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SCAVENGERS FOR OXIDIZED DEVELOPING AGENT

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Int. Cl. G03c 7/00
U.S. Cl. 96—3 10 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to novel immobile reducing agents of the p-aminophenol type which may be defined as Zwitter ionic (inner) salts of p-aminophenols containing an anchoring or immobilizing moiety.

BACKGROUND OF THE INVENTION

The copending application of Stanley M. Bloom and Howard G. Rogers, Ser. No. 655,440, filed concurrently describes and claims certain photographic procedures for forming positive color transfer images wherein a photosensitive element containing at least one light-sensitive silver halide emulsion and an associated layer of color-providing material is exposed and then developed with an aqueous alkaline processing composition including a silver halide solvent and a silver halide developing agent. As a function of development, an imagewise distribution of soluble silver complex is formed, and this imagewise distribution migrates to the associated color-providing material where it is reduced and the color-providing material is in turn liberated for transfer to a superposed stratum to impart thereto a positive color transfer image.

In the practice of this photographic procedure, care must be taken to avoid a redox reaction between oxidized developing agent formed as a function of development and the color-providing material, since this redox reaction interferes with the system upon which selective transfer of color-providing material to the superposed stratum to form the desired image is predicated.

One system for obviating this redox reaction is to incorporate in the photosensitive element a reducing agent or "scavenger" for the oxidized developer which will reduce the latter before it has had opportunity to react with the color-providing material. The "scavenger" should ideally provide an immobile reaction product so that it will be unable to migrate to the superposed stratum where it might adversely affect the color and/or stability of the desired color image.

SUMMARY

The present invention is directed to a novel class of reducing agents which are of particular use in the aforementioned photographic processes and in procedures generally where it is desired that the reducing agent be immobile or non-migratory. The reducing agents of this invention are also silver halide developing agents.

The novel reducing agents of this invention contain an immobilizing or "anchoring" substituent which effectively precludes unwanted migration of the compound from its layer in the photosensitive element, which migration may adversely affect image formation by the previously described photographic system.

As was mentioned previously, the present invention is directed to novel reducing agents.

A primary object of this invention, therefore, is to provide a novel class of reducing agents.

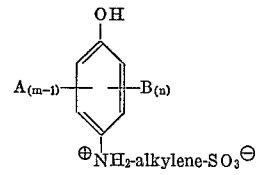
Another object is to provide a novel class of reducing agents or "scavengers" of the foregoing description.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the product possessing the features, properties and the relation of components which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

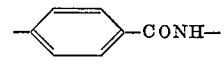
The novel reducing agents of this invention may be represented by the following formula:



wherein:

A represents an "anchoring" or immobilizing substituent rendering the compound non-diffusible, e.g., higher alkyl, e.g., of at least eight carbon atoms, such as octyl, decyl, dodecyl, stearyl, oleyl, etc., linked directly to the aromatic nucleus or linked indirectly thereto through an appropriate linking group, e.g.,

—CONH; -alkylene-CONH;



etc., an aromatic ring, e.g., of the benzene or naphthalene series which rings may be either bonded to a single carbon atom of the aromatic nucleus or fused thereto, i.e., bonded to a pair of adjacent carbon atoms, or A may be a plurality of short chain radicals which together provide the anchoring moiety, each of the short chain radicals being linked directly or indirectly to a different carbon atom on the benzene nucleus;

B is carboxy, alkoxy, alkyl, chloro or an amide substituent;

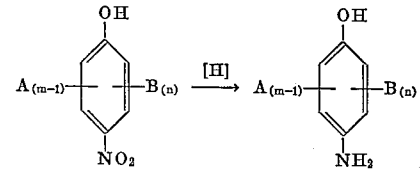
n is a positive integer from 1 to 3;

The alkylene moiety contains at least two carbon atoms, e.g., from 2 to 18 carbon atoms, and preferably from 2 to 4 carbon atoms, and may be a straight or a branched chain; and

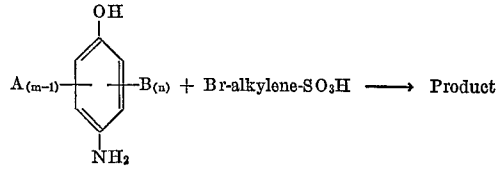
m is a positive integer from 1 to 2, provided that where the alkylene moiety alone or together with said B substituent provides an anchoring or immobilizing substituent *m* may be 1, but when it does not, then *m* must be 2.

The compounds of this invention may be prepared by the following sequence of steps:

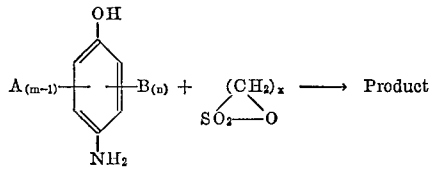
I



II



Where the alkylene moiety contains from 2–4 carbon atoms, the desired compound may also be obtained by employing as step II, the following reaction:

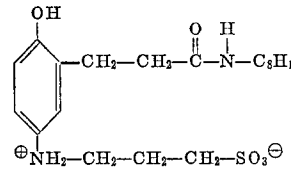


X=2-4

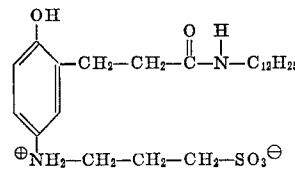
The particular reaction conditions, e.g., time, temperature, pressure, etc. are not critical and will be readily apparent to those skilled in the art.

As examples of novel reducing agents contemplated by this invention, mention may be made of the following:

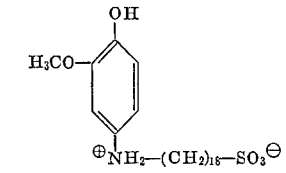
(1)



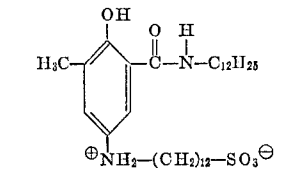
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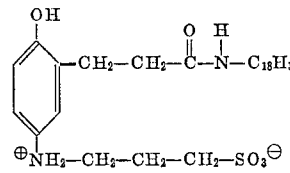
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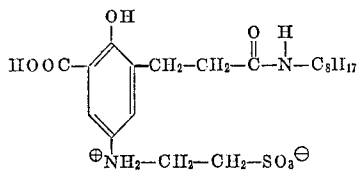
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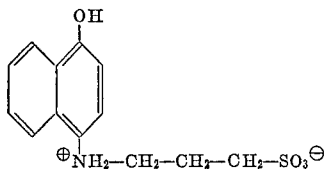
(5)



(6)



(7)



As was mentioned previously, the compounds of this invention are particularly useful in the previously described photographic systems to avoid the undesired redox reaction between oxidized developing agent and the color-providing material present in the photosensitive element.

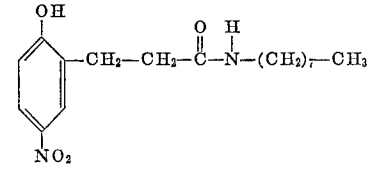
Because of the anchoring moiety rendering the compound non-diffusible from the layer in which it is present, migration of the compound to the layer containing the color-providing material is effectively precluded, thereby in turn precluding unwanted competition between scavenger and color-providing material for reduction of the soluble silver complex formed as a function of development.

The inner salt or Zwitter ionic form of the p-aminophenol-type compound affords significant advantages over p-aminophenols in general in that the latter are not stable in the photosensitive element and, upon contact, will desensitize the emulsion; whereas the inner salt form of this invention is highly stable and does not so desensitize the emulsion.

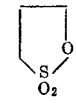
The following examples show by way of illustration and not by way of limitation the practice of this invention.

EXAMPLE 1

38.6 g. of 6-nitrodehydrocoumarin was dissolved in 400.0 cc. of methyl Cellosolve. 28.4 g. of n-octylamine were added and the mixture was heated on a steam bath for 30 minutes and then cooled. Filtration yielded 40.2 g. of a light yellow compound, M.P. 179–180° C. of the formula:



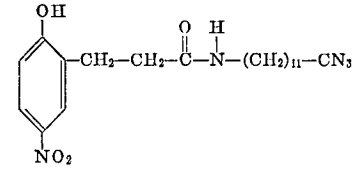
40.2 g. of the last-named nitro compound 15.8 g. of



propane sultone, 200.0 cc. of methanol and 5% palladium/barium sulfate were placed in a pressure vessel. Hydrogen was introduced and the reaction mixture was shaken for four hours after theoretical hydrogen uptake. 100.0 cc. more of methanol were then added and the mixture was boiled and then filtered. Cooling of the filtrate yielded 23 g. of the pure white compound of Formula 1, M.P. 196–197° C.

EXAMPLE 2

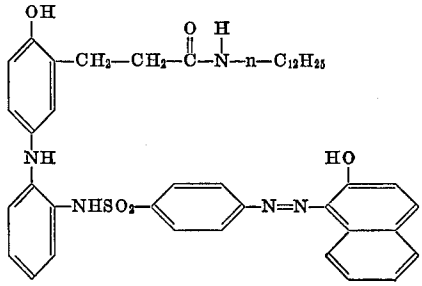
11.0 g. of 6-nitrodehydrocoumarin was dissolved in 100.0 cc. of methyl Cellosolve. 12.0 g. of n-dodecylamine were then added. (The reaction was exothermic and a yellow solid separated out.) The mixture was heated until a clear solution was obtained and then cooled to give 14.0 g. of light yellow crystals, M.P. 168–170° C., an amide of the formula:



27.5 g. of the above amide (prepared in the foregoing manner) and 9.28 g. of propane sultone (10% excess) were placed in a pressure vessel. 200.0 cc. of methanol and 5% $Pd/BaSO_4$ were added and the mixture was then hydrogenated at 40 p.s.i. The reaction mixture was shaken for four hours after theoretical hydrogen uptake. An additional 100.0 cc. of methanol were then added and the mixture was heated to boiling, filtered and cooled. After cooling, 11.65 g. of the compound of Formula 2 were obtained, a white solid, M.P. 207–208° C. An additional 2 g. of this compound were obtained after concentration of the filtrate.

EXAMPLE 3

A photosensitive element of the type disclosed in the aforementioned copending application Ser. No. 655,440, was prepared by coating on a cellulose acetate support a gelatin layer containing a colloidal silver silver-precipitating agent and non-diffusible color-providing compound of the formula:



to provide a caluculated coverage of 136 mgm. per square foot of each of the color-providing compound and the silver precipitating agent; applying over this a layer containing a calculated coverage of 136 mgm. per square foot of gelatin and the same amount of a compound of Formula 1; and finally coating on a light-sensitive gelatino silver iodobromide emulsion. This element was then exposed and developed by spreading between the thus exposed element and a superimposed dyeable sheet material at a gap of .0026 a processing composition containing the following proportions of ingredients:

Water	cc.	100.0
Hydroxyethyl cellulose	g.	3.9
Sodium hydroxide	g.	5.0
Sodium triosulfate	g.	2.0
Sodium sulfite	g.	2.0
Metol	g.	1.6

After an imbibition time of about two minutes, the elements were separated to reveal a positive dye transfer image.

EXAMPLE 4

A similar photosensitive element containing no scavenger was exposed and developed in the manner described in Example 3. When the elements were separated following imbibition, dye had transferred in both exposed and unexposed areas so that no image formation was observable.

EXAMPLE 5

A photosensitive element was prepared as in Example 3, except that the compound of Formula 1 was included in the silver halide emulsion layer at a calculated coverage of 68 mgm. per square foot. This photosensitive element was exposed and developed in the manner described in Example 3 with a developing composition containing the following proportions of ingredients:

Water	cc.	100.0
Hydroxyethyl cellulose	g.	3.9
Sodium hydroxide	g.	5.0
Sodium thiosulfate	g.	1.0

The gap employed was .0016". After two minutes the elements were separated to reveal a positive dye image.

From the procedure described in Example 5, it will be observed that the compounds of this invention may be employed as silver halide developing agents. While they are primarily intended for use in the processes described above, and illustrative Example 5 so indicates their usefulness in such processes, it will be apparent that they may find use as silver halide developing agents in other photographic processes, e.g., processes wherein the use of an immobile or relatively immobile developer is desirable. Accordingly, it is to be expressly understood that the photographic utilization of the compounds of this invention is not restricted to products and processes such as were described in Examples 3–5.

By way of recapitulation the compounds of this invention are particularly useful in the photographic systems described and claimed in the aforementioned Ser. No. 655,440 wherein a photosensitive element including at least one light-sensitive silver halide emulsion having associated therewith a non-diffusible color-providing material which is capable of providing an oxidation product which can auto-react intramolecularly to effect ring-closure and to eliminate the color-providing moiety of said material for transfer is exposed and then developed with an aqueous alkaline processing composition including a silver halide solvent and a silver halide developing agent the oxidation product of which is reducible by a redox reaction with the color-providing material; and imagewise distribution of soluble silver complex is formed in terms of unexposed areas of the emulsion; the non-diffusible color-providing material is contacted with the imagewise distribution of soluble silver complex where, in the presence of silver-precipitating nuclei, the complex is reduced as a function thereof an imagewise distribution of oxidized color-providing material is formed; the oxidized material is allowed to auto-react intramolecularly to eliminate the color-providing moiety to provide an imagewise distribution of diffusible color-providing moiety in terms of unexposed areas of the emulsion; and this imagewise distribution of color-providing moiety is transferred, at least in part, by imbibition, to a superimposed stratum to impart thereto a positive color transfer image. In one procedure described in this copending application, a scavenger for oxidized developer is positioned in a layer in the photosensitive element between the emulsion layer and the layer of color-providing material, so that oxidized developer formed as a function of development is reduced before it can migrate to the layer of color-providing material and there undergo an undesired redox reaction with the color-providing material.

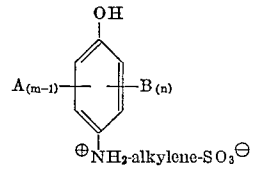
Since the novel compounds of this invention are effectively immobile in their reduced form, they cannot migrate to the layer of color-providing material where they would compete with the color-providing material as reducing agents for the soluble silver complex, which competing would be detrimental to proper image formation.

Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a process for forming positive color transfer images wherein a photosensitive element containing at least one light-sensitive silver halide emulsion and an associated layer of a non-diffusible compound containing a color-providing moiety is exposed and then developed with an aqueous alkaline processing composition including a silver halide solvent and a silver halide developing agent, the oxidation product of said developing agent being reducible by a redox reaction with said compound; and an imagewise distribution of soluble silver complex formed as a function of development migrates to said compound wherein said complex is reduced and the color-providing moiety of said compound is in turn liberated for transfer to a superposed stratum to impart thereto a positive color transfer image, said process being performed in the presence of a scavenger for reducing oxidized developing agent formed as a function of development to prevent said redox reaction with said compound;

the improvement which comprises employing as said scavenger a compound of the formula:



wherein:

A represents an anchoring substituent rendering the compound non-diffusible, said substituent containing a higher alkyl, aromatic, or heterocyclic ring bonded to a single carbon atom of the benzene nucleus or an aromatic ring fused thereto by being bonded to a pair of adjacent carbon atoms of said benzene nucleus, or a plurality of short chain alkyl radicals which together provide said anchoring moiety, each of said short chain radicals being linked directly or indirectly to a different nuclear carbon atom;

B is a carboxy, alkoxy, alkyl, chloro, or an amide substituent;

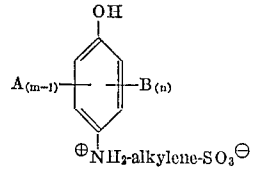
the alkylene moiety contains from 2 to 18 carbon atoms;

n is a positive integer from 1 to 3;

and *m* is a positive integer from 1 to 2, provided that where the alkylene moiety alone or together with said B substituent provides an anchoring or immobilizing substituent *m* may be 1 but when it does not provide such a substituent, then *m* must be 2.

2. In a process of forming positive color transfer images comprising the steps of (1) exposing a photosensitive element including at least one light-sensitive silver halide emulsion having associated therewith a non-diffusible color-providing material which is capable of providing an oxidation product which can auto-react intramolecularly to effect ring-closure and to eliminate the color-providing moiety of said material for transfer; (2) developing said exposed silver halide emulsion with an aqueous alkaline processing composition including a silver halide developing agent; (3) forming as a function of development an imagewise distribution of soluble silver complex in terms of unexposed areas of said emulsion; (4) contacting said non-diffusible color-providing material with said imagewise distribution of soluble silver complex to reduce said silver complex as a function thereof forming an imagewise distribution of oxidized color-providing material; (5) allowing said oxidized material to auto-react intramolecularly to eliminate said color-providing moiety, thereby forming an imagewise distribution of diffusible color-providing moiety in terms of unexposed areas of said emulsion; and (6) transferring said imagewise distribution of said color-providing moiety to a superposed stratum to impart thereto a positive color transfer image, said process being performed in the presence of a scavenger comprising a material for reducing oxidized developing agent formed as a function of development of said silver halide emulsion;

the improvement which comprises employing as said scavenger a compound of the formula:



wherein:

A represents an anchoring substituent rendering the compound non-diffusible, said substituent containing a higher alkyl, aromatic, or heterocyclic ring bonded to a single carbon atom of the benzene nucleus or an aromatic ring fused thereto by being bonded to a pair of adjacent carbon atoms of said benzene nucleus, or a plurality of short chain alkyl radicals which together provide said anchoring moiety, each of said short chain radicals being linked directly or indirectly to a different nuclear carbon atom;

B is a carboxy, alkoxy, alkyl, chloro, or an amide substituent;

the alkylene moiety contains from 2 to 18 carbon atoms;

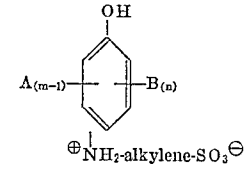
n is a positive integer from 1 to 3;

and *m* is a positive integer from 1 to 2, provided that where the alkylene moiety alone or together with said B substituent provides an anchoring or immobilizing substutuent *m* may be 1 but when it does not provide such a substituent, then *m* must be 2.

3. A process as defined in claim 1 wherein said compound is selected from those identified in the specification as Formulae 1–7.

4. In a photographic product comprising a support, a light-sensitive silver halide emulsion in a layer on said support, said emulsion having associated therewith a non-diffusible compound containing a color-providing moiety, said compound being capable upon development of said emulsion of providing a reaction product which can auto-react intramolecularly to effect ring-closure and to eliminate said color-providing moiety, said eliminated moiety being diffusible in an aqueous alkaline processing composition, said compound being in a layer on the same side of said support as said emulsion, and a layer containing a scavenger for oxidized silver halide developing agent, said scavenger comprising a material for reducing oxidized development agent formed as a function of development of said silver halide emulsion, said non-diffusible compound containing said color-providing moiety being in a layer between said support and said layer containing said scavenger;

the improvement which comprises employing as said scavenger a compound of the formula:



wherein:

A represents an anchoring substituent rendering the compound non-diffusible, said substituent containing a higher alkyl, aromatic, or heterocyclic ring bonded to a single carbon atom of the benzene nucleus or an aromatic ring fused thereto by being bonded to a pair of adjacent carbon atoms of said benzene nucleus, or a plurality of short chain alkyl radicals which together provide said anchoring moiety, each of said short chain radicals being linked directly or indirectly to a different nuclear carbon atom;

B is a carboxy, alkoxy, alkyl, chloro, or an amide substituent;

the alkylene moiety contains from 2 to 18 carbon atoms;

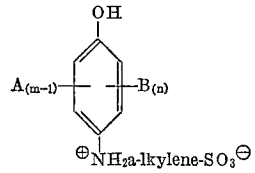
n is a positive integer from 1 to 3;

and *m* is a positive integer from 1 to 2, provided that where the alkylene moiety alone or together with said B substituent provides an anchoring or immobilizing substutuent *m* may be 1 but when it does not provide such a substituent, then *m* must be 2.

5. A product as defined in claim 4 wherein said compound is selected from those identified in the specification as Formulae 1–7.

6. A photographic product including a photosensitive

element having a layer containing a light-sensitive silver halide emulsion and a compound of the formula:



wherein:

A represents an anchoring substituent rendering the compound non-diffusible, said substituent containing a higher alkyl, aromatic, or heterocyclic ring bonded to a single carbon atom of the benzene nucleus or an aromatic ring fused thereto by being bonded to a pair of adjacent carbon atoms of said benzene nucleus, or a plurality of short chain alkyl radicals which together provide said anchoring moiety, each of said short chain radicals being linked directly or indirectly to a different nuclear carbon atom;

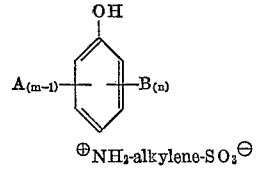
B is a carboxy, alkoxy, alkyl, chloro, or an amide substituent;

the alkylene moiety contains from 2 to 18 carbon atoms;

n is a positive integer from 1 to 3;

and *m* is a positive integer from 1 to 2, provided that where the alkylene moiety alone or together with said B substituent provides an anchoring or immobilizing substituent *m* may be 1 but when it does not provide such a substituent, then *m* must be 2.

7. A process which comprises developing an exposed light-sensitive silver halide emulsion containing a developable image with a compound of the formula:



wherein:

A represents an anchoring substituent rendering the compound non-diffusible, said substituent containing a higher alkyl, aromatic, or heterocyclic ring bonded to a single carbon atom of the benzene nucleus or an aromatic ring fused thereto by being bonded to a pair of adjacent carbon atoms of said benzene nucleus, or a plurality of short chain alkyl radicals which together provide said anchoring moiety, each of said short chain radicals being linked directly or indirectly to a different nuclear carbon atom;

B is a carboxy, alkoxy, alkyl, chloro, or an amide substituent;

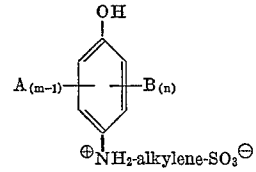
the alkylene moiety contains from 2 to 18 carbon atoms;

n is a positive integer from 1 to 3;

and *m* is a positive integer from 1 to 2, provided that where the alkylene moiety alone or together with said B substituent provides an anchoring or immobilizing substituent *m* may be 1 but when it does not provide such a substituent, then *m* must be 2.

8. In a process for forming images by diffusion transfer wherein a photosensitive element including a layer comprising an exposed light-sensitive silver halide emulsion containing a developable image is developed with a silver halide developing agent, an imagewise distribution of a soluble silver complex is formed in terms of unexposed and undeveloped areas of said emulsion, and the imagewise distribution of soluble silver complex is transferred, at least in part, by imbibition to a superposed silver-receptive stratum to impart thereto a silver transfer image;

the improvement which comprises employing as said silver halide developing agent a compound of the formula:



wherein:

A represents an anchoring substituent rendering the compound non-diffusible, said substituent containing a higher alkyl, aromatic, or heterocyclic ring bonded to a single carbon atom of the benzene nucleus or an aromatic ring fused thereto by being bonded to a pair of adjacent carbon atoms of said benzene nucleus, or a plurality of short chain alkyl radicals which together provide said anchoring moiety, each of said short chain radicals being linked directly or indirectly to a different nuclear carbon atom;

B is a carboxy, alkoxy, alkyl, chloro, or an amide substituent;

the alkylene moiety contains from 2 to 18 carbon atoms;

n is a positive integer from 1 to 3;

and *m* is a positive integer from 1 to 2, provided that where the alkylene moiety alone or together with said B substituent provides an anchoring or immobilizing substituent *m* may be 1 but when it does not provide such a substituent, then *m* must be 2.

9. A process as defined in claim **7** wherein said compound is contained initially in the layer in said photosensitive element containing said silver halide emulsion.

10. A process as defined in claim **7** wherein said compound is selected from those identified in the specification as Formulae 1–7.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,459,548 August 5, 1969

Stanley M. Bloom et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 31, "superimposed" should read -- superposed --; line 37, "triosulfate" should read -- thiosulfate --. Colum 7, line 42, after "including" insert -- a silver halide solvent and --. Column 8, line 70, "substutuent" should read -- substituent --. Column 9, line 5, "NH_2a-lkylene-$SO_3^{\ominus}$" should re -- NH_2-alkylene-$SO_3^{\ominus}$ --.

Signed and sealed this 17th day of November 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents