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(54) Method of processing holographic material.

(57) Treatment of processed holographic material by means of aqueous solutions containing at least one compound which has a cathodic reduction potential of more than -1 Volt versus a standard calomel electrode.

Method of processing holographic material

The present invention relates to a method of processing holographically exposed silver halide sensitised holographic material.

In one method of forming holograms from silver halide photographic material a silver image is formed and the developed silver is bleached leaving in the processed hologram the unexposed silver halide in the gelatin binder. The presence of the unexposed silver halide helps to form brighter holograms than those holograms wherein the unexposed silver halide has been fixed out during the processing.

Processed holograms are often stored in daylight and very commonly are exposed to a strong light source for long periods of time to reconstruct the image. When holograms which contain residual silver halide are so treated after a period of time the residual silver halide tends to print out silver. Whilst this does not affect directly the reconstruction of the hologram it is unsightly and tends to lessen the brightness of the hologram on reconstruction.

It is therefore an object of the present invention to reduce the print-out tendency of silver halide based holograms which comprise residual silver halide.

According to the present invention there is provided a method of processing holographically exposed silver halide sensitised holographic material which comprises developing the material in a photographic developing solution, and bleaching the developed silver, the method being characterised in that it comprises treating the material after the bleaching step with an aqueous solution of at least one compound which has a cathodic reduction potential of more than -1 volt versus a standard calomel electrode as determined by the cyclic voltammetric method hereinafter defined.

Preferably the material is treated with an aqueous solution of a compound which has a cathodic reduction potential of more than 0.4 volts versus a standard calomel electrode as determined by the cyclic voltammetric method.

Usefully the strength of the aqueous solution used to treat the material after the bleaching step is between 1 to 3 g of the compound per litre. However the length of treatment is also important. If for example the strength of the aqueous solution is 2g per litre then a suitable treatment time is two minutes.

Cyclic voltammetry is a technique used in electrochemical investigations such as the determination of redox potentials.

Cyclic voltammetry is described in detail in the Journal of Chemical Education, Volume 60, Number 9 of September 1983 pages 697 to 701. The three electrode system referred to in this article was used to determine the cathodic reduction potential of the compounds tested.

However when comparing the cathodic reduction potential of compounds it is necessary to state a number of the parameters of the cyclic voltammetry technique employed as these affect the apparant cathodic reduction potential. These parameters are the solvent used for the compound being tested, the supporting electrolyte used if the compound being tested has low electroconductivity, the nature of the three electrodes employed, viz, the standard electrode, the working electrode and the auxilary electrode. Further the sweep range of potential and the sweep rate in minivolts per second should be defined. Two other parameters which should be noted are the concentration of the compound in the solvent and the temperature at which the determination was carried out.

In the case of the compounds tested in connection with this application the following conditions applied:-

a) the solvent for the compound being tested in all cases was acetonitrile,

b) the supporting electrolyte which was used in all cases was tetrabutylammonium perchlorate Im molar in the solvent,

c) the standard electrode used in all cases was a saturated calomel electrode,

d) in all cases both the working electrode and the auxilary electrode was a platinum electrode,

e) the sweep range of potential was from -2 volts to + 2 volts,

f) the sweep rate was 50 millivolts per second,

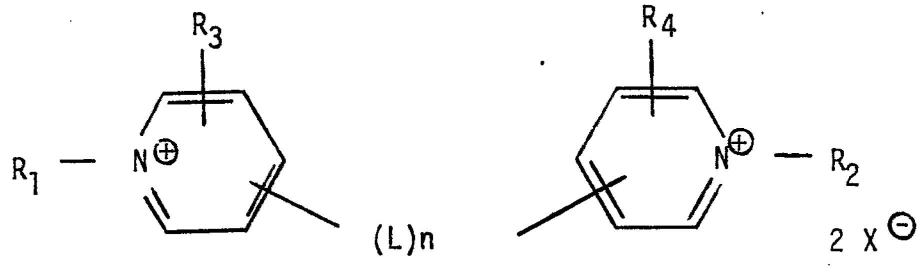
g) the concentration of the compound in the acetronitrile was 1.0 m molar,

h) all the determinations were carried out at room temperature.

A B.B.C. microcomputer was used to provide the required ramped voltage. The voltammograms shown on the computer screen were dumped onto a Epson plotter and the cathodic reduction potential of each compound was determined from the voltammogram.

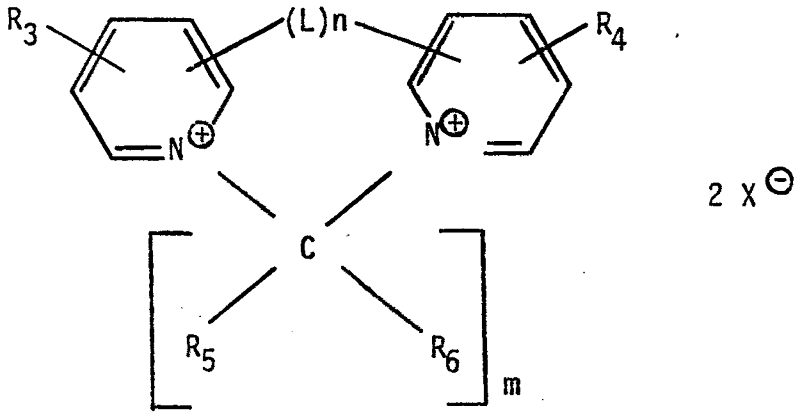
Particularly useful classes of compounds which have a cathodic reduction potential of more than -1 volt versus a standard calomel electrode are compounds of the general formula

(1)



and compounds of the general formula

(2)



wherein each of R_1 and R_2 are optionally substituted alkyl, cycloalkyl, aralkyl or aryl, R_3 and R_4 are each hydrogen, halogen, or optionally substituted alkyl or alkoxy containing 1 to 4 carbon atoms, R_5 and R_6 are each hydrogen or optionally substituted alkyl containing 1 to 4 carbon atoms, L is a direct link, an unsaturated link or a direct link and an unsaturated link, X⊖ is an anion, n is 0, 1 or 2, m is 2, 3 or 4.

The prefered compounds of formula (1) are those wherein R_3 and R_4 are each hydrogen and R_1 and R_2 are each optionally substituted alkyl having 1 to 4 carbon atoms.

Preferably in formula (1) L is -CH=CH-and n is 1 or L is a direct link.

A specially preferred aralkyl group is benzyl.

The preferred compounds of formula (2) are those wherein each of R_3, R_4, R_5 and R_6 are hydrogen atoms.

Preferably in the compounds of formula (2) L is a direct link or is a direct link and an unsaturated link and m is 2.

The compounds of both formula (1) and (2) all have a cathodic reduction potential versus a standard calomel electrode of more than 0.4 volts.

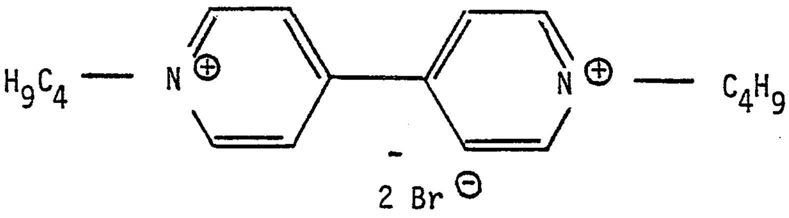
Another group of compounds for use in the present invention are nitro-substituted aromatic or heterocyclic compounds with a cathodic reduction potential versus a standard calomel electrode of more than -1 volts.

Especially suitable compounds are nitro -or dinitro -substituted benzimidazoles.

These compounds however have a cathodic reduction potential versus a standard calomel electrode of between -1 and -0.4 volts.

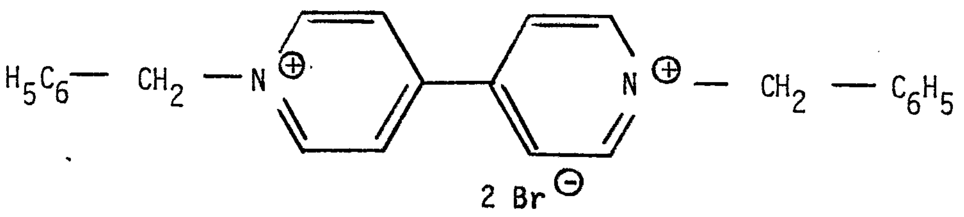
Particularly useful compounds of formula (1) are:

Compound A



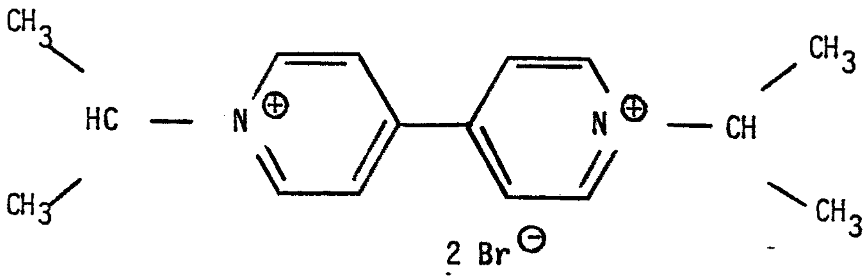
R.P. = 0.48 volts

Compound B



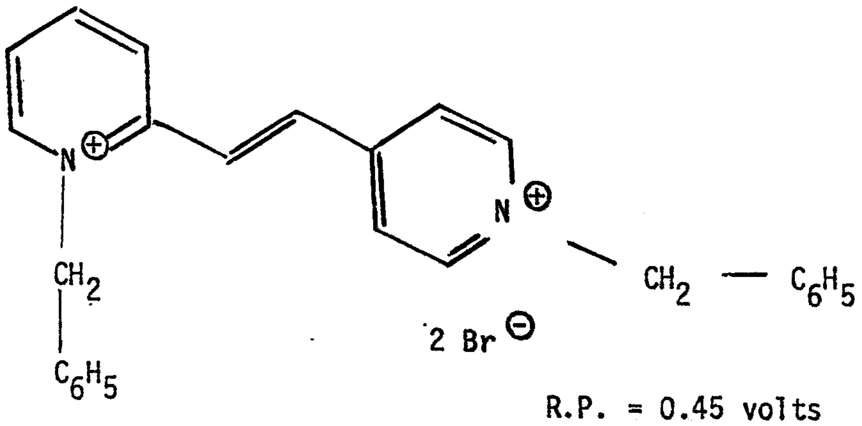
R.P. = 0.48 volts

Compound C



R.P. = 0.45 volts

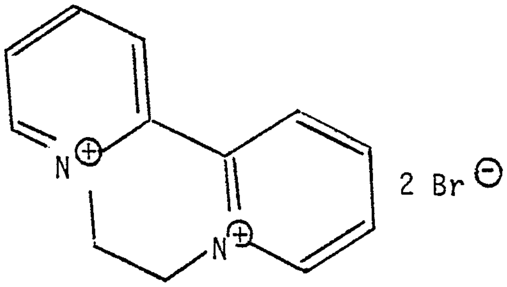
and Compound D



R.P. = 0.45 volts

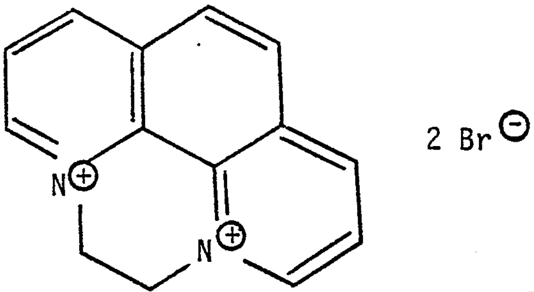
Particularly useful compounds of formula (2) are:

Compound E



R.P. = 0.55 volts

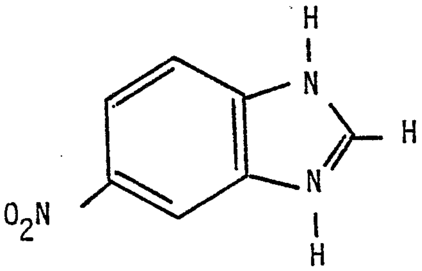
and Compound F



R.P. = 0.59 volts

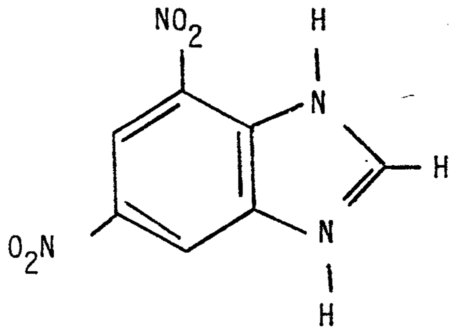
Especially useful nitro-benimidazole compounds are:

Compound G



R.P. = -0.98 volts

and Compound H



R.P. = - 0.40 volts

Wherein R.P. is the cathodic reduction potential versus a standard calomel electrode.

Preferably in the process of the present invention a stop bath is used between the development step and the silver bleaching step. Also most preferably the holographic material is washed after the silver bleaching step and before the treatment of the material in an aqueous solution of a compound which has a cathodic reduction potential versus a standard calomel electrode of more than -1 volt.

The compounds of formula (1) and (2) which as hereinbefore stated have a standard reduction potential of greater than 0.4 volts have an additional use in that they can be used to reduce the blacking caused by silver which has already printed out. Thus in this aspect of the method of the present invention the time interval between the silver bleaching step and the step of treating the holographic material with an aqueous solution of a compound of formulae (1) or (2) may be several months or even years.

The silver bleaching step may be any process of removing the developed silver but which leaves the unexposed silver halide in situ. It is to be understood that the developed silver may be converted to silver halide some of which may remain in the holographic material.

Examples of bleaching techniques are solvent bleaching methods in which the developed silver is removed from the material and rehalogenating bleaching methods, in which the developed silver is converted to silver halide.

Some of the compounds of formulae (1) and -(2) have been described as being used in silver halide photographic emulsions. For example in British patent specification 714290 the use of some of the compounds of formula (1) is described in order to prepare direct positive silver halide emulsions.

In British patent specification 133044 the use of some of the compounds of formulae (1) and (2) to prepare silver halide material of low sensitivity is described. However in neither of these British patent specifications is the use of the compounds of formulae (1) and (2) after the development of the silver image described or implied. In fact the compounds of formula (1) and (2) act on the silver halide in one case before exposure and in the other case during exposure of the silver halide material and there is no residual effect on the exposed and processed material.

Compound G has been described in L.F.A. Mason's Photographic Processing Science. Focal Press 1975 edition as being of use as an antifoggant in a silver halide developing solution. The object of this additive is to retard development to some extent and so prevent fogging. Thus use of Compound G is entirely different to its proposed use in the prevent invention.

Usually the silver halide in the holographic material will be predominantly silver bromide having an average grain size of 0.02 to 0.1 µm.

Thus the material is inherently low scattering because of the grain size. Any photographic type fog is removed during the bleaching and fixing steps. As the silver halide in the exposed areas is converted to developed silver, oxidised and then fixed out a net shrinkage of emulsion layer and compression of the interference fringe spaceing occurs. This causes a shift to shorter wavelength between the exposure wavelength and the replay wavelength when the hologram is made as a reflection holgram.

The following Examples will serve to illustrate the invention.

Example 1

Holographic material was prepared by coating onto a transparent photographic film base a gelatino silver halide emulsion which was substantially pure silver bromide having a mean crystal size of 0.03 µm at a silver coating weight of 30mg/dm2. The emulsion was optically sensitised with a red sensitising dye so that it was optically sensitive to 633mm the colour of a He:Ne laser.

This material was holographically exposed using a Denisyuk exposure method using a brushed aluminium plate as an object to yield (after processing) a reflective hologram.

The material was then developed for 2 minutes in a solution of the following formulation:

Sodium Sulphite Anydrous 30g

Hydroquinone 10g

Sodium Carbonate 60g

Water to 1000ml

The samples were then transferred to an acidified dichromate bleach bath of the following composition:

Ammonium Dichromate 20g

Sulphuric Acid (conc.) 0.5 ml

Water to 1000ml

until all silver metal had been bleached out which was about 2 minutes.

The samples were then washed in running water for 1 minute and transferred to an aqueous bath which comprised 2g of Compound A (as hereinbefore set forth) in 1 litre for 2 minutes. The material was then dried.

Strips of the dried material were then transferred to an accelerated light-stability tester called a Xenotester in which 12 days is equivalent to 120 days of normal daylight. The strips were then examined and substantially no print-out of the residual silver halide could be observed. On a Macbeth Densitometer the average density reading of the strip was 0.03.

Coated strips of the same holographic film which had been prepared and processed except that they had not been subjected to the final aqueous bath which comprised compound A were also transferred to the Xenotester for 12 days. After this period maroon coloured silver had printed out causing the strips to be greatly discoloured. When measured on a Macbeth densitometer an average density of 0.45 was recorded.

The holographic image on both sets of strips both before treatment with the aqueous bath comprising compound A, after treatment with this bath and after 12 days on the Xenotester was examined using white light to reconstruct the image. A bright holographic image was obtained in all cases except with the strips which had not been treated with the aqueous solution of compound A but which had been treated in a Xenotester for 12 days and as a result exhibited considerable silver print-out. In this case a markedly less bright reconstructed holographic image was observed.

Similar results are obtained when the compounds B to H were used instead of compound A.

However when an aqueous solution of comound J which has an R.P. of −1.48 volts was used to treat a hologram in a similar manner after 2 days on the Xenotester the hologram had darkened noticeably. When this hologram was reconstructed with white light a markedly less light reconstructed holographic image was observed than that observed when the holograms which had been treated with compounds A to H were reconstructed.

Example 2

Another example of holographic material was prepared as in Example 1. After a similar holographic exposure it was developed, bleached and washed as set forth in Example 1. The density of this film at a corner was then measured.

The hologram was then attached to a window for 2 months to allow silver print-out to occur.

The film was then cut into two and one half of the film was treated for 2 minutes in an aqueous solution of compound E at a strength of 2g/litre. After this treatment this half of the film had a pale yellow appearance compared with the other half of the film which had a blackish appearance due to silver print-out.

The densities at a corner of these two halves of film were then measured.

Density of whole hologram before being attached to window was 0.08.

Density of half holographic film treated with solution of compound E was 0.07

Density of half of holographic film not treated with solution of compound E was 0.31.

This shows that the method of the present invention is able not only to prevent silver print-out but to reverse the effects of silver print-out.

Claims

1. A method of processing holgraphically exposed silver halide sensitised holographic material which comprises developing the material in a photographic developing solution and bleaching the developed silver, the method being characterised in that it comprises treating the material after the bleaching step with an aqueous solution of at least one compound which has a cathodic reduction potential of more than -1 volt versus a standard calomel electrode as determined by the cyclic voltammetric method.

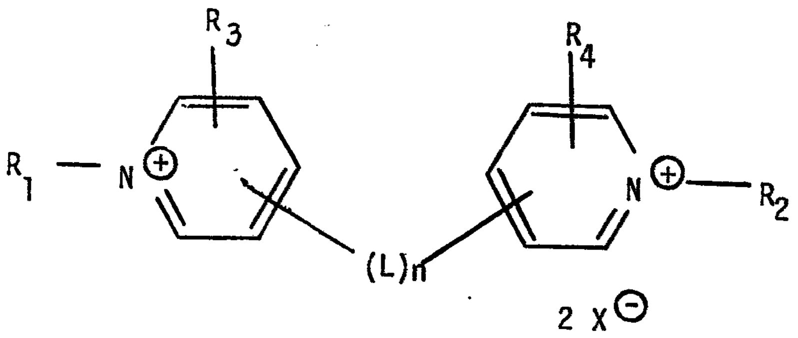
2. A method according to claim 1 wherein the material is treated with an aqueous solution of a compound which has a cathodic reduction potential of more than 0.4 volts.

3. A method according to claim 1 wherein the strength of the aqueous solution used to treat the material after the bleaching step is between 1 to 3 g of the compound per litre.

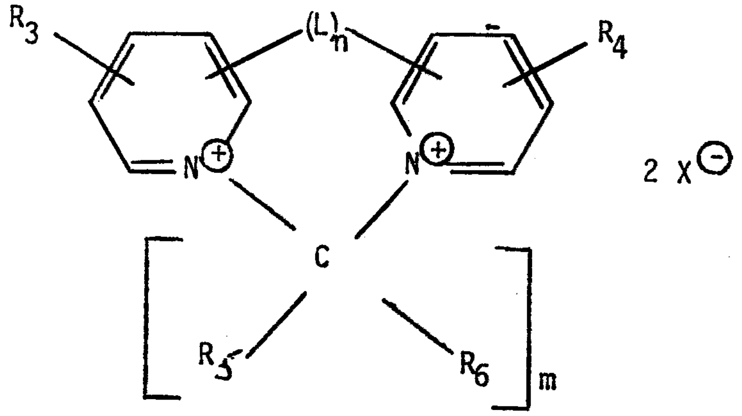
4. A method according to claim 3 wherein the strength of the aqueous solution is 2g/litre and the treatment time is 2 minutes.

5. A method according to claim 2 wherein the compounds which have a cathodic reduction potential of more than 0.4 volts are compounds of either general formula

(1)



(2)



wherein each of R_1 and R_2 are optionally substituted alkyl, cycloalkyl, aralkyl or aryl, R_3 and R_4 are each hydrogen or halogen or alkyl or alkoxy containing 1 to 4 carbon atoms R_5 and R_6 are each hydrogen or optionally substituted alkyl containing 1 to 4 carbon atoms, L is a direct link, an unsaturated link or a direct link and an unsaturated link, Xe is an anion, n is 0, 1 or 2 and m is 2, 3 or 4.

6. A method according to claim 5 where in the comopunds of formula (1) R_3 and R_4 each hydrogen and R_1 and R_2 are each optionally substituted alkyl having 1 to 4 carbon atoms.

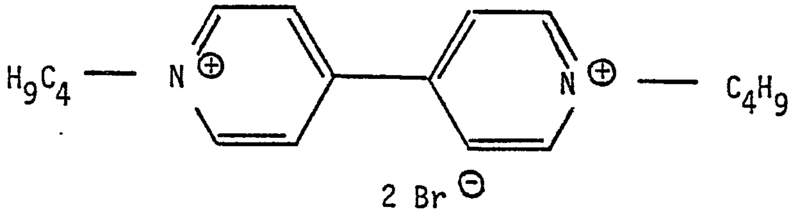
7. A method according to claim 5 where in the compounds of formula (1) R_3 and R_4 are each hydrogen and R_1 and R_2 are each benzyl.

8. A method according to claim 5 where in the compound of formula (1) L is -CH=CH-or a direct link and n is 1.

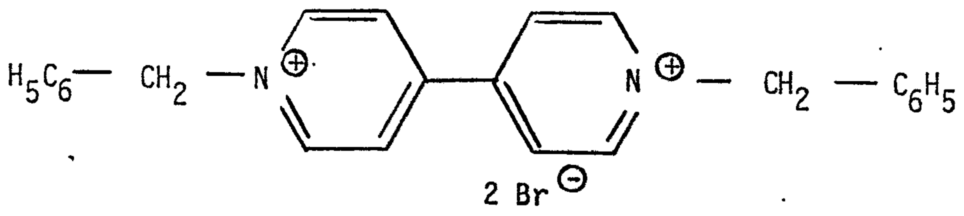
9. A method according to claim 5 where in the compounds of formula (2) each of R_3, R_4, R_5 and R_6 are hydrogen.

10. A method according to claim 9 where in the compounds of formula (2) L is a direct link or is a direct link and an unsaturated link and m is 2.

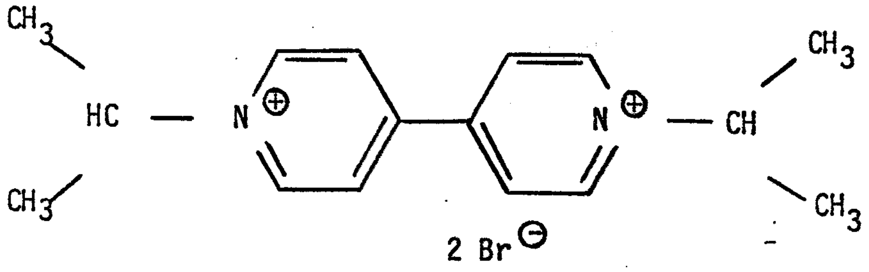
11. A method according to claim 5 where in the compound used is at least one of the compounds of the formulae



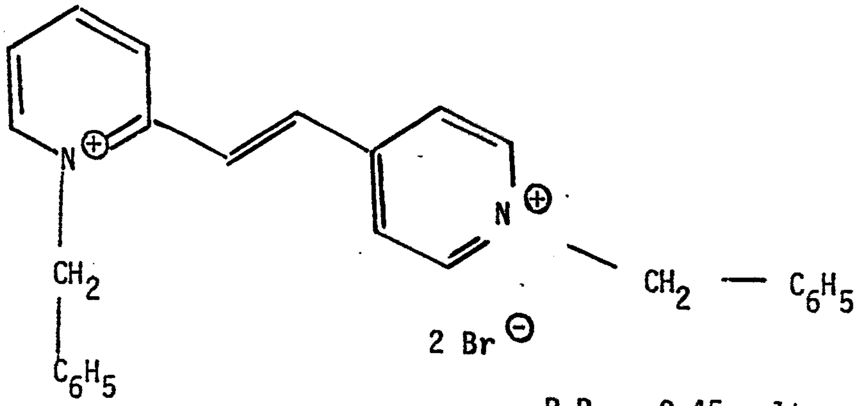
R.P. = 0.48 volts



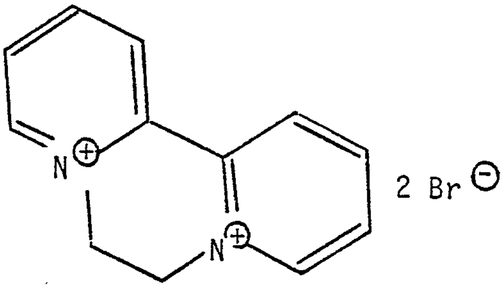
R.P. = 0.48 volts



R.P. = 0.45 volts

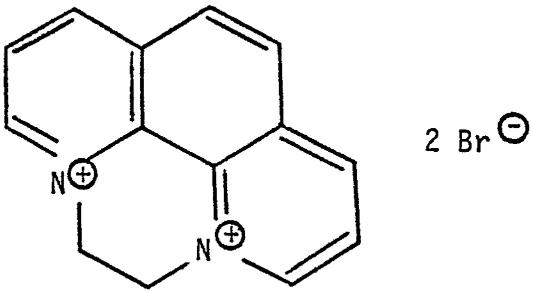


R.P. = 0.45 volts



R.P. = 0.55 volts

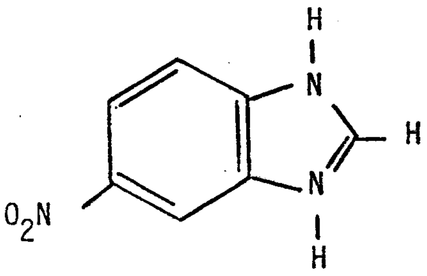
or



R.P. = 0.59 volts

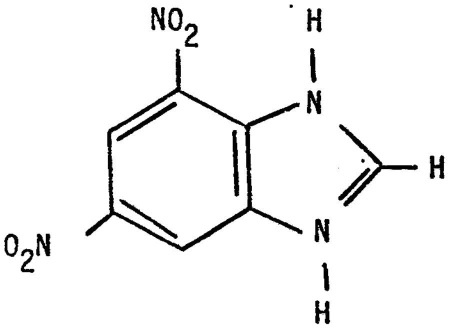
12. A method according to claim 1 wherein the compound which has a cathodic reduction potential versus a standard calomel electrode of more than -1 volts is a nitro-substituted aromatic or hetrocyclic compound.

13. A method according to claim 12 where the nitro-substituted aromatic compound is either compound (G) of the formula



R.P. =-0.98 volts

or (H) of formula



R.P. = - 0.40 volts

14. A method according to claim 1 wherein the holographic material is treated with a stop bath between the development step and the silver bleaching step.

15. A method according to claim 1 wherein the holographic material is water washed after the silver bleaching step and before the treatment of the material in an aqueous solution of the compound which has a cathodic reduction potential of more than -1 volts.

16. A method of reducing the effect of silver print-out which comprising treating a hologram which has been developed and bleached and which exhibits silver print out which comprises treating the hologram with an aqueous solution of a compound of formula (1) or of formula (2) as set forth in claim 5.

17. A silver halide sensitized hologram which has been processed by the method according to claim 1.

18. The use of a compound which has a cathodic reduction potential of more than -1 volt versus a standard calomel electrode as determined by the cyclic voltametric method hereinbefore defined to treat exposed and processed silver sensitized holograms to reduce the tendency for the residual silver halide to print-out.

19. The use of a compound of either formula - (1) or of formula (2) as set forth in claim 5 to treat a silver sensitized hologram and which exhibits silver print-out to reduce the silver print-out.