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3,345,166 10/1967 Land et al. 96/29
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[54] **SILVER HALIDE DEVELOPING AGENTS AND
PHOTOGRAPHIC PROCESS**
8 Claims, No Drawings

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96/63, 96/16
[51] Int. Cl. G03c 5/24;
G03c 5/54
[50] Field of Search 96/29, 63,
76, 95

[56] **References Cited**
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ABSTRACT: Photographic process and product employing silver halide developing agents of quaternary ammonium compounds of the formula:

DEV—LINK—QUAT

wherein DEV is a dihydroxyaryl silver halide developing radical or a dialkoxyaryl or dialkoxymethoxyaryl precursor thereof; LINK is a hydrocarbon radical of at least 2 and preferably 3 carbon atoms or a hydrocarbon radical preceded by and/or interrupted by individual atoms of oxygen or sulfur with the proviso that an interrupting atom of oxygen or sulfur cannot be closer than two carbon atoms away in the chain from the positively charged nitrogen atom of the quaternary ammonium radical QUAT bonded to LINK through the pentavalent nitrogen atom. The preferred mode of preparation of these compounds is by the alkylation of an amine. These compounds are especially useful in photography as silver halide developing agents.

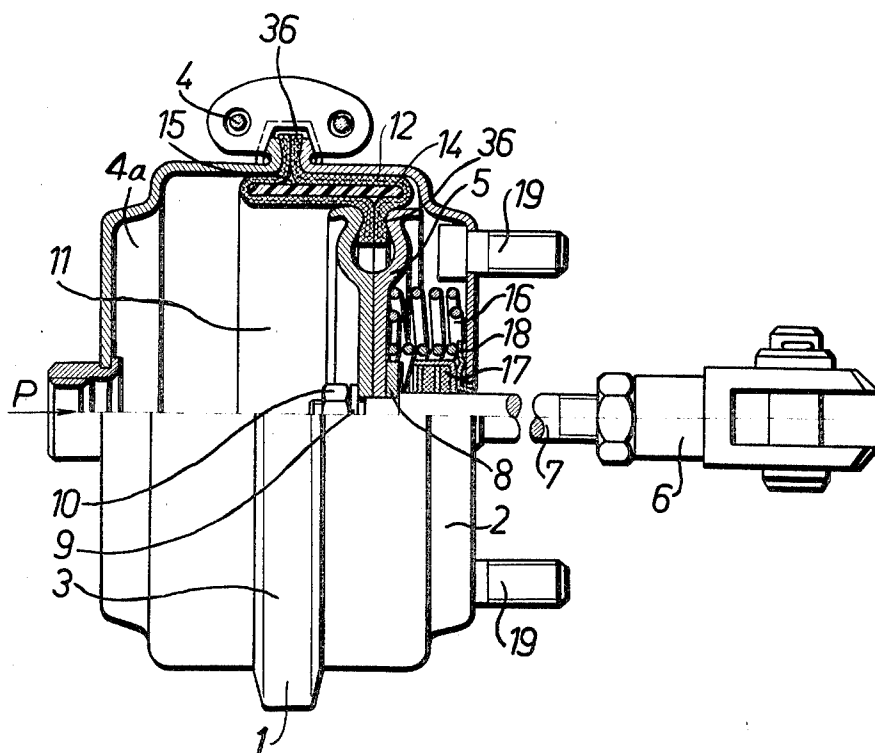


Fig. 1

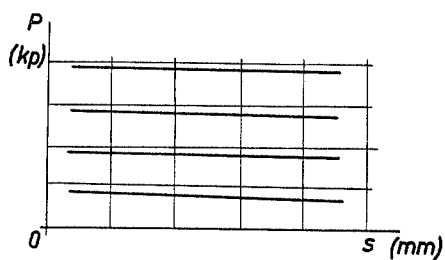


Fig. 2

INVENTOR

ISTVÁN RASKÓ

BY

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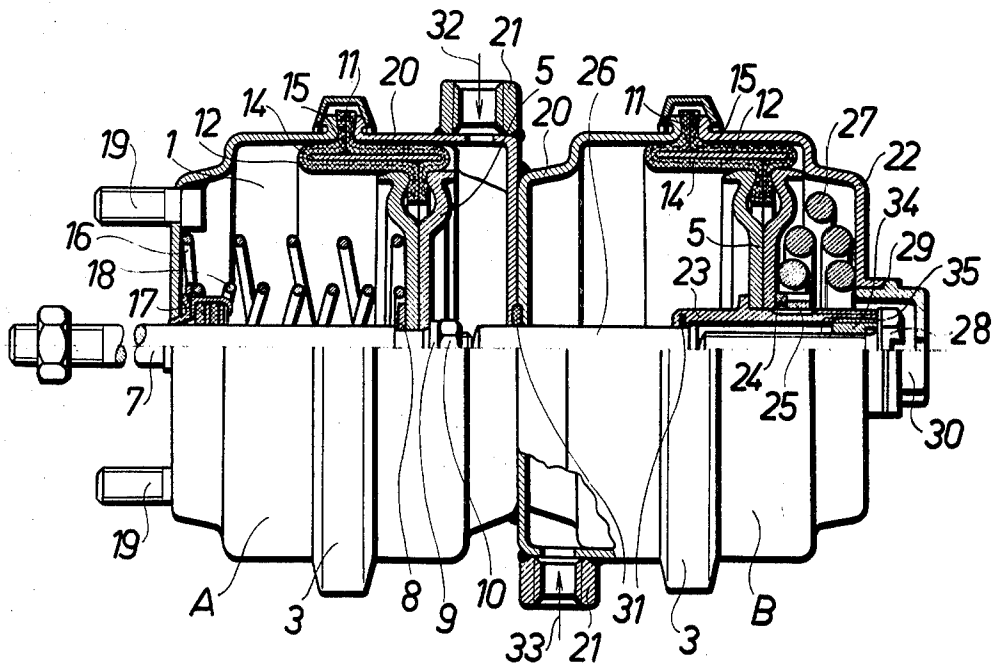


Fig.3

INVENTOR

ISTVÁN RASKÓ

BY

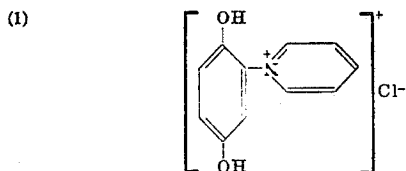
Young & Thompson

ATTORNEYS

SILVER HALIDE DEVELOPING AGENTS AND PHOTOGRAPHIC PROCESS

This invention relates to photography and, more particularly, to novel silver halide developing agents.

Mees, in *The Theory of the Photographic Process*, revised edition, copyright 1954, at page 556, indicates that Kumetat in *Zeitschrift für wissenschaftliche Photographie*, volume 43, page 113 et seq., 1948, states that hydroquinone derivatives in which one hydrogen atom of an aromatic ring is substituted by a pyridinium ring, e.g.,



are good silver halide developing agents. The introduction of positive substituents such as $-\text{CH}_3$ and $-\text{OCH}_3$ onto the hydroquinone nucleus of such derivatives increases the development capability of such compounds whereas the introduction of negative substituents decreases it. The positive charge of the pyridinium group might be expected to weaken the developing agent by the withdrawal of electrons from the hydroquinone system. The positive charge on the pyridinium group would be expected to make it easier for the hydroquinone ion to penetrate the negative charge barrier surrounding the silver halide grains, and this action may more than offset the electron withdrawal effect.

When such developing agents were utilized in diffusion transfer processing compositions which, as is known in the art, have a high pH of about 13, it was found that the developing agent fragmented. It has now been found that if a linking group containing at least two and preferably three carbon atoms is present between the positively charged nitrogen atom and the hydroquinone radical, or at least two carbon atoms between the positively charged nitrogen atom and any other atoms, such as oxygen or sulfur atoms, comprising a part of said linking group that such fragmentation will not occur. The utilization of the linking group also overcomes any electron withdrawing effect attributed to the quaternary nitrogen atom while still maintaining the benefits to be derived from the positive charge in regard to the penetration of the negative charge barrier.

Accordingly, it is one object of the present invention to provide novel quaternary ammonium compounds which are alkali stable silver halide developing agents suitable for use in diffusion transfer processes.

Another object is to provide novel processes and processing compositions for forming images by a diffusion transfer process wherein the novel compounds are utilized as the silver halide developing agent.

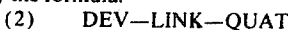
Still another object is to provide procedures for the preparation of the novel compounds.

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

The invention accordingly comprises the processes involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the products and compositions possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

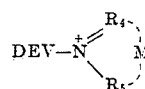
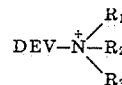
For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

The novel compounds of this invention may be represented by the formula:

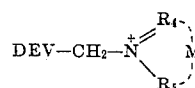
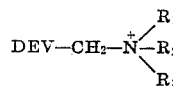


wherein DEV is a dihydroxyaryl silver halide developing radical; or a dialkoxyaryl or dialkoxy methoxy precursor thereof, or a monoamine monohydroxy silver halide developing radical; or a nitroalkoxyaryl or nitroalkoxymethoxyaryl precursor thereof; LINK is a divalent organic radical bonded to a nuclear carbon atom of DEV and to QUAT through a pentavalent nitrogen atom of QUAT, wherein the atom of LINK next adjacent to DEV is selected from among oxygen, sulfur and carbon, the remainder of said radical being a linear two to nine carbon atom hydrocarbon chain or a hydrocarbon chain which is interrupted by individual oxygen or sulfur atoms, with the proviso that an interrupting atom of oxygen or sulfur is not bonded to the carbon atom of LINK bonded to said pentavalent nitrogen atom of QUAT, and QUAT is a cyclic or acyclic quaternary ammonium radical which is bonded through the pentavalent nitrogen atom thereof to LINK and which radical when acyclic has three of its valences filled by three unsubstituted or halogen substituted hydrocarbon groups, and which radical when entirely cyclic comprises a heterocyclic ring which fills three of its valences, and which radical when partially cyclic and partially acyclic, contains an acyclic unsubstituted or halogen substituted hydrocarbon group to fill one valence, two other valences being filled by a heterocyclic ring, said rings containing in addition to the nitrogen atom bonded to the $-\text{LINK}-$ radical, carbon atoms, hydrogen atoms and optionally an atom selected from the group consisting of nitrogen, oxygen, selenium and sulfur.

As noted above, it has unexpectedly been discovered that these dihydroxyaryl containing developing agents are stable in high concentrations of alkali and as such can be utilized in diffusion transfer processing compositions, which as is known in the art, are generally of the pH of about 13 or more. This is surprising in view of the fact that compounds of the formula:

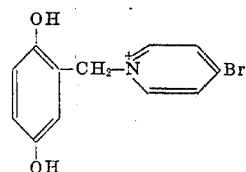


as well as

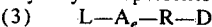


and

wherein DEV is a dihydroxyaryl silver halide developing radical; R_1 , R_2 , R_3 , R_4 and R_5 are hydrocarbon substituents and M comprises the atoms necessary to complete a heterocyclic ring, when placed in strongly alkaline media, liberate the pertinent amine compound. This liberation is easily attested to as, for instance, by the smell of pyridine being liberated from an alkaline solution of the compound:

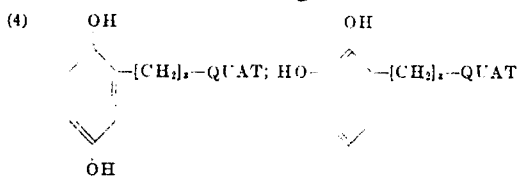


The novel compounds of this invention for ease and simplicity may be represented by the formula:



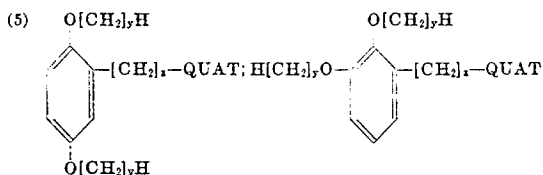
wherein L is an unsubstituted, alkylsubstituted or halogen substituted monovalent radical selected from the group consisting of phenyl and naphthyl rings substituted in ortho or para posi-

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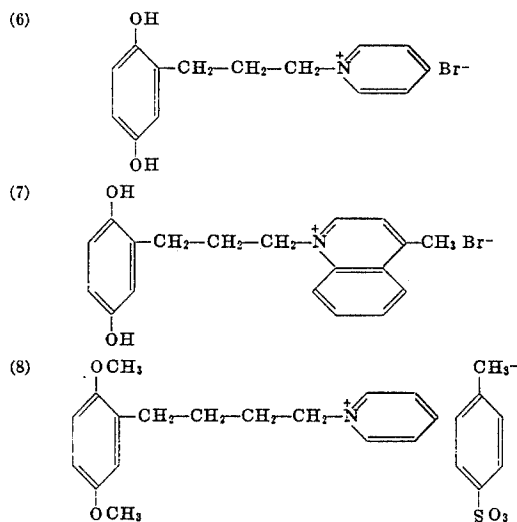
wherein z is an integer of from 2 to 10 inclusive.

Another preferred embodiment comprises compounds wherein L is a bisdialkoxypheyl radical, $A-R$ and D are of the significance indicated at formula (5). Such compounds are represented by the formulas

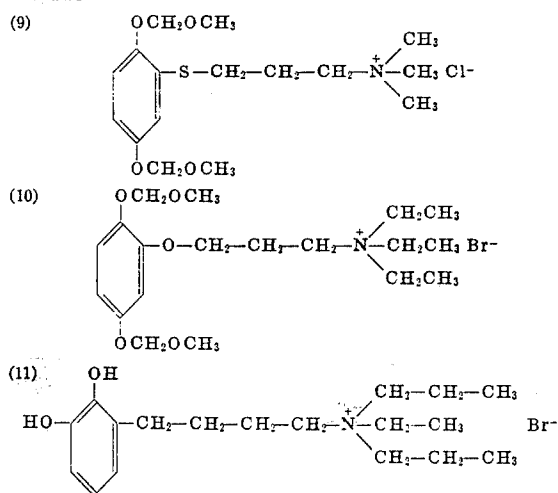


wherein z is an integer of from 2 to 10 inclusive, and y is an integer of from 1 to 5 inclusive.

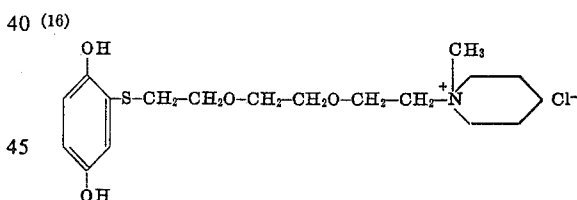
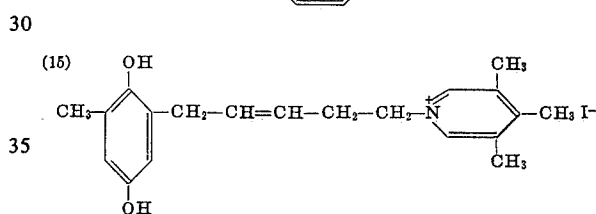
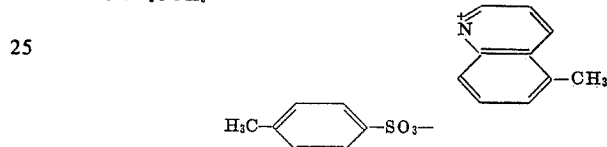
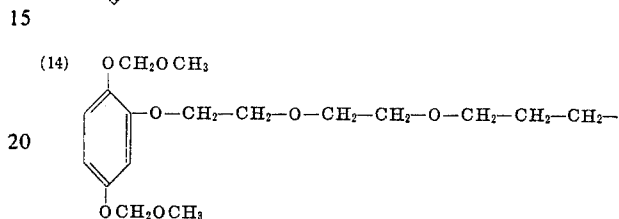
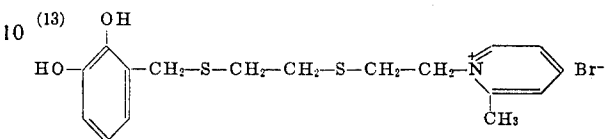
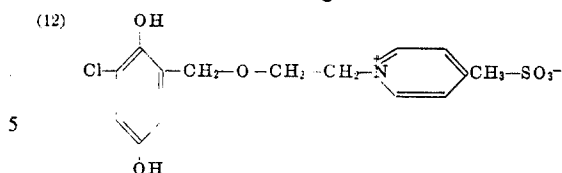
In the scope of formulas (4) and (5), typical preferred compounds include 1-(2,5'-dihydroxyphenyl) propyl-3-pyridinium bromide, N-γ(2,5'-dihydroxyphenyl) propyl-4-methylquinolinium bromide and N-γ(2,5'-dimethoxyphenyl)butyl-pyridinium tosylate, which are of the formulas:



Other compounds within the scope of this invention include:



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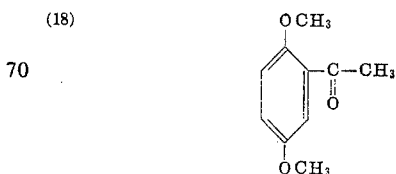


In general, the novel compounds of this invention can be prepared by several methods. One such method comprises reacting a tertiary amine, such as pyridine, with a halogen substituted alkyl acetal, such as a compound of the formula:



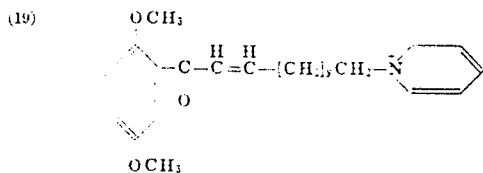
wherein y is an integer of from 1 to 5 inclusive

This intermediate product is reacted with hydrogen ion, such that the aldehyde derivative is prepared. This aldehyde compound is reacted in base with an acetophenone such as the compound of the formula:

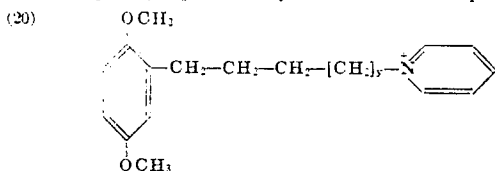


to give rise to a product of the formula:

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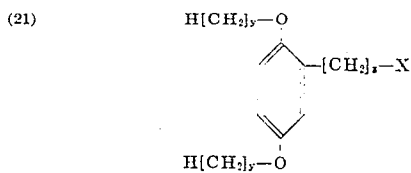


which can then be reduced, such as by hydrogen, to a dialkoxyphenyl quaternary ammonium compound,



Subsequent treatment of the alkoxy groups with a dealkylating agent gives rise to the hydroxyl derivative of the alkoxy compound, if such is desired. Details on this step will be set forth further on in the specification.

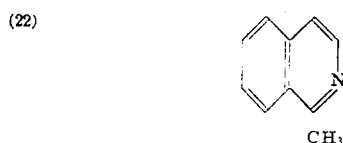
The preferred means of preparing compounds of the present invention which do not contain the optional A group, i.e., oxygen or sulfur, and which have an all hydrocarbon R, is by the alkylation of a tertiary amine, in the absence of heat, so as to avoid side reactions. This reaction can be illustrated as follows, a compound of the formula:



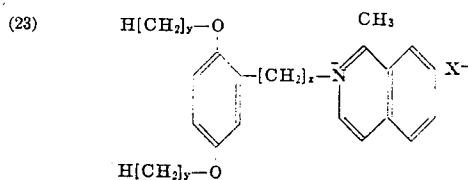
wherein y and z are as previously defined, and X is halogen,



or $\text{CH}_3\text{—SO}_3\text{—}$, or its ortho dialkoxy equivalent, is reacted with a tertiary amine, as for instance a compound of the formula:



and a product of the formula:

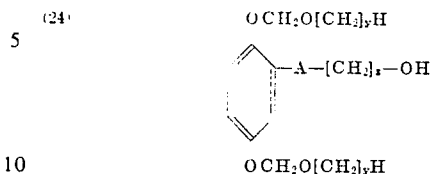


is obtained. Dealkylation of the alkoxy groups prepares the dihydroxy compound, if such is desired.

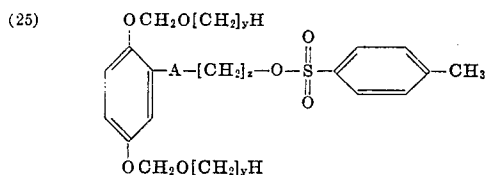
Compounds containing the optional A group, namely an atom of oxygen or sulfur, and an all hydrocarbon R, are prepared by a slightly different alkylation process. This is necessary in view of the fact that the dihydroxy compounds cannot be prepared by the aforementioned synthesis in view of the inability of any reagent to differentiate between the alkoxy groups in the 2,5 positions and the alkoxy group that would be in the 1 position. Therefore, to prepare compounds containing

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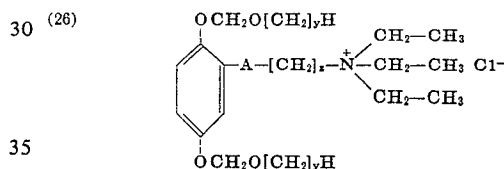
the optional A_e group, an alkoxyalkoxy compound such as the one of the formula



or its ortho equivalent, wherein A, y and z are as previously defined, is reacted with a compound such as toluene sulfonyl chloride in an organic base such as pyridine to prepare an intermediate of the formula:

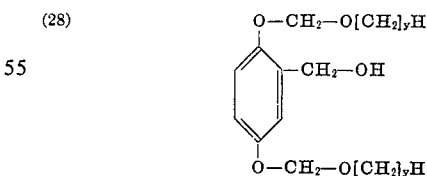
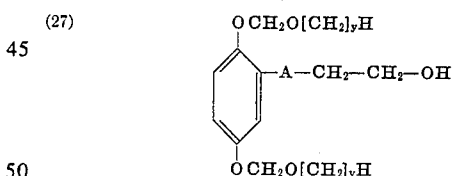


which is then reacted with any tertiary amine, such as triethyl amine to yield an end product of the formula:



Treatment of the above with dilute mineral acid removes the alkoxy groups and prepares the dihydroxy product.

Compounds containing ether or thioether groups in the "R" unit of $L\text{—}A_e\text{—}R\text{—}D$ are prepared by treating compounds of the following formulas:



y and A are as previously defined, or their ortho equivalents with reagent such as NaH in dimethylsulfoxide followed by the addition of one mole of ethylene oxide or its sulfur counterpart. More than one ether or thioether units can be added to increase the size of "R" by increasing the number of moles of ethylene oxide or ethylene sulfide added in the addition step. The preferred mode, however, is the unimolar addition followed by a NaH treatment between the additions of each mole of ethylene oxide or sulfide. Following the addition of the ether units to the starting materials, the same alkylation processes are carried out as well as same treatment to remove the alkoxy groups. It is, of course, understood that other epoxide units such as propylene oxide, etc., can be added in like manner.

The removal of the protective alkoxy groups to form the desired hydroxy-substituted compounds may be accomplished by known hydrolysis techniques. A typical dealkylation process involves complexing the group to be removed with boron tribromide, followed by decomposition of the resulting complex with water. Another dealkylation process comprises treatment of the methoxy intermediate with aqueous HBr or HBr in acetic acid.

The various reaction conditions, e.g., time, temperature, pressure, selection of solvents to form the reaction mixture, etc., are not critical to the practice of this invention unless so indicated within the confines of this application, and will therefore be readily apparent to the skilled artisan in the light of the foregoing descriptive material. The essence of the invention is, therefore, the aforementioned selection of steps, in the order described to obtain the desired end product, as well as the end product itself.

The invention will be illustrated in greater detail in conjunction with the following specific examples which set out representative preparations of the novel compounds of this invention, which, however, are not limited to the details therein set forth and are intended to be illustrative only.

EXAMPLE I

Preparation of N- γ (2', 5'-dihydroxyphenyl) propyl pyridinium bromide.

In a nitrogen atmosphere, 15 g. of lithium aluminum hydride (M.W. 37.95), 0.4 moles, was slurried in 200 cc. of dry ether. 87 g. of 2,5-dimethoxydihydrocinnamic acid, 0.416 moles, in 550 cc. of dry ether was added dropwise. The addition of the ether caused the dihydrocinnamic acid to reflux without the addition of extra heat. Stirring was continued for a period of 1 hour. Sufficient water was added dropwise, to decompose excess lithium aluminum hydride.

620 cc. of 10 percent H_2SO_4 were added to the reaction vessel. A two layer system resulted. The ether layer was separated and washed several times with an aqueous solution of $NaHCO_3$, cautiously, and then with water and dried. The ether was evaporated off leaving a fluid oil comprising 2,5-dimethoxyphenyl propyl alcohol. 54 g. of the approximately 70 g. of said alcohol were cooled to $-10^\circ C$. To this was added 40 g. of PBr_3 , 0.14 moles dropwise. The temperature was permitted to reach room temperature and the mixture was stirred for 2 hours and then allowed to stand overnight. It was heated to $80^\circ C$. for 0.5 hours and then cooled and poured onto ice mixed with water. The end product which was 2', 5'-dimethoxyphenyl 3-propyl bromide was extracted with ether, washed and dried. 52 g. (0.2 moles) of the bromide and 15.8 g. (0.2 moles) of pyridine in 200 cc. of dioxane were heated for 52 hours, with two layers being formed. The desired product, a yellow viscous oil, was separated and then refluxed overnight in approximately 350 cc. of 48 percent HBr, while under nitrogen. The nitrogen blanket was maintained until most of the liquid evaporated. The remainder was cooled and acetone was added. The resulting precipitate was washed in acetone, collected and dried under vacuum. Approximately 16 g. of an orange-tan product was obtained. The product was recrystallized from ethanol, melting point $167^\circ C$. for analysis. The analysis was in agreement with the assignment of the structure as N- γ (2', 5'-dihydroxyphenyl)propyl pyridinium bromide.

Analysis.—Calculated for $C_{14}H_{18}NO_2Br$ (percent): Nitrogen, 4.52%. Found (percent): Nitrogen, 4.52%.

EXAMPLE II

Preparation of N- γ (2', 5'-dihydroxyphenyl) propyl-4-methylquinolinium bromide.

3-(2', 5'-dimethoxyphenyl) propanal, 34.0 g., 0.2 moles, was dissolved in 400 ml. of 95 percent ethanol. Sodium borohydride, 7.4 g., 0.2 moles, was added and the reaction mixture refluxed two hours. The solvent was removed *in vacuo* and water and ethyl ether were added. The ether extract was washed with water, dried (anhydrous magnesium sulfate) and concentrated to a heavy oil. The oil, 27 g., 79 percent, 3-(2', 5'-dimethoxyphenyl)propanol was used directly. An infrared analysis showed that no aldehyde remained unreacted.

The 3-(2', 5'-dimethoxyphenyl)propanol, 27 g., 0.137 moles, was cooled to -10° and phosphorous tribromide 20 g., 0.074 moles, was added dropwise with stirring. The reaction was allowed to rise to room temperature and was stirred for an additional two hours and finally heated at 80° for one-half hour. The reaction mixture was poured into ice water and the product extracted into ethyl ether. The ether was washed with water and dried. The crude 3-(2', 5'-dimethoxyphenyl)propyl bromide was obtained by removal of the ether.

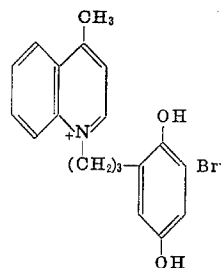
Attempts to purify a sample of the crude product by distillation at 18 mm. pressure and a temperature of $155^\circ C$. gave a clear liquid which was largely converted to a methoxy chroman. Because of this sensitivity to heat, the crude product was used directly in the synthesis of the quaternary salt.

The propyl bromide product, 5.6 g., 0.04 moles, and 4-methylquinoline, 5.6 g., 0.04 moles, were dissolved in 40 ml. dioxane and heated on the steam cone two days. On cooling, two layers were obtained. The dioxane layer was decanted and ethyl ether-ethyl acetate trituration was used to obtain the product. The crude solid was taken up in 60 ml. of concentrated hydrobromic acid and the reaction mixture refluxed $2\frac{1}{2}$ hours. The HBr was removed by evaporation on the steam cone using a nitrogen stream. Trituration of the residue with acetone gave 2 g. of N- γ (2', 5'-dihydroxyphenyl)propyl-4'-methylquinolinium bromide which was crystallized from ethanol, m.p. $238-9^\circ$.

The photographic utilization of the novel compounds of this invention will be illustrated in greater detail in conjunction with the following specific examples which set forth representative processes and which are not intended to be limiting, but are meant to be illustrative only.

EXAMPLE III

A photosensitive element was prepared by coating a gelatin subcoated film base at a speed of 15 feet per minute with a solution comprising 2 g. of a compound of the formula:



processing dissolved in 100 cc. of a solution containing 5.0 g. cellulose acetate hydrogen phthalate in a 1:1 mixture, by volume, of methoxyethanol and ethanol. After this coating dried, a green-sensitive silver iodobromide emulsion was coated thereupon at a speed of 10 feet per minute and allowed to dry. This photosensitive element was exposed and processed by spreading an aqueous processing composition between the thus exposed photosensitive element and a superposed spreader element, i.e., a sheet used to retain the processing composition, said aqueous processing composition comprising:

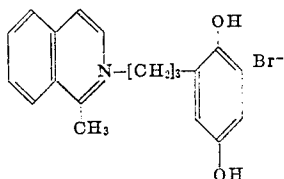
Water	100cc.
NaOH	5g.
Hydroxyethyl cellulose	3.9g.
Benzotriazole	1g.

After an imbibition period of approximately 1 minute, the spreader element was separated and it was found that a good negative image was present in the photosensitive element

In the following example, the novel compounds of this invention are utilized in a diffusion transfer process wherein unreduced (i.e., the hydroquinone form) quaternary ammonium developing agent is transferred by imbibition to an image-receiving layer and upon aerial oxidation, e.g., by oxygen in the air upon separation of the image-receiving layer from the photosensitive element, is caused to undergo an oxidative coupling with a second molecule of the quaternary ammonium developing agent. In this reaction, an active methylene group present on the QUAT portion of one molecule couples to the quinonyl portion of an oxidized DEV—LINK—QUAT molecule, whereby a colored immobile "polymeric" compound is formed in the image-receiving element in the areas corresponding to the undeveloped areas of the photosensitive element. Such a transfer process forms the subject matter of a copending application Ser. No. 741,548 in the name of Stanley M. Bloom herewith, now U.S. Pat. No. 3,537,852. It is to be understood that not all compounds of the formula DEV—LINK—QUAT are capable of participating in an oxidative reaction of this nature. Only the compounds which are capable of generating an enamine can so participate and then only if the pH has been adjusted to facilitate the self coupling reaction.

EXAMPLE IV

A photosensitive element was prepared by coating a gelatin subcoated film base at a speed of 10 feet per minute with a solution comprising 1 g. of a compound of the formula:



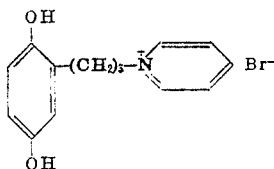
which was dissolved in 100 cc. of a solution containing 5.0 g. cellulose acetate hydrogen phthalate in a 1:1 mixture, by volume, of methoxyethanol and ethanol. After this coating dried, a blue-sensitive silver iodobromide emulsion was coated thereupon at a speed of 10 feet per minute and allowed to dry. This photosensitive element was exposed and processed by spreading an aqueous processing composition between the thus exposed photosensitive element and a superposed image-receiving element, said aqueous processing composition comprising:

Water 100cc.
NaOH 5g.
Hydroxyethyl cellulose 3.9g.
Benzotriazole 2g.
4'-methyl-phenyl hydroquinone 0.1g.

The image-receiving element comprised a 2:1 mixture, by weight, of gelatin and poly-4-vinyl pyridine containing a small amount of 1-phenyl-5-mercaptotetrazole coated upon a pigmented plastic base. After an imbibition period of approximately one minute, the image-receiving element was separated and contained a dense blue-positive transfer image.

EXAMPLE V

Utilizing a pair of standard iodobromide panchromatic sensitized negatives, the compound



was tested as a developing agent against 4-methylphenyl-hydroquinone, a control developing agent whose developing characteristics are well known in a diffusion transfer process.

The processing compositions utilized comprised 100 cc. of water to which was added 3.8 g. of hydroxyethyl cellulose, 11.2 g. of 85 per cent pure KOH, 0.93 g. of the test compound and 0.6 g. of 4'-methylphenyl hydroquinone, respectively. In duplicate tests, the negatives are exposed under conditions so that one-half of each negative is totally unexposed and the other half of the negative is totally exposed. The thus exposed negative and an image-receiving element are brought into superposed relationship and the processing composition is spread therebetween as the exposed negative and the image-receiving element are advanced at a constant rate between a pair of rollers. The resulting sandwich is scanned by infrared light. All the components of the sandwich are transparent to infrared light except for silver formed by development. It is to be noted that no silver is deposited on the receiving layer by diffusion transfer since a silver solvent is not present in the processing compositions. The reduction in infrared transmission due to silver formation as a function of imbibition time is reproduced electronically as a trace on a time and density grid on an oscilloscope tube, and the resulting oscilloscope tracing is photographed. The upper line in each such oscilloscope tracing represents the initiation of the development of exposed silver halide and the amount of silver developed in a given time in the fully exposed areas of the negative. The lower line represents the initiation of the development of unexposed silver halide in the totally unexposed areas of the negative and the amount of unexposed silver halide developed and therefore is a direct representation of the amount of fog development. The results of this test indicating the difference in fog buildup by the two developing agents are set forth graphically below:

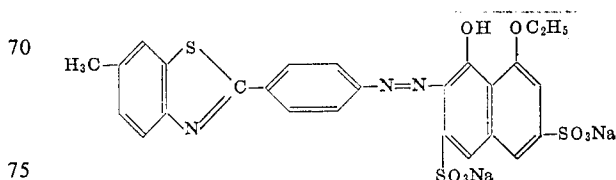
	Ag buildup, sec.			Fog buildup, sec.		
	5	10	60	5	10	60
Test.....	0.45	0.51	0.54	0.02	0.04	0.08
Control (MPHQ).....	0.52	0.57	0.63	0.14	0.19	0.19

It is seen that the test compound is a better discriminatory developer, i.e., the delta density difference between exposed and unexposed areas was greater with the test compound than with the 4'-methylphenyl hydroquinone.

The compounds of the present invention can also be utilized as mordanting developing agents in accordance with the concepts of the novel image forming process of Howard C. Haas, the subject matter of which is found in copending application Ser. No. 740,965, filed June 28, 1968, now abandoned. The following nonlimiting example is incorporated herein from said copending application to illustrate the utilization of the compounds of the present invention as silver halide developing agents which will interact with gelatin when they are oxidized to form in the photosensitive emulsion an imagewise distribution of a mordant for a negatively charged dye, such as an acid dye. When such a dye is associated with the instant compounds, it is mordanted in place in the developed areas of the photosensitive emulsion where it is free to transfer from the undeveloped areas to form a transfer image.

EXAMPLE VI

A photosensitive element was prepared as follows: 3.75 g. of C.I. 15080 Direct Red 3, Benzo Brilliant Geranine B, of the formula:



was dissolved in 45 cc. of water. This solution was emulsified by means of a high shear mechanical agitator, with an aqueous solution of 5 g. of 10 percent gelatin, to obtain a uniformly blended mixture. 50 cc. of the resulting dye dispersion were mixed with 78 cc. of water and then coated upon a subcoated film base. After this coating dried, a blue-sensitive silver iodobromide emulsion was coated thereupon at a coverage of 317.9 mg. per square foot of silver and allowed to dry. This photosensitive element was exposed and processed by spreading, between the thus exposed photosensitive element and a superposed image-receiving element, an aqueous processing composition comprising:

Water 90g.

NaOH 4g.

Hydroxyethyl cellulose 3g.

N- γ (2', 5'-dihydroxyphenyl) propyl-pyredinium bromide 3g.

The image-receiving element comprised baryta paper coated with a layer of a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinyl-pyridine. After an imbibition period of approximately one minute, the image-receiving element was separated and contained a red-positive image.

From the examples above, it is evident that the compounds of the present invention have particular utility as silver halide developing agents in diffusion transfer processes, both dye and silver.

It will be apparent that the relative proportions of developing agents and other ingredients and materials illustrated in the above examples may be varied to suit the requirements of one skilled in the art. Thus, it is within the scope of this invention to substitute alkalies other than sodium hydroxide in the processing composition. Likewise, it is also contemplated that where desirable the processing or developing compositions may be modified by the inclusion of other common components of developer compositions such as restrainers, preservatives, accelerators, etc. Where the processing compositions are to be employed in silver diffusion transfer processes, they may have incorporated in them as a further ingredient a silver halide solvent such as sodium thiosulfate. If the processing composition is to be applied to the emulsion by being spread thereon in a thin layer, it may also include a film-forming thickening agent such, for example, as a high molecular weight polymer, e.g., hydroxyethyl cellulose or sodium carboxymethyl cellulose. Thus, by adding sodium thiosulfate to the pertinent compositions, e.g., Example III, illustrated above and using an image-receiving layer containing silver precipitating agents as is well known in the art, in conjunction with the photosensitive element, a silver transfer image may be obtained.

It will be apparent that, by appropriate selection of the support and coatings forming the image-receiving element from among suitable known opaque and transparent materials, it is possible to obtain either a positive reflection print or a positive transparency.

As examples of useful color image-receiving materials, mention may be made of nylon, e.g., N-methoxymethyl-polyhexamethylene adipamide, polyvinyl alcohol, and gelatin, particularly polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine.

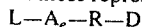
The utility of the compounds of this invention is by no means limited to diffusion transfer processes for they may be satisfactorily employed in conventional multistage multibath photographic processes in black-and-white or color photography. A typical developer composition would include in addition to a compound of this invention, ingredients as sodium hydroxide, sodium sulfite and potassium bromide. After development is completed, any unreacted developing agent is washed out of the photosensitive element preferably with an alkaline washing medium or other medium in which unreacted developing agent is soluble.

In the preceding portions of the specification, the expression "color" has been used. This expression is intended to include the use of a plurality of colors to obtain black.

Since certain changes may be made in the above products and processes and compositions 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.

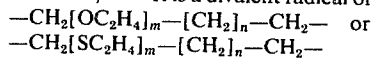
I claim:

1. In a diffusion transfer process which comprises the steps of developing an exposed silver halide emulsion with an aqueous alkaline solution of a silver halide developing agent, forming an imagewise distribution of a diffusible image-forming component, and transferring at least a portion of said imagewise distribution of said image-forming component by diffusion in alkaline solution to an image-receiving layer to provide a transfer image, the improvement which comprises said process in the presence of at least one compound selected from those represented by the formula:



wherein L is an unsubstituted, alkylsubstituted or halogen substituted monovalent radical selected from the group consisting of phenyl and naphthyl rings substituted in ortho or para positions with respect to each other by $\Delta-OH$ and $\Delta-NH_2$, at least one of said positions being substituted by $\Delta-OH$;

A is selected from the group consisting of oxygen and sulfur; e is 1 or 0; R is a divalent radical of the formula:



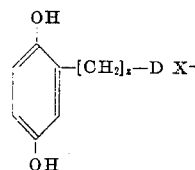
wherein m is a number from 0 to 4 inclusive; n is a number from 0 to 8 inclusive; the sum of m+n being not greater than 8;

D is a cyclic, acyclic, or part cyclic part acyclic quaternary ammonium radical selected from the group of radicals of the formulae:

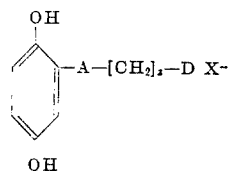


wherein each Q and T are acyclic hydrocarbon or halogen substituted hydrocarbon groups, M represents the atoms necessary to complete a heterocyclic ring and may contain in addition to carbon and hydrogen atoms, an atom selected from the group consisting of nitrogen, oxygen, sulfur and selenium, and X is an anion selected from the group consisting of halide, methyl sulfonate and p-toluenesulfonate.

2. (Amended) The process of claim 1, the step which comprises conducting said process in the presence of at least one compound selected from those represented by the formulae:



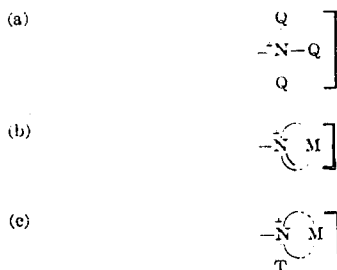
and



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wherein z is an integer of from 2 to 10 inclusive, and A is selected from the group consisting of oxygen and sulfur; and

D is a cyclic, acyclic or part cyclic part acyclic quaternary ammonium radical selected from the group of radicals of the formulae:



wherein each Q and T are acyclic hydrocarbon or halogen substituted hydrocarbon groups, M represents the atoms necessary to complete a heterocyclic ring and may contain in addition to carbon and hydrogen atoms, an atom selected from the group consisting of nitrogen, oxygen, sulfur and selenium, and X is an anion selected from the group consisting of halide, methyl sulfonate and p-toluenesulfonate.

3. The process as defined in claim 1 wherein the compound represented by the formula:

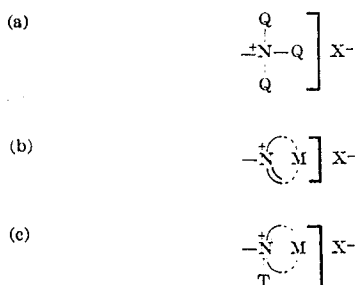
$1-A_e-R-D$ is selected from the group consisting of N- γ (2', 5' dihydroxyphenyl) propyl- pyridinium bromide, N- γ (2', 5'-dihydroxyphenyl) propyl-2''-methylquinolinium bromide and N- γ (2', 5'-dihydroxyphenyl) propyl- 4''-methylquinolinium bromide.

4. The process of developing a latent image in a silver halide emulsion which comprises treating said emulsion with an aqueous alkaline solution in the presence of a compound selected from those represented by the formula:

$L-A-R-D$ wherein L is an unsubstituted, alkylsubstituted or halogen substituted monovalent radical selected from the group consisting of phenyl and naphthyl rings substituted in ortho or para positions with respect to each other by $\Delta-OH$ and $\Delta-NH_2$, at least one of said positions being substituted by $\Delta-OH$;

A is selected from the group consisting of oxygen and sulfur; e is 1 or 0; R is a divalent radical of the formula: $-CH_2[OC_2H]_m-[CH_2]_n-CH_2-$ or $-CH_2[SC_2H_4]_m-[CH_2]_n-CH_2-$ wherein m is a number from 0 to 4 inclusive; n is a number from 0 to 8 inclusive; the sum of $m+n$ being not greater than 8;

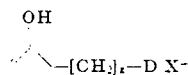
D is a cyclic, acyclic, or part cyclic part acyclic quaternary ammonium radical selected from the group of radicals of the formulae:



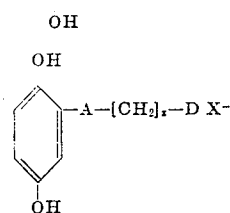
wherein each Q and T are acyclic hydrocarbon or halogen substituted hydrocarbon groups, M represents the atoms necessary to complete a heterocyclic ring and may contain in addition to carbon and hydrogen atoms, optionally an atom selected from the group consisting of nitrogen, oxygen, sulfur and selenium, and X is an anion selected from the group consisting of halide, methyl sulfonate and p-toluenesulfonate.

5. (Amended) The process of developing a latent image as in claim 4 which comprises treating said emulsion with a compound selected from those represented by the formulae:

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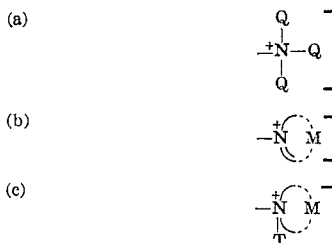


and



wherein z is an integer of from 2 to 10 inclusive, and A is selected from the group consisting of oxygen and sulfur;

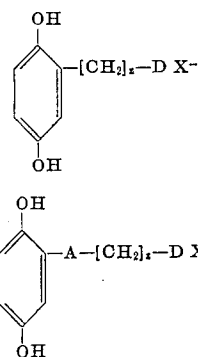
D is a cyclic, acyclic or part cyclic part acyclic quaternary ammonium radical selected from the group of radicals of the formulae:



wherein each Q and T are acyclic hydrocarbon or halogen substituted hydrocarbon groups, M represents the atoms necessary to complete a heterocyclic ring and may contain in addition to carbon and hydrogen atoms, an atom selected from the group consisting of nitrogen, oxygen, sulfur and selenium, and X is an anion selected from the group consisting of halide, methyl sulfonate and p-toluenesulfonate.

6. A process of developing a latent image in a silver halide emulsion which comprises treating said emulsion with an aqueous alkaline solution in the presence of a compound selected from the group consisting of N- γ (2', 5'-dihydroxyphenyl) propyl-pyridinium bromide, N- γ (2', 5'-dihydroxyphenyl) propyl-4- methylquinolinium bromide and N- γ (2', 5'-dihydroxyphenyl)propyl-2-methylquinolinium bromide.

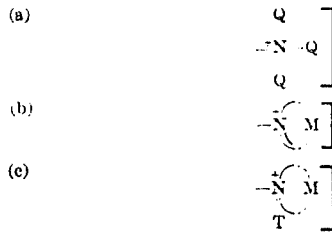
7. (Amended) A photographic product comprising a plurality of layers, at least one of said layers including a silver halide emulsion, and at least one of said layers including a compound selected from those of the formulae:



wherein z is an integer of from 2 to 10 inclusive, and A is selected from the group consisting of oxygen and sulfur;

D is a cyclic, acyclic or part cyclic part acyclic quaternary ammonium radical selected from the group of radicals of the formulae:

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wherein each Q and T are acyclic hydrocarbon or halogen substituted hydrocarbon groups, M represents the atoms

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necessary to complete a heterocyclic ring and may contain in addition to carbon and hydrogen atoms, optionally an atom selected from the group consisting of nitrogen, oxygen, sulfur and selenium, and X is an anion selected from the group consisting of halide, methyl sulfonate and p-toluenesulfonate.

8. A photographic product comprising a plurality of layers, at least one of said layers including a silver halide emulsion, and at least one of said layers including a compound selected from the group consisting of N- γ (2', 5'-dihydroxyphenyl)propyl-pyridinium bromide, N- γ (2',5'-dihydroxyphenyl)propyl-4-methylquinolinium bromide and N- γ (2', 5'-dihydroxyphenyl) propyl-2-methylquinolinium bromide.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,590,692 Dated July 6, 1971

Inventor(s) Stanley M. Bloom

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

IN THE CLAIMS:

Claim 1, line 14, after "comprises" insert "conducting".

Claim 1, line 21, " Δ —OH" should read "—OH".

Claim 1, line 21, " Δ —NH₂" should read "—NH₂".

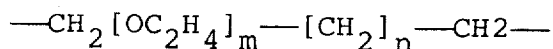
Claim 1, line 22, " Δ —OH" should read "—OH".

Claim 4, line 41, " Δ —OH" should read "—OH".

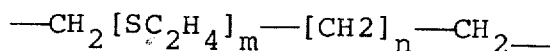
Claim 4, line 41, " Δ —NH₂" should read "—NH₂".

Claim 4, line 42, " Δ —OH" should read "—OH".

Claim 4, lines 44-46, the formulae should read:



or



Signed and sealed this 27th day of June 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents