United States Patent

[11] 3,622,603

[72] Inventors **Stanley M. Bloom**
Waban;
Paul S. Huyffer, Lynnfield, both of Mass.

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[73] Assignee **Polaroid Corporation**
Cambridge, Mass.

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[54] **REDUCING AGENTS FOR PHOTOGRAPHIC PROCESSES**
6 Claims, No Drawings

[52] **U.S. Cl.** ..... **260/397.7,** 260/347.2, 260/347.3, 260/347.4, 200/347.7, 200/401, 200/403, 260/404.5, 260/408, 260/471 R, 260/473 R, 260/556 A, 260/558 A, 260/559 R, 260/941, 260/944, 260/556 AR, 260/558 R

[51] **Int. Cl.** **C07c 143/74,** C07c 143/78

[50] **Field of Search** ..... 260/397.7, 556 A, 556 AR

[56] **References Cited**

UNITED STATES PATENTS

3,474,107 10/1969 Thiele 260/295.5

Primary Examiner—Henry R. Jiles
Assistant Examiner—C. M. Shurko
Attorneys—Brown and Mikulka and Alvin Isaacs

ABSTRACT: This invention relates to novel immobile reducing agents which, upon oxidation, auto-react intramolecularly in such a way as to form a new heterocyclic ring.

REDUCING AGENTS FOR PHOTOGRAPHIC PROCESSES

This application is a division of copending U.S. Ser. No. 655,324, filed July 24, 1967, now U.S. Pat. No. 3,482,971 patented Dec. 1969.

BACKGROUND OF THE INVENTION

The copending application of Stanley M. Bloom and Howard G. Rogers Ser. No. 655,440, now U.S. Pat. No. 3,443,940 patented May 13, 1969, 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 predicted.

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 nonmigratory. 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 their migration and subsequent competition with the color-providing material in the aforementioned photographic systems and further, upon oxidation, undergo a ring-closing reaction to form a new heterocyclic ring which also contributes to the immobility of the resulting compound Moreover, this ring-closure precludes any possibility of subsequent reduction which may be undesirable in the photographic system described above.

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.

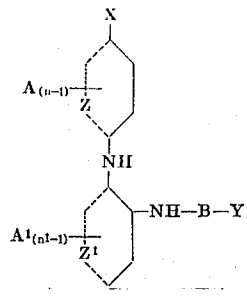
Other objects of the invention will in part be obvious and will in part appear hereinafter.

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:

(A)



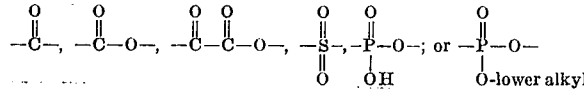
wherein:

Z and Z¹ each represent the atoms necessary to complete a benzene or naphthalene ring;

X is hydroxy or amino, e.g., a primary, secondary or tertiary amino substituent of the formula:

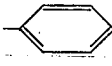


wherein each R may be hydrogen, a hydrocarbon radical, e.g., alkyl such as methyl, ethyl, butyl, dodecyl, etc., aryl such as phenyl or naphthyl attached through a carbon atom thereof to the nitrogen atom, a cyclic alkyl such as cyclopentyl or cyclohexyl, i.e., where both R's are alkylene comprising together with a nitrogen atom a heterocyclic ring, a substituted alkyl, such as hydroxyethyl, methoxyethoxyethyl, polyglycoloxyethyl, carboxymethyl, ethylcarboxymethyl, benzyl, phenylethyl, sulfo-phenylethyl, acetylamino-phenylethyl, succinylamino-phenylethyl, furanemethyl, etc.; or a substituted aryl such as methylphenyl, ethylphenyl, etc.; B is



Y is a substantially colorless substituent, e.g., an aryl radical such as phenyl, naphthyl, or substituted derivatives thereof, e.g., a nitro, alkyl or alkoxy-substituted phenyl or naphthyl, alkyl, alkoxy, hydroxyalkyl, haloalkyl, e.g., trifluoromethyl etc. wherein the alkyl moiety of the aforementioned substituents contains from one–18 carbon atoms,

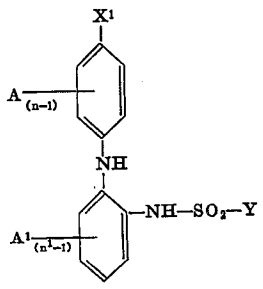
A and A¹ each represent an "anchoring" or immobilizing substituent rendering the compound nondiffusible, e.g., higher alkyl such as decyl, dodecyl, stearyl, oleyl, etc. linked directly to the aromatic nucleus or linked indirectly thereto through an appropriate linking group,

e.g., —CONH—; —alkylene—CONH—;  —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 and A¹ each 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 designated aromatic nuclei;

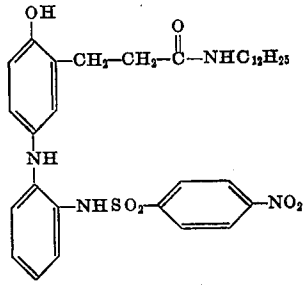
and n and n¹ are 1 or 2, provided that when X is a secondary or tertiary amino comprising an anchoring moiety rendering said compound nondiffusible, Y is a substituent providing an anchoring moiety, or X and Y together provide an anchoring moiety, n and n¹ may be 1, but when X and Y alone or together do not provide such a substituent, at least one of n and n¹ must be 2; and nuclear substituted derivatives of these compounds, e.g., where any of the nuclear carbon atoms not containing one of the specifically designated substituents may contain an alkyl such as methyl, ethyl, etc., alkoxy such as methoxy, ethoxy, etc., carboxy, chloro or amide substituent.

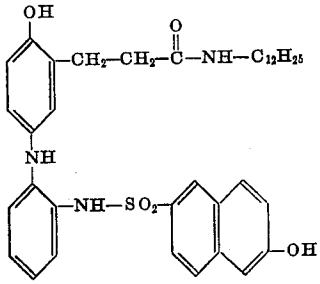
The preferred class of compounds within formula A may be represented by the following formula:

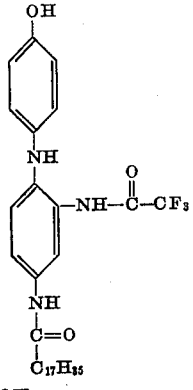
(B) 

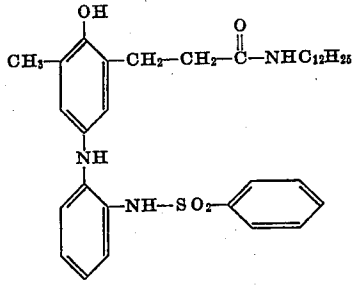
wherein X^1 is hydroxy or primary amino and the other moieties have the meanings heretofore noted; and nuclear substituted derivatives thereof, e.g., derivatives such as mentioned previously in the description of the compounds of formula A.

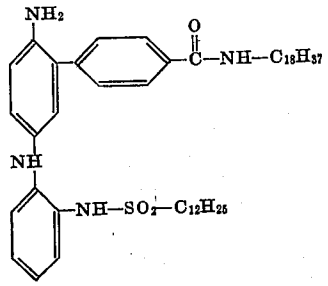
As examples of novel reducing agents contemplated by this invention, mention may be made of the following:

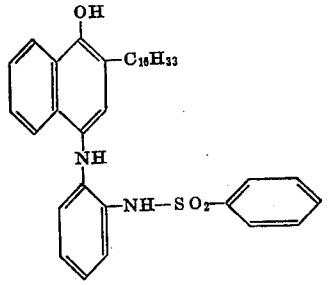
1. 

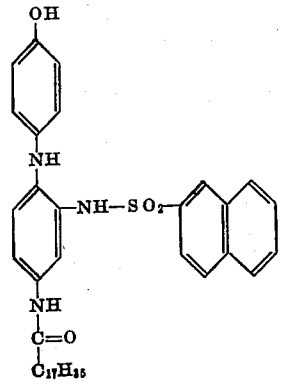
2. 

3. 

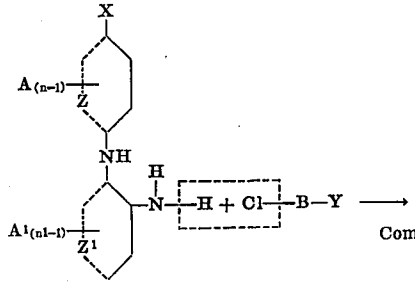
4. 

5. 

6. 

7. 

In general, the compounds of this invention may be readily synthesized by appropriate reaction between an acid salt: Cl–B–Y and the 3-amino substituent of the aromatic ring, as follows:

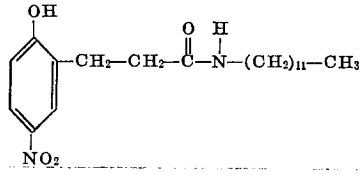


It may be desired for the X moiety to be in some other form during the above coupling reaction. For example, where X is hydroxy, it may be necessary or advisable for it to be present as a protected derivative, e.g., an alkoxy substituent, during coupling, in which event the desired hydroxy analogue may subsequently be obtained by hydrolysis. Where X is primary amino, it may be necessary or advisable to employ the corresponding 1-nitro analogue in the coupling reaction, followed by reduction, e.g., with hydrogen in the presence of a Raney nickel catalyst, to form the desired amino compound.

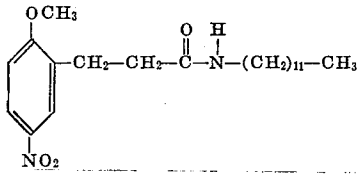
The following examples show by way of illustration and not by way of limitation the preparation of the novel compounds of this invention and their usefulness in the photographic processes described and claimed in the aforementioned copending application, Ser. No. 655,440, now U.S. Pat. No. 3,443,940, patented May 13,1969.

EXAMPLE 1

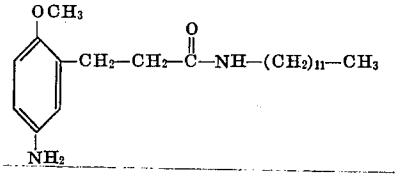
11.0 g. (0.05mole) of 6-nitrodehydrocoumarin was dissolved in 100.0 cc. of methyl cellosolve. 12.0 g. (0.064 mole) of n-dodecylamine was then added. [The reaction was exothermic and a yellow solid separated out.] The mixture was heated until a clear solution was obtained and then cooled to give 14.0 g. of light yellow crystals, m.p. 168–170, an amido of the formula:



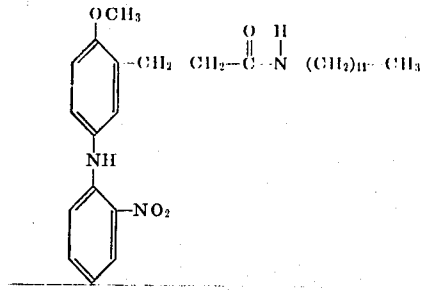
A mixture of 16.5 g. (0.0437 mole) of this amide, prepared in the manner described above, 7,0 g. (0.056 mole) of dimethylsulfate, 9.2 g. (0.066 mole) of potassium carbonate and 250 ml. of xylene was refluxed overnight. The xylene was then removed by steam distillation and an oily product crystallized on standing. Recrystallization of this product from hexane-chloroform yielded 13.3 g. of light tan needles, m.p. 106°–108 °C. of the formula:



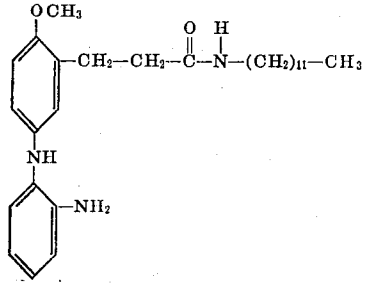
13.3 g. of this latter amide was hydrogenated in 95 percent ethanol in the presence of Raney-Nickel catalyst. The reaction mixture was filtered and the filtrate evaporated. The resulting solid was recrystallized from hexane-ether to obtain 9 g. of a pure white amine, m.p. 80°–82° C. of the formula:



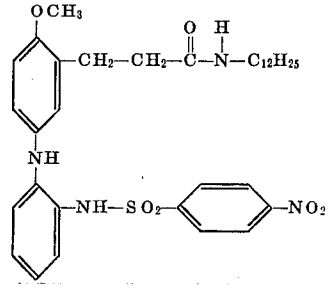
52 g. (0.145 mole) of the amine prepared in the above manner, 21.0 g. (0.145 mole) of 2-fluoronitrobenzene, 7.85 g. (0.195 mole) of magnesium oxide and 100.0 ml. of water were heated in a sealed bomb at 180° C. for 18 hours. The contents of the bomb were then filtered and the solid obtained by filtering was stirred in boiling ethyl acetate and filtered. Cooling of the filtrate yielded 40 g. of a light yellow solid, m.p. 125°–126° C., of the formula:



10.0 g. of the last-named product was hydrogenated with 5 % Pd/BaSO4 in ethyl acetate to reduce the nitro group to the corresponding amine. The reaction mixture was filtered and the filtrate was then cooled in dry ice. Filtration yielded 9 g. of an off-white solid, m.p. 81°–83° C. an amine of the formula:



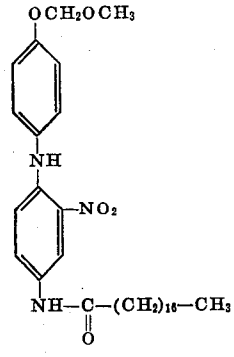
7.0 g. of the above amine and 3.5 g. of p-nitrobenzene-sulfonyl chloride were allowed to stand overnight in 50.0 ml. of dry pyridine. The mixture was then poured into a mixture of 250.0 ml. of 10 % HCl and about 50.0 g. of ice. The resulting solid was filtered and recrystallized from ethanol-water (80–20) to yield 7.0 g. of a sulfonamide, m.p. 120°–121° C. of the formula:



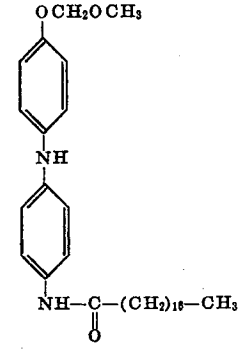
7 g. of the above sulfonamide in 50.0 cc. of dry dichloromethane was treated with excess boron tribromide and allowed to stand overnight. Water was added to destroy the excess boron tribromide and the resulting solid was filtered, stirred in boiling water and filtered again. Recrystallization from hexane-chloroform yielded 5.0 g. of the compound of formula 1, a light tan solid, m.p. 139°–141° C.

EXAMPLE 2

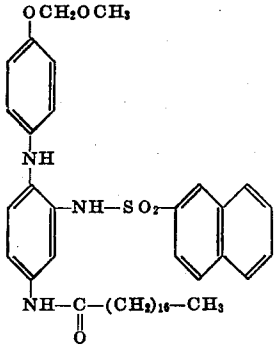
14.5 g. of p-methoxymethoxyaniline, 8.0 g. of 2-fluoro-4-stearamido-nitrobenzene, 4.0 g. of magnesium oxide and 100.0 ml. of water were heated with shaking at 180° C. for 2 days. After cooling, the mixture was filtered to recover a solid which was recrystallized from ethyl acetate to yield 6.0 g. of an orange crystalline solid, m.p. 118°–119° C. of the formula:



6.0 g. of this nitro compound was hydrogenated in ethyl acetate using 5 percent palladium on barium sulfate as catalyst. After theoretical hydrogen uptake was completed, the reaction mixture was heated to boiling and then filtered through celite. After cooling, the filtrate was filtered to yield 4.0 g. of a white solid amine, m.p. 113°–114° C. of the formula:



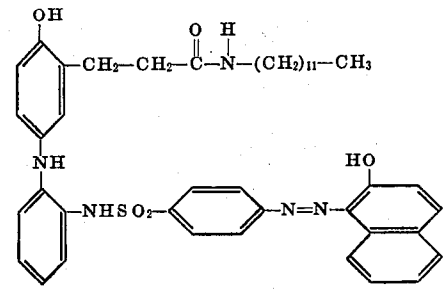
15.8 g. of the above amine (prepared in the foregoing manner) and 6.8 g. of 2-naphthalene-sulfonyl chloride were heated in 75.0 ml. of pyridine under nitrogen on a steam bath for 2 hours. The mixture was then poured into a mixture of 250.0 ml. of 10 percent sodium bicarbonate solution and about 50.0 g. of ice. The resulting solid was filtered and recrystallized from ethanol to yield 14.0 g. of an off white solid, m.p. 123°–124° C., of the formula:



A mixture of 14.0 g. of the above compound, 50.0 ml. of ethanol and 2.0 ml. of concentrated HCl was heated under nitrogen on a steam bath for 2 hours. The mixture was then stirred into ice water and the resulting solid was collected by filtration. After several dissolutions in ethanol and precipitations from water, the resulting solid was dried to yield 11.0 g. of the compound of formula 7, m.p. 87°–89° C.

EXAMPLE 3

A photosensitive element of the type disclosed in the aforementioned copending application Ser. No. (Case No. 3387), was prepared by coating on a cellulose acetate support a gelatin layer containing a colloidal silver silver-precipitating agent and nondiffusible color-providing compound of the formula:



to provide a calculated 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 superposed dyeable sheet material at a gap of 0.0026 a processing composition containing the following proportions of ingredients.

Water	100.0 cc.
Hydroxyethyl cellulose	3.9 g.
Sodium hydroxide	4.0 g.
Sodium thiosulfate	2.0 g.
Sodium sulfite	2.0 g.
Metol	1.6 g.

After an imbibition time of about 2 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 may be prepared as in example 3, except that the compound of formula 1 may be included in the silver halide emulsion layer at a calculated coverage of, for example, 68 mgm. per square foot. Such a photosensitive element may be exposed and developed in the manner described in example 3 with a developing composition containing no silver halide developing agent, e.g., a composition containing the following proportions of ingredients:

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

Employing a gap of 0.0016 inch, after 2 minutes the elements may be separated to provide a positive dye image.

From the procedure illustrated 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, 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.

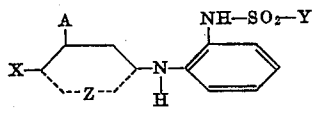
By way of recapitulation the compounds of this invention are particularly useful in the photographic systems described and claimed in the aforementioned Ser. No. 655,440, now U.S. Pat. No. 3,443,940, patented May 13, 1969 wherein a photosensitive element including at least one light-sensitive silver halide emulsion having associated therewith a nondiffusible 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, an imagewise distribution of soluble silver complex is formed in terms of unexposed areas of the emulsion; the nondiffusable color-providing material is contacted with the imagewise distribution of silver complex where, in the presence of silver-precipitating nuclei, the complex is reduced and 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 superposed 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 these compounds are even more nonmigratory in their oxidized form, owing to ring-closure as a function of oxidation, the oxidized form also cannot leave the layer in the photosensitive element where they are employed and thereby adversely affect the quality and/or stability of the color transfer image.

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:

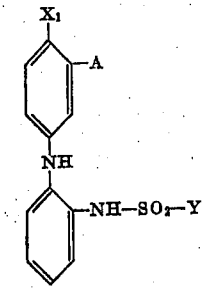
1. A compound of the formula:



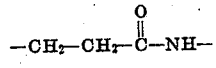
wherein Z represents the atoms necessary to complete a benzene or naphthalene ring or a monolower alkyl substituted benzene or naphthalene ring; X is hydroxy or amino; A is an anchoring moiety rendering the compound nondiffusible and said moiety is higher alkyl of from 12–18 carbon atoms bonded to the aromatic nucleus through the group

and Y is a colorless substituent selected from the group consisting of higher alkyls having from 12–18 carbon atoms, phenyl, naphthyl or mono-hydroxy, mono-lower alkoxy, mono-lower alkyl, mono-nitro substituted derivatives of phenyl or naphthyl.

2. A compound of the formula

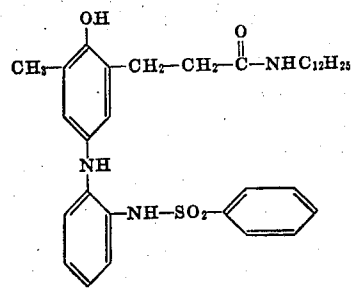


wherein X^1 is hydroxy or primary amino; A is an anchoring moiety of high alkyl having from 12–18 carbon atoms connected to the aromatic nucleus through

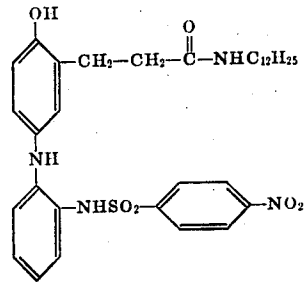


and Y is a substantially colorless substituent chosen from the group consisting of phenyl, naphthyl, mono-hydroxy substituted derivatives of phenyl or naphthy or mono-nitro substituted derivatives of phenyl or naphthyl.

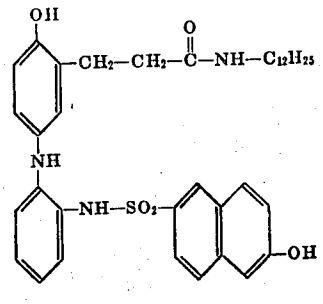
3.



4.



5.



6.

