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3,467,658

## QUATERNARY LEUCOAURAMINE COMPOUNDS

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11 Claims

### ABSTRACT OF THE DISCLOSURE

There are provided quaternary bis(p-dialkylaminophenyl)-methyl amine derivatives in which the amino N attached to the methyl C constitutes part of the residue of a primary or secondary amine also containing at least one other nitrogen atom, which other nitrogen atom is capable of being quaternized. These compounds are valuable as color precursors for colorless carbon paper and impact printing systems.

It is known that leucoauramines of various types, which compounds are colorless or essentially colorless, undergo a color reaction, changing to a deep blue or violet shade, when brought into adsorption contact with an acidic electron acceptor material such as attapulgite, bentonite, kaolin, a zeolite, silica gel, aluminum sulfate, and magnesium trisilicate or a solid organic acid such as succinic acid, benzoic acid, and fumaric acid.

This property finds extensive use in the production of colorless carbon paper, manifold record systems, and similar impact-printing arrangements. In general, in the preparation of such a system, the under surface of a sheet of paper, called the transfer sheet, is coated with a composition containing the leucoauramine color precursor; and the top surface of another sheet of paper, called the copy sheet, is coated with a composition containing an acidic material of the indicated type. When the transfer sheet is superimposed on the copy sheet and a written or imprinted impression is made on the top surface of the transfer sheet, the impression will be duplicated in color on the copy sheet at the point of pressure.

The leucoauramine compounds commonly employed for this purpose have not proved entirely satisfactory in practice. Thus, for example, they tend to migrate to the surface of the coating especially where a crack is formed in the coating as by folding of the paper. This action results in premature coloration and smudging of the copy sheet.

Some of these leucoauramine compounds also respond slowly to color development following impact pressure. In addition, often these leucoauramines produce a blurry or fuzzy imprint on impact of printing or writing.

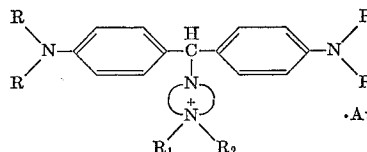
I have now found that, surprisingly, leucoauramine compounds can be employed for this extremely useful application in such a manner that not only are the above-mentioned and other disadvantages eliminated or substantially mitigated but an improved imprint on impact pressure is also produced. This unexpected result is obtained by introducing a quaternizable nitrogen atom into the leucoauramine compound and effecting quaternization of the same, with conversion of such leucoauramine compound from its non-ionic state to an ionic form.

According to the invention there are thus provided quaternary bis(p-dialkylaminophenyl)-methyl amine derivatives in which the amino N attached to the methyl C constitutes part of the residue of a primary or secondary amine also containing at least one other nitrogen atom, which other nitrogen atom is capable of being quaternized.

These quaternary leucoauramine compounds of the pres-

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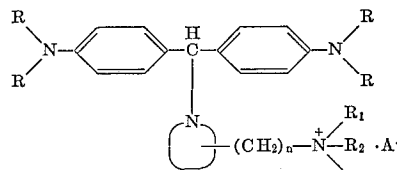
ent invention comprise (1) those compounds having the formula



wherein R is an alkyl group,



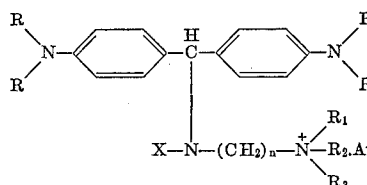
represents a heterocyclic nucleus containing 5 to 6 ring members of which at least two are nitrogen atoms, one of such nitrogen atoms being quaternizable, R<sub>1</sub> is an alkyl group, a cycloalkyl group, or an aralkyl group, R<sub>2</sub> is an alkyl group, and A<sup>-</sup> is an anion; (2) those compounds having the formula



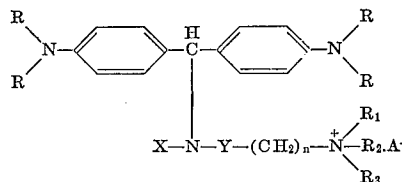
wherein R, R<sub>1</sub>, R<sub>2</sub> and A<sup>-</sup> respectively have the same meaning as above,



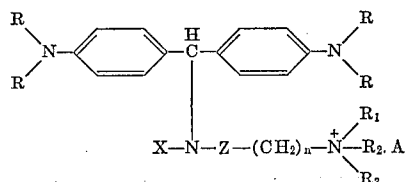
represents a heterocyclic nucleus containing 5 to 6 ring members of which at least one is a nitrogen atom, n is an integer from 1 to 18, R<sub>3</sub> is an alkyl group, and R<sub>2</sub> and R<sub>3</sub> may together with the N<sup>+</sup> atom also comprise a heterocyclic alkyl group; (3) those compounds having the formula



wherein R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, n and A<sup>-</sup> respectively have the same meaning as above, and X is a hydrogen or an alkyl group, an aryl group, an aralkyl group, or an alkaryl group; (4) those compounds having the formula



wherein R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, X, n and A<sup>-</sup> respectively have the same meaning as above, and Y is an aryl group; and (5) those compounds having the formula



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wherein R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, X, n and A<sup>-</sup> respectively have the same meaning as above, and Z is a heterocyclic nucleus containing 5 to 6 ring members and connected to the N atom through a ring carbon atom.

As indicated, R is an alkyl group, which may have a straight-chain structure or a branched-chain structure. Usually, however, R is a lower alkyl group having 1 to 4 carbon atoms; and preferably it is a methyl group or an ethyl group. Ordinarily each R is the same, but they may be different as desired.

Each phenylene group attached to the methyl C is generally a phenylene group per se. Either or both phenylene groups may, however, contain one or more substituents such as an alkyl group, an aralkyl group, an alkoxy group, group, or a halogen provided that any such substituent is itself inert and is not rendered reactive by reason of its manner of association with the phenylene group. The tolylene, methoxyphenylene, and chlorophenylene groups comprise typical examples of such "substituted" phenylene groups.

The heterocyclic nucleus represented by



contains, as indicated, 5 to 6 ring members of which at least two are nitrogen atoms. One such nitrogen atom forms the linking point to the methyl C, and the other such nitrogen atom must be quaternizable. Besides carbon and nitrogen atoms, this heterocyclic nucleus may contain an oxygen atom and/or a sulfur atom as a ring member. In addition, such heterocyclic nucleus may contain one or more substituents such as an alkyl group, an aralkyl group, a hydroxyalkyl group, an alkoxy group or a halogen provided that any such substituent is itself inert and is not rendered reactive by reason of its manner of association with the heterocyclic nucleus. This term "heterocyclic nucleus" also includes within its scope a condensed or fused polynuclear group, part of which is comprised of the above-indicated 5- or 6-membered heterocyclic nucleus itself and which may also be substituted as indicated above. A typical 5-membered heterocyclic nucleus of this type comprises the imidazolidine nucleus; typical 6-membered heterocyclic nuclei of this type include the piperazine nucleus and the 2-methyl piperazine nucleus; and a typical condensed heterocyclic nucleus of this type comprises the 1,2,3,4-tetrahydroquin-oxaline nucleus.

R<sub>1</sub> represents the group introduced into the leucoauramine compound as the result of its quaternization. As indicated, R<sub>1</sub> may be an alkyl group, in which event it may be a straight-chain group or a branched-chain group. In such case, however, R<sub>1</sub> is usually a lower alkyl group having 1 to 4 carbon atoms; and preferably it is a methyl group or an ethyl group. R<sub>1</sub> may also be a cycloalkyl group such as the cyclohexyl group, or it may be an aralkyl group such as the benzyl group.

The alkyl group represented by R<sub>2</sub> may have a straight-chain structure or a branched-chain structure. In addition, such alkyl group may contain a substituent such as a halogen or a hydroxyl group provided that such substituent is not itself reactive and is not rendered reactive by reason of its manner of association with the alkyl group. Usually, however, R<sub>2</sub> is a lower alkyl group having 1 to 4 carbon atoms; and preferably it is a methyl group or an ethyl group. An example of such a "substituted" alkyl group is the hydroxy ethyl group.

The anion represented by A<sup>-</sup> is, of course, the anion derived from the quaternizing agent utilized in producing the desired quaternary leucoauramine compound. Any quaternizing agent providing the appropriate R<sub>1</sub> group may be employed for this purpose so that A<sup>-</sup> represents whatever anion results from the use of such quaternizing agent. Ordinarily, however, A<sup>-</sup> is a chloride, bromide or iodide anion or a mono-alkyl sulfate anion. In the latter

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case the alkyl portion of the anion usually has 1 to 4 carbon atoms and is preferably a methyl group or an ethyl group. As will be appreciated, when A<sup>-</sup> is such a monoalkyl sulfate anion, R<sub>1</sub> is generally an alkyl group corresponding to the alkyl portion of such anion.

The heterocyclic nucleus represented by



contains, as indicated, 5 to 6 ring members of which at least one is a nitrogen atom, such nitrogen atom providing the linking point to the methyl C. Besides carbon and nitrogen atoms, this heterocyclic nucleus may contain an oxygen atom and/or a sulfur atom as a ring member. In addition, such heterocyclic nucleus may contain one or more substituents such as an alkyl group, an aralkyl group, a hydroxyalkyl group, an alkoxy group or a halogen provided that any such substituent is itself inert and is not rendered reactive by reason of its manner of association with the heterocyclic nucleus. This term "heterocyclic nucleus" also included within its scope a condensed or fused polynuclear group, part of which is comprised of the above-indicated 5- or 6-membered heterocyclic nucleus itself and which may also be substituted as indicated above. Typical 5-membered heterocyclic nuclei of this type include the imidazoline nucleus and the pyrazoline nucleus; typical 6-membered heterocyclic nuclei of this type include the piperidine nucleus and the morpholine nucleus; and typical condensed heterocyclic nuclei of this type include the indole nucleus, the benzotriazole nucleus, and the carbazole nucleus.

The alkylene chain represented by —(CH<sub>2</sub>)<sub>n</sub>— may contain 1 to 18 carbon atoms as indicated. This alkylene chain may be branched in structure but is generally a straight-chain group. In addition, such alkylene chain may include an ether linkage or a thio linkage provided that such a linkage is not itself reactive and is not rendered reactive by reason of its manner of association with the alkylene chain.

R<sub>3</sub> represents an alkyl group of the same type as represented by R<sub>2</sub> and, like R<sub>2</sub>, is usually a lower alkyl group having 1 to 4 carbon atoms. R<sub>2</sub> and R<sub>3</sub> are generally the same but may be different as desired. In addition, R<sub>2</sub> and R<sub>3</sub> together with the N atom to which they are attached may also comprise a heterocyclic alkyl group, which may contain other hetero atoms such as oxygen in its ring. Typical examples of such heterocyclic alkyl groups include the piperidino group and the morpholino group.

As indicated, X may be hydrogen or any of several hydrocarbon groups. Where X is an alkyl group, it may be a straight-chain group or a branched-chain group, or it may have a cyclic structure. In such a case, however, X is usually a lower alkyl group having 1 to 4 carbon atoms; and preferably it is a methyl group or an ethyl group. Where X is an aryl group, it may be mononuclear or polynuclear. Where X is an aralkyl group or an alkaryl group, similar comments respectively apply to the alkyl portion and to the aryl portion of such a group. A typical example of such an aryl group is the phenyl group; a typical example of such an aralkyl group is the benzyl group; and a typical example of such an alkaryl group is the tolyl group. In addition, any such hydrocarbon group may contain a substituent such as an alkoxy group or a halogen provided that such substituent is itself inert and is not rendered reactive by reason of its manner of association with the hydrocarbon group.

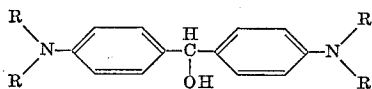
The aryl group represented by Y may be mononuclear or polynuclear in structure. In addition, such aryl group may contain a substituent such as an alkyl group, an alkoxy group or a halogen provided that any such substituent is itself inert and is not rendered reactive by reason of its manner of association with the aryl group.

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Typical examples of such aryl groups include those groups respectively derived from benzene, naphthalene, anthracene and biphenyl.

Z represents a heterocyclic nucleus having, as indicated, 5 to 6 ring members, one carbon atom of which serves as the linking point to the N atom attached to the methyl C. The hetero atom or atoms included in such heterocyclic nucleus may comprise oxygen, nitrogen and/or sulfur. In addition, such heterocyclic nucleus may contain one or more substituents such as an alkyl group, an aralkyl group, a hydroxyalkyl group, an alkoxy group or a halogen provided that any such substituent is itself inert and is not rendered reactive by reason of its manner of association with the heterocyclic nucleus. This term "heterocyclic nucleus" also includes within its scope a condensed or fused polynuclear group, part of which is comprised of the above-indicated 5- or 6-membered heterocyclic nucleus itself and which may also be substituted as indicated above. A typical 5-membered heterocyclic nucleus of this type comprises the pyrrole nucleus; a typical 6-membered heterocyclic nucleus of this type comprises the pyridine nucleus; and typical condensed heterocyclic nuclei of this type include the benzofuran nucleus, the dibenzofuran nucleus, the benzothiazole nucleus, and the quinoline nucleus.

In general, the quaternary leucoauramine compounds of the present invention may be prepared by initially condensing a bis(p-dialkylaminophenyl)-methyl hydrol (or 4,4'-bis(dialkylamino)-benzhydrol) having the formula



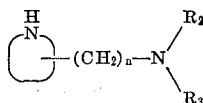
wherein R has the same meaning as above and each phenylene group has the same scope as given above, with (1) a secondary amine having the formula



wherein



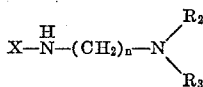
and R<sub>2</sub> respectively have the same meaning as above, or (2) a secondary amine having the formula



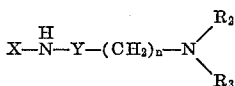
wherein



R<sub>2</sub>, R<sub>3</sub> and n respectively have the same meaning as above, or (3) a primary or secondary amine having the formula



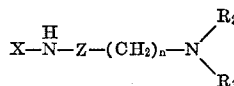
wherein R<sub>2</sub>, R<sub>3</sub>, X and n respectively have the same meaning as above, or (4) a primary or secondary amine having the formula



wherein R<sub>2</sub>, R<sub>3</sub>, X, Y and n respectively have the same

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meaning as above, or (5) a primary or secondary amine having the formula



wherein R<sub>2</sub>, R<sub>3</sub>, X, Z and n respectively have the same meaning as above. The resulting leucoauramine compound is then treated with a quaternizing agent containing the appropriate R<sub>1</sub> group to give the corresponding quaternary leucoauramine compound.

More particularly, the initial condensation of the benzhydrol with the primary or secondary amine is conducted by refluxing substantially equimolar proportions of the two reactants in the presence of a solvent in which both reactants are at least partially soluble and which has a boiling point between 60 and 150° C. Examples of suitable solvents for this purpose include aromatic hydrocarbons such as benzene, toluene and xylene and alcohols such as methanol, ethanol, propanol and butanol. Upon completion of the refluxing, the reaction mixture is cooled in order to precipitate the resulting leucoauramine compound, which is then separated as by filtration and which may be purified, if desired, by subsequent recrystallization from a suitable solvent. Solution of such leucoauramine compound is thereafter effected in a suitable non-polar solvent such as one of the aromatic hydrocarbons at a temperature of about 50 to 70° C. The appropriate quaternizing agent is then added, preferably dropwise, to such solution. The quaternization reaction being mildly exothermic, there is a rise in temperature, usually on the order of 10 to 15° C., of the reaction mixture during the addition of the quaternizing agent. The resulting quaternary leucoauramine compound, being insoluble in the non-polar solvent, precipitates out during the course of the reaction and is subsequently separated as by filtration.

Examples of benzhydrols suitable for use in such initial condensation reaction include:

- 4,4'-bis(dimethylamino)-benzhydrol (Michler's hydrol)
- 4,4'-bis(diethylamino)-benzhydrol
- 4,4'-bis(dibutylamino)-benzhydrol
- 4,4'-bis(dimethylamino)-2,2'-dichloro-benzhydrol.

Examples of primary and secondary amines that can be typically employed in such initial condensation reaction include:

- N-methyl piperazine
- N-ethyl piperazine
- 2-(2-dimethylaminoethyl) morpholine
- 4-(2-diethylaminoethyl) piperidine
- 6-dimethylaminoethyl indole
- 3-(3-diethylaminopropyl) indole
- N,N-dimethyl octamethylene diamine
- N-ethyl-N',N'-dimethyl hexadecylmethylene diamine
- N-benzyl-N-methyl dodecylmethylene diamine
- 4-(2-diethylaminoethyl) aniline
- 4-(N,N-dimethylaminomethyl)-1-naphthyl amine
- 2-(4-dimethylaminobutyl)-4-amino-pyridine
- 2-(3-diethylaminopropyl)-8-amino-quinoline
- 6-(2-dimethylaminoethyl)-2-methylamino-benzothiazole.

Quaternizing agents typically suitable for effecting the quaternization of the resulting leucoauramine compound include dimethyl sulfate, diethyl sulfate, methyl chloride, methyl bromide, methyl iodide, ethyl chloride, ethyl bromide, ethyl iodide, cyclohexyl chloride, cyclohexyl bromide, benzyl chloride, and benzyl bromide.

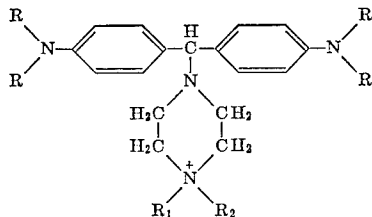
Alternatively, the quaternary leucoauramine compounds may be prepared by initially quaternizing the quaternizable nitrogen atom contained in the primary or secondary amine and then condensing the benzhydrol with the resulting quaternized primary or secondary amine. Such quaternization of the primary or secondary amine can be effected by treating the primary or secondary amine with a quaternizing agent providing the appropriate

R<sub>1</sub> group in the presence of a suitable solvent medium such as an alcohol. The benzhydrol can then be added to the resulting solution of the quaternized primary or secondary amine for condensation therewith; and the resulting quaternized leucoauramine compound can be recovered as by evaporation of the solvent medium. A quaternized primary amine typically suitable for this purpose comprises N',N'-diethyl-N'-methyl trimethylene diammonium bromide; and a quaternized secondary amine typically suitable for this purpose comprises ([3-N-methylaminophenyl]methyl) - ethyldimethyl ammonium ethyl sulfate.

The quaternary leucoauramine compounds of the invention, as will be appreciated, include a positively charged nitrogen atom and are thus ionic in nature. As a result, in contrast to the corresponding leucoauramines themselves, these quaternized compounds are insoluble in non-polar solvents or media such as petroleum hydrocarbons, aromatic hydrocarbons, waxes and vegetable oils. Being ionizable, however, these quaternary leucoauramine compounds are readily soluble in water; and they also possess greater solubility in polar and semi-polar solvents such as ethanol and acetone than the corresponding unquaternized leucoauramine compounds.

Moreover, these quaternary leucoauramine compounds not only retain the color-producing property of the corresponding leucoauramines themselves, but improved results are obtained when such a quaternary leucoauramine compound is utilized as the color precursor in an impact-printing system. For example, because of their water-solubility, these quaternary leucoauramine compounds can be incorporated in the internal phase of an aqueous wax emulsion of the water-in-oil type for use as the coating on the transfer sheet of an impact-duplicating arrangement, with the result that migration of the quaternary leucoauramine compound through such coating is effectively prevented and the production of premature color development in the acidic-material coating on the associated copy sheet is avoided. The present quaternary leucoauramine compounds also produce an instantaneous, intense color formation on the copy sheet upon impact pressure in contrast to the relatively slow color formation encountered with many of the corresponding leucoauramines themselves. Such imprint on the copy sheet, in addition, is clear and sharp as contrasted with the indistinct and otherwise unclear imprint frequently obtained when the corresponding leucoauramine compounds themselves are utilized as color precursors.

Those quaternary leucoauramine compounds which are obtained by condensing a benzhydrol of the type indicated above with an N-alkyl piperazine followed by appropriate quaternization of the resulting condensation product are particularly effective in producing such improved results. Such compounds, which constitute a preferred embodiment of the present invention, have the formula



wherein R is an alkyl group having 1 to 4 carbon atoms, R<sub>1</sub> is an alkyl group having 1 to 4 carbon atoms or an aralkyl group, R<sub>2</sub> is an alkyl group having 1 to 4 carbon atoms, and A<sup>-</sup> is a chloride, bromide, or iodide anion or a mono-alkyl sulfate anion of which the alkyl portion has 1 to 4 carbon atoms. Preferably, R is a methyl or ethyl group; R<sub>1</sub> is a methyl or ethyl group or a benzyl group; and R<sub>2</sub> is a methyl or ethyl group. Generally, R, R<sub>1</sub> and R<sub>2</sub> are the same, in which case each may be a methyl group or an ethyl group. These three substituents may, however, be different, depending upon the R<sub>1</sub> group pro-

vided by the quaternizing agent and/or the R<sub>2</sub> group contained in the initial piperazine reactant.

The following examples will illustrate the invention:

#### EXAMPLE 1

A solution of 638 g. of Michler's hydrol (technical grade, 90% strength; 2.125 moles) and 213 g. (2.125 moles) of N-methyl piperazine in 3700 ml. of 95% methanol was heated at reflux temperature for 43 hours. The reaction mass was then cooled to room temperature and filtered. The filter cake was washed with 300 ml. of ethanol and dried in a vacuum oven at 40 to 45° C. The resulting crystalline, essentially colorless product, comprising bis(p-dimethylaminophenyl)-N'-methyl-piperazinyl methane, melted at 174° C. It was thereafter recrystallized from toluene.

A 3-liter, 3-neck flask, fitted with a condenser, an agitator, a thermometer and a dropping funnel, was charged with 264 g. (.075 mole) of such leucoauramine compound and 1320 ml. of dry benzene. The mixture was heated to 60° C. to effect solution. To the hot solution was added dropwise 94.5 g. (71 ml.; 0.75 mole) of dimethyl sulfate over a period of about 1 hour. The temperature rose to 73° C.; and a white granular precipitate formed during such addition. The reaction mass was allowed to cool overnight; and the precipitate was then collected on a Buchner funnel, using gentle suction, and was washed with 100 ml. of dry benzene. The washed product was covered with a polyethylene dam and suction-dried for 4 hours. After transfer to a vacuum drier, the product was further dried at room temperature overnight. The yield of N - bis(p - dimethylaminophenyl)-methyl-N',N'-dimethyl piperazinium methyl sulfate was 317 g. (90% of theory); it melted at 156 to 158° C.

An aqueous solution of this quaternary leucoauramine compound gave an instantaneous intense blue-violet color upon contact with filter paper impregnated with succinic acid.

#### EXAMPLE 2

To a 75° C. solution (protected by a drying tube) of 35.2 g. (0.1 mole) of bis(p-dimethyl-aminophenyl)-N'-methyl-piperazinyl methane (prepared as in Example 1) in 165 ml. of toluene, 15.4 g. (0.1 mole) of diethyl sulfate was added dropwise over 20 minutes. The resulting pale brown-yellow solution gradually became greenish, and an oily greenish product slowly separated. Heating was continued for an additional hour and 20 minutes. After cooling of the reaction mixture and decantation of the solvent, a brown gummy material remained. This residue was extracted with 100 ml. of hot (90° C.) Skellysolve C (a petroleum hydrocarbon mixture having a boiling point range of 88 to 99° C. and consisting predominantly of heptane) for about 20 minutes; then the solvent was decanted hot. The taffy-like residue was cooled to ambient temperature and then placed for a few minutes in an ice bath, during which time it changed to a resinous glass. After recovery, this resinous product was air-dried and ground, yielding a brownish powder. The yield of N - [bis(p-dimethylaminophenyl) - methyl]-N'-ethyl-N'-methyl piperazinium ethyl sulfate was 37.6 g. (70% of theory).

When brought into contact with filter paper impregnated with attapulgite and with filter paper impregnated with bentonite, an aqueous solution of this quaternary leucoauramine compound gave respectively an intense blue-violet color and an intense blue color. Similar contact of such aqueous solution with filter paper impregnated with succinic acid gave an immediate intense blue color.

#### EXAMPLE 3

To a 100° C. solution (protected by a drying tube) of 35.2 g. (0.1 mole) of bis(p-dimethylaminophenyl)-N'-methyl piperazinyl methane (prepared as in Example 1) in 165 ml. of toluene, 12.6 g. (0.1 mole) of benzyl

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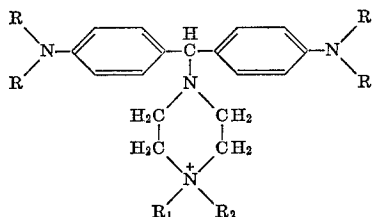
chloride was charged over 35 minutes. The solution slowly darkened, and a precipitate gradually deposited. Heating was continued for 5 hours at 100 to 110° C. After cooling of the reaction mixture to ambient temperature, a grey solid was recovered on a filter, successively washed with 100 ml. of toluene and 100 ml. of Skellysolve C, and then air-dried (using a protective plastic cover) for 4 hours. The yield of N-[bis(p-dimethylaminophenyl)-methyl]-N'-benzyl-N'-methyl piperazinium chloride was 33.4 g. (70% of theory).

When brought into contact with filter paper impregnated with attapulgite and with filter paper impregnated with bentonite, an aqueous solution of this quaternary leucoauramine compound gave respectively an intense blue-violet color and an intense blue color. Similar contact of such aqueous solution with filter paper impregnated with succinic acid gave an immediate intense blue coloration.

I claim:

1. A quaternary leucoauramine compound according to claim 10, in which A<sup>-</sup> is a mono-alkyl sulfate anion.

2. A quaternary leucoauramine compound having the formula



wherein R is an alkyl group having 1 to 4 carbon atoms, R<sub>1</sub> is a member selected from the class consisting of alkyl groups having 1 to 4 carbon atoms and phenyl alkyl having 1 to 4 carbon atoms in the alkyl moiety, R<sub>2</sub> is an alkyl group having 1 to 4 carbon atoms, and A<sup>-</sup> is an anion selected from the class consisting of chloride, bromide, and iodide anions and mono-alkyl sulfate anions of which the alkyl portion has 1 to 4 carbon atoms.

3. A quaternary leucoauramine compound according to claim 9, in which R, R<sub>1</sub> and R<sub>2</sub> are each a methyl group.

4. A quaternary leucoauramine compound according to claim 9, in which R, R<sub>1</sub> and R<sub>2</sub> are each an ethyl group.

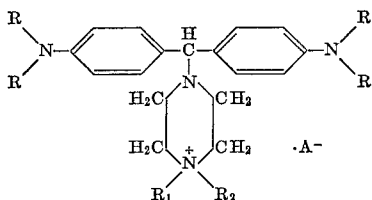
5. A quaternary leucoauramine compound according to claim 9, in which R<sub>1</sub> is a benzyl group.

6. N - [bis(p - dimethylaminophenyl) - methyl]-N',N'-dimethyl piperazinium methyl sulfate.

7. N - [bis(p - dimethylaminophenyl) - methyl] - N'-ethyl-N'-methyl piperazinium ethyl sulfate.

8. N - [bis(p - dimethylaminophenyl) - methyl] - N'-benzyl-N'-methyl piperazinium chloride.

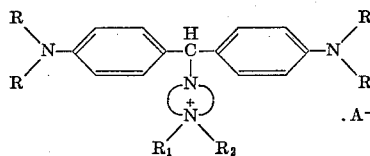
9. A quaternary leucoauramine compound having the formula



wherein R and R<sub>2</sub> are alkyl groups having 1 to 4 carbon atoms, R<sub>1</sub> is a member selected from the class consisting of alkyl groups having 1 to 4 carbon atoms and benzyl groups and A<sup>-</sup> is an anion selected from the class consisting of chloride, bromide, and iodide anions and mono-alkyl sulfate anions of which the alkyl portion has 1 to 4 carbon atoms.

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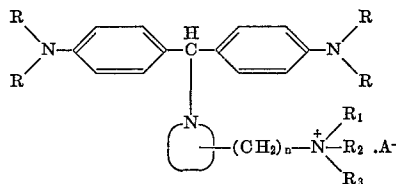
10. A quaternary leucoauramine compound selected from the class consisting of (1) those compounds having the formula



wherein R is an alkyl group having 1 to 4 carbon atoms;



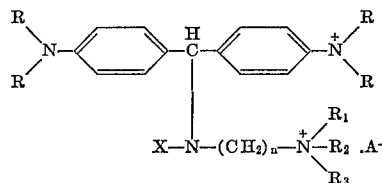
is a heterocyclic nucleus selected from the group consisting of piperazine, and methylpiperazine, R<sub>1</sub> is a member selected from the group consisting of alkyl groups having 1 to 4 carbon atoms, cyclohexyl and phenylalkyl having 1 to 4 carbon atoms in the alkyl moiety; R<sub>2</sub> is an alkyl group having 1 to 4 carbon atoms, and A<sup>-</sup> is an anion selected from the group consisting of chloride, bromide, iodide and mono-alkyl sulfate; (2) those compounds having the formula



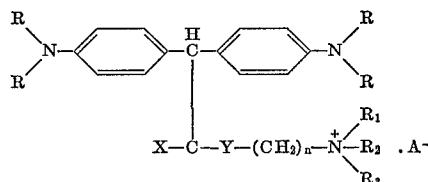
wherein R, R<sub>1</sub>, R<sub>2</sub> and A<sup>-</sup> respectively have the same meaning as above,



is piperidine; n is an integer from 1 to 18, R<sub>3</sub> is an alkyl group having 1 to 4 carbon atoms and R<sub>2</sub> and R<sub>3</sub> may together with the N atom form a piperidine group radical; (3) those compounds having the formula



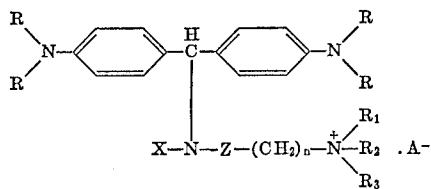
wherein R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, n and A<sup>-</sup> respectively have the same meaning as above, and X is a member selected from the group consisting of hydrogen, alkyl groups, having 1 to 4 carbon atoms, phenyl, benzyl and tolyl; (4) those compounds having the formula



wherein R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, X, n and A<sup>-</sup> respectively have the same meaning as above, and Y is an aryl group selected from the group consisting of phenyl, naphthyl, anthracyl

## 11

and biphenyl; and (5) those compounds having the formula



wherein R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, X, n and A<sup>-</sup> respectively have the same meaning as above, and Z is a heterocyclic nucleus selected from the group consisting of piperidine, piperazine, methylpiperazine and quinoline connected to the N atom through a ring carbon atom.

## 12

11. The compound of claim 10 wherein R<sub>1</sub> is an alkyl group having 1 to 4 carbon atoms, X is hydrogen or an alkyl group having 1 to 4 carbon atoms, and Y is phenyl.

## References Cited

## UNITED STATES PATENTS

3,375,279 3/1968 Moffett ..... 260—268 X

ALEX MAZEL, Primary Examiner

D. G. DAUS, Assistant Examiner

U.S. Cl. X.R.

106—22; 117—36.8; 260—239, 247.5, 250, 286, 288, 293, 296, 304, 305, 308, 309.6, 309.7, 310, 313.1, 315, 326.15, 346.2, 501.15, 515, 537, 567.6, 570, 578, 583, 648, 650

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,467,658 Dated September 16, 1969

Inventor(s) Benjamin Lipka

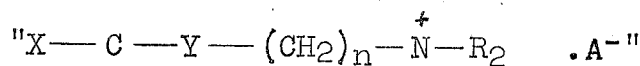
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the claims, claim 10, line 47 reading,

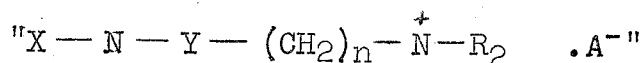
"together with the N atom form a piperidine group radical;"  
should read

"together with the  $\overset{+}{N}$  atom form a piperidine group;"

, line 70, that portion of  
the formula reading,



should read



SIGNED AND  
SEALED  
MAY 12 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.  
Attesting Officer

WILLIAM E. SCHUYLER, JR.  
Commissioner of Patents