent No. 635,605 (1936) and in Photographische Korrespondenz, Band 72, Seite 148, the use of diphenyliodonium salts in emulsions and in the various processing baths is recommended for the prevention of this fog. Treatment with a bath of sodium sulfite and potassium cyanide has also been suggested as a means of removing the yellow fog after its formation (Cassel's Cyclopaedia of Photography, 1912, Vol. I, page 266). These methods cannot be considered wholly satisfactory since they often cause flat gradation, formation of grey fog, lowered sensitivity, or other disadvantages.

One object of our invention is to provide a new class of fog inhibitors which tend to prevent the formation of yellow fog in photographic materials without the difficulties and disadvantages of the prior art.

Another object is to provide anti-yellow fog agents which may be included in a photographic emulsion or in a surface or substratum layer without a noticeable decrease in the sensitivity of the emulsion.

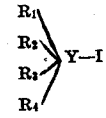
A further object is to provide new yellow fog inhibitors which may be incorporated in the developing bath itself or in a separate processing bath.

Still further objects and advantages will appear from the following specification.

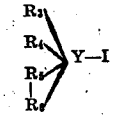
We have found that the above objects are accomplished by the use of phosphonium iodides and the related arsonium and antimonium compounds as well as the addition products or salts of the above compounds with various metal and alkyl iodides, as yellow fog inhibitors.

These compounds all contain the quaternary grouping

wherein Y is phosphorus, arsenic, or antimony, and I represents iodine. Although we do not wish to limit ourselves to any particular theory, it is our belief based on experience that the essential feature responsible for the excellent results produced by these compounds is the pentavalent Y grouping, of which one valence is "taken up" by an iodine atom. Thus it is immaterial how the remaining four valences of the Y-atom are supplied, as long as they are supplied by organic radicles. Accordingly, our invention includes compounds of the general formulae

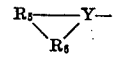


and



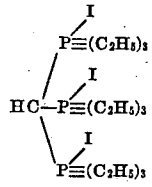
wherein Y is phosphorus, arsenic, or antimony, as above, and wherein the substitutes R_1, R_2, R_3 and R_4 may be substituted or unsubstituted alkyl,

aryl, aralkyl, cycloalkyl, or heterocyclic groups and may be like or unlike, and wherein

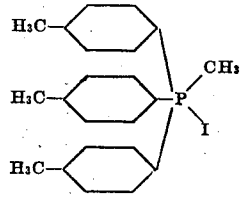


is a heterocyclic grouping.

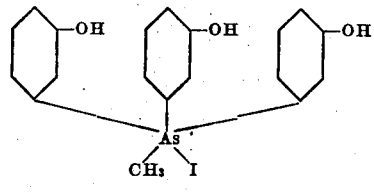
Typical compounds having these desirable properties thus include: alkyl phosphonium-, arsonium-, and antimonium iodides such as methyl-triethyl phosphonium iodide, tetra-ethyl-phosphonium iodide, tetra-ethyl-arsonium iodide, tetra-methyl-antimonium iodide, tetra-ethyl-antimonium iodide, and methenyl-tris-triethyl phosphonium iodide



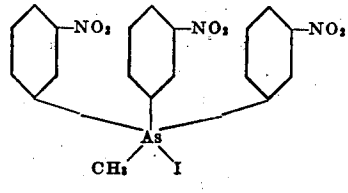
alkyla-aryl phosphonium-, arsonium-, and antimonium iodides such as methyl-triphenyl-phosphonium iodide, ethyl-triphenyl-phosphonium iodide, allyl-triphenyl-phosphonium iodide, trimethyl-phenyl phosphonium iodide, methyl-diethyl-phenyl-phosphonium iodide, methyl-tri-p-tolyl phosphonium iodide



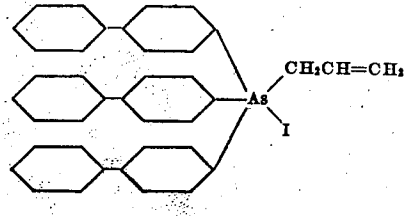
methyl-triphenyl-arsonium iodide, ethyl-triphenyl-arsonium iodide, allyl-triphenyl arsonium iodide, trimethyl-phenyl arsonium iodide, methyl-diethyl-phenyl-arsonium iodide, methyl-tri-p-tolyl arsonium iodide, methyl-tri-(3-hydroxyphenyl) arsonium iodide



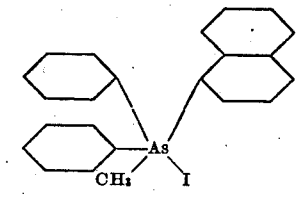
methyl-tri (3 nitrophenyl) arsonium iodide



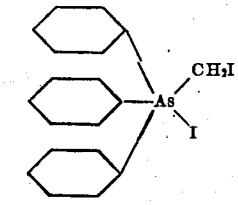
methyl-tri-(3-aminophenyl) arsonium iodide, allyl-tribiphenyl arsonium iodide



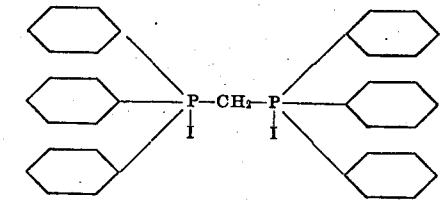
methyl-diphenyl-α-naphthyl arsonium iodide



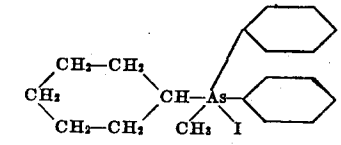
iodomethyl-triphenyl arsonium iodide



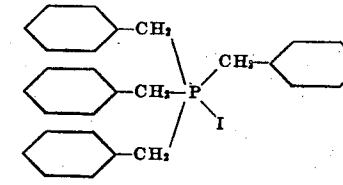
and methylene-bis-tri-phenyl-phosphonium iodide



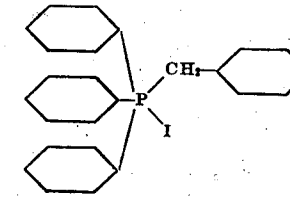
alkyl-cycloalkyl-aryl phosphonium-, arsonium-, and antimonium iodides, such as methyl-cyclohexyl-diphenyl arsonium iodide



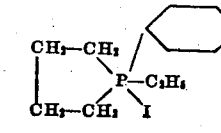
aryl phosphonium-, arsonium-, and antimonium iodides, such as tetraphenyl-arsonium iodide; aralkyl phosphonium-, arsonium-, and antimonium iodides, such as tetrabenzyl-phosphonium iodide



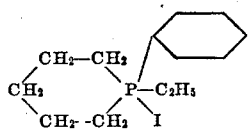
and tetrabenzyl arsonium iodide; aryl-aralkyl phosphonium-, arsonium-, and antimonium iodides, such as triphenyl-benzyl phosphonium iodide



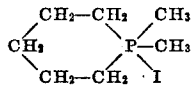
and triphenyl benzyl arsonium iodide; heterocyclic phosphonium-, arsonium-, and antimonium iodides, such as ethyl-phenyl-tetramethylene-phosphonium iodide



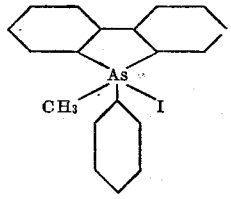
ethyl-phenyl-pentamethylene-phosphonium iodide



ethyl-phenyl-tetramethylene-arsonium iodide, dimethyl-pentamethylene-phosphonium iodide.



and methyl-phenyl-O.O'-diphenylaresonium iodide



and finally, addition products or salts of any of the above compounds with various metal and alkyl iodides, for example with bismuth iodide, and mercuric iodide.

Typical examples of such addition product are:

$[(C_2H_5)_4P\cdot I]_2HgI_2$
$[(C_2H_5)_4PI]_3[BiI_3]_2$
$[(CH_3)_4AsI]HgI_2$
$[(CH_3)\ (C_2H_5)_3SbI]HgI_2$

In order that those skilled in the art may better understand the nature and scope of this invention, the following specific examples are given without any intention of limiting the invention thereto.

Example 1

To 500 g. of a light sensitive gelatino-silver halide emulsion which normally shows yellow fog, melted at 40° C., are added from 10 to 20 mg. of methyl-triphenyl-arsonium iodide. The mixture is coated on a suitable support, chilled, and dried in the customary manner. The emulsion thus treated is free from yellow fog.

Example 2

The methyl-triphenyl-arsonium iodide of the preceding example may be applied to the emulsion by including it in a surface coating. In such a case the amount used should be so chosen that the same concentration of arsonium iodide per unit area of coated film based on relative thickness of surface and emulsion coatings, is obtained as in Example 1. Thus, if the surface coating is one-tenth the thickness of the emulsion coating, approximately ten times as much methyl-triphenyl-arsonium iodide, or from 100 to 200 mgr., is added to 500 g. of surface coating solution. The film having a surface coating thus treated is free from yellow fog.

Example 3

To one liter of a common developer solution, such as any standard metol-hydroquinone formula, is added 20 to 30 mg. of methyl-triphenyl phosphonium iodide. A film having an emulsion which normally exhibits a tendency to form yellow fog may be developed in this solution without the formation of such fog.

Example 4

To 500 g. of a light sensitive gelatino-silver halide emulsion as in Example 1, melted at 40° C., are added from 10 to 20 mg. of tetraphenyl arsonium iodide. The mixture is coated on a suitable support, chilled and dried in the usual way. The emulsion thus treated is free from yellow fog.

Example 5

To 500 g. of a light sensitive gelatino-silver halide emulsion as in Example 1, melted at 40° C., are added from 10 to 20 mg. of allyl-triphenyl-arsonium iodide. The mixture is coated on a suitable support, chilled and dried in the usual way. The emulsion thus treated is free from yellow fog.

Example 6

To 500 g. of a light sensitive gelatino-silver halide emulsion as in Example 1, melted at 40° C., are added from 10 to 20 mg. of allyl-triphenyl-phosphonium iodide. The mixture is coated on a suitable support, chilled and dried in the usual way. The emulsion thus treated is free from yellow fog.

Example 7

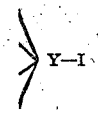
To 500 g. of a light sensitive gelatino-silver halide emulsion as in Example 1, melted at 40° C., are added from 10 to 20 mg. of methyl-phenyl-O.O'-diphenyl arsonium iodide. The mixture is coated on a suitable support, chilled and dried in the usual way. The emulsion thus treated is free from yellow fog.

The quantities of the compounds used may, of course, be varied slightly to suit the particular conditions involved.

Since the presence of these new compounds tends to prevent yellow fog whether they are incorporated directly into the emulsion, added to a separate surface or substratum layer, added to the developing bath, or used in a separate processing bath, we have used the term "photographic material" in the appended claims in a broad sense as including each of these possible applications.

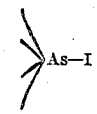
We claim:

1. A photographic material containing as a yellow fog inhibitor for silver halide emulsions an organic compound containing the grouping



wherein Y is a pentavalent atom selected from the group consisting of phosphorus, arsenic, and antimony and wherein the dangling valences are supplied by organic radicles.

2. A photographic material containing as a yellow fog inhibitor for silver halide emulsions an organic compound having the grouping

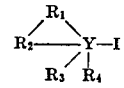


wherein the dangling valences are supplied by organic radicles.

3. A photographic material containing as a yellow fog inhibitor for silver halide emulsions an organic compound corresponding to the formula

wherein Y is a pentavalent atom selected from the group consisting of phosphorus, arsenic, and antimony and wherein the dangling valences are supplied by organic radicles.

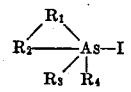
4. A photographic material containing as a yellow fog inhibitor for silver halide emulsions a substance corresponding to the formula



wherein Y is a pentavalent atom selected from the group consisting of phosphorus, arsenic, and antimony,

is a heterocyclic group, and R_3 and R_4 are members selected from the group consisting of alkyl, cycloalkyl, aryl, aralkyl, and heterocyclic groups.

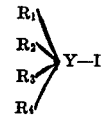
5. A photographic material containing as a yellow fog inhibitor for silver halide emulsions a substance corresponding to the formula



wherein

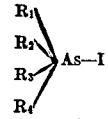
is a heterocyclic group, and R_3 and R_4 are members selected from the group consisting of alkyl, cycloalkyl, aryl, aralkyl, and heterocyclic groups.

6. A photographic material containing as a yellow fog inhibitor for silver halide emulsions a substance corresponding to the formula



wherein Y is a pentavalent atom selected from the group consisting of phosphorus, arsenic, and antimony, R_1, R_2 and R_3 represent aryl groups, and R_4 represents an alkyl group.

7. A photographic material containing as a yellow fog inhibitor for silver halide emulsions a substance corresponding to the formula



wherein R_1, R_2 and R_3 represent aryl groups, and R_4 represents an alkyl group.

8. A photographic material containing methyl-triphenyl-arsonium iodide as a yellow fog inhibitor for silver halide emulsions.

9. A light sensitive photographic gelatino-silver halide emulsion containing from 10 to 20 mg. of methyl-triphenyl-arsonium iodide per 500 g. of emulsion, as a yellow fog inhibitor.

10. A photographic material containing allyl-triphenyl-arsonium iodide as a yellow fog inhibitor for silver halide emulsions.

11. A light sensitive photographic gelatino-silver halide emulsion containing from 10 to 20 mg. of allyl-triphenyl-arsonium iodide per 500 g. of emulsion, as a yellow fog inhibitor.

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