PHOTOGRAPHIC COLOR DEVELOPING SOLUTIONS CONTAINING P-TOLUENESULFONIC ACID SALTS OF P-PHENYLENEDIAMINES

Inventors: Dietmar Schellenberg; Richard L. Bent, both of Rochester, N.Y.

Assignee: Eastman Kodak Company, Rochester, N.Y.

Filed: Dec. 3, 1971

App. No.: 204,725

U.S. Cl.................... 96/55, 96/22, 96/66 R
Int. Cl...................... G03c 7/00
Field of Search............ 96/55, 66, 66.3, 66.4, 96/66 HD

References Cited

UNITED STATES PATENTS
3,656,950 4/1972 Bent et al..................... 96/66 R

Primary Examiner—J. Travis Brown
Attorney, Agent, or Firm—Alfred P. Lorenzo

ABSTRACT

The p-toluenesulfonic acid salts of certain p-phenylenediamine color developing agents have been found to possess extraordinarily and unexpectedly high solubility in aqueous alkaline solution. Thus, extremely concentrated solutions of these materials can be prepared to provide developer "concentrates" which are extremely economical to ship and working developer solutions which possess abnormally high developing agent concentrations and which are therefore capable of producing unusually high dye density levels in very short periods of time. Specifically preferred among these p-phenylenediamine salts are the di-p-toluenesulfonic acid salts of 3-alkyl and 3-alkoxy N-alkyl-N-alkoxyalkyl-p-phenylenediamine developing agents.

9 Claims, No Drawings
PHOTOGRAPHIC COLOR DEVELOPING SOLUTIONS CONTAINING P-TOLUENESULFONIC ACID SALTS OF P-PHENYLENEDIAMINES

This invention relates to color photography and more particularly to color photographic developing agents which are capable of forming unusually highly concentrated aqueous alkaline solutions and hence, provide faster rates and shorter times of color development.

In the process of color photography, it is known to use p-phenylenediamines in conjunction with couplers to produce colored images. A summary of this process is described by Thistle et al., Encyclopedia of Chemical Technology, Vol. 5, pp. 812-845 (1964), John Wiley & Sons, Inc. The color developing agent is oxidized by the silver halide in the presence of a latent image in a photographic element to produce silver metal and oxidized color developing agent. The oxidized color developing agent then couples with color-producing compounds present to produce a dye image-wise with respect to silver development.

Color development of the differently sensitized emulsion layers in color photographic elements containing non-diffusible couplers is advantageously performed in a single color development step to produce a color negative image reproduction when this development step is the first development step, or to produce a color reversal image if a negative black-and-white development step is used followed by a step in which the residual unexposed and undeveloped silver halide is made developable and then color developed. In reversal color photographic elements that do not contain non-diffusible couplers, diffusible couplers are used in the aqueous alkaline color developer solutions that are used to selectively color develop one silver halide emulsion layer at a time. The reversal processing of such a multicolor, multilayer element (containing no incorporated couplers) requires a negative black-and-white process followed by a step in which residual unexposed and undeveloped silver halide in each emulsion layer is selectively made developable, then that layer is color developed with a color developing solution containing a diffusible coupler that forms a nondiffuse dye that is complementary in color to the light-sensitivity of that layer, then the unexposed and undeveloped silver halide in a second emulsion layer is selectively made developable and color developed with another color developing solution containing a diffusible coupler that forms a nondiffuse dye that is complementary in color to the light-sensitivity of that layer. Following completion of the color development, the silver and any residual silver halide are removed by silver bleaching and then fixing the photographic element. In any such color process, it is important that as large as practical and possible a quantity of color developing agent be brought into contact with the exposed, black-and-white developed etc. element within the shortest possible period of time so that maximum density dye images are produced with optimum efficient usage of the silver present in the photographic element in the minimum amount of time.

Also, in recent years, in order to eliminate the need for complex, expensive mixing equipment at the processor's location, it has become the custom in the trade to provide processing chemicals in the form of concentrated aqueous solutions which, while they are easier to dissolve or dilute with water than the dry processing chemicals, provide similar results. This dissolution of dry chemicals often required several hours of intense mixing with expensive equipment, and sometimes resulted in solutions containing substantial amounts of undissolved solute which rendered practical usage thereof impossible.

In view of the costs of shipping such concentrates attempts have continually been made to reduce the amount of water which had to be shipped in the concentrates and consequently to increase the concentration of the working chemicals (i.e., developer, bleach, fix, etc.) to the highest practical levels which provide a stable solution.

Thus, in the photographic arts there has existed a definite need and desire for, among other things, more concentrated solutions of p-phenylenediamine color developing agents which provide faster rates of color development and hence shortened color development times for color photographic elements and simultaneously permit the preparation of extremely concentrated solutions of color developer for shipment from the supplier to the processor customer.

Among the prior art suggesting methods for increasing the solubility of p-phenylenediamine developing agents are a large number of references which suggest the formation of the inorganic e.g. HCl salts of such compounds. More recently attempts to increase the solubility of these materials have been directed to the formation of organic salts thereof. Among this art is U.S. Pat. No. 2,618,558 to Vittum et al., which suggests the use of a benzene sulfonate of the formula:

\[
\text{R-SO}_2\text{M}
\]

wherein R is hydrogen or a lower alkyl radical and M is ammonium or alkali metal to increase solubility. British Patent No. 837,491 to Imperial Chemical Industries Ltd. suggests the use of an acid with the formula X-\text{Ar-SO}_2\text{H} wherein \text{Ar} represents an arylene radical and X is a carboxylic or sulphonlic acid group.

As will be demonstrated hereinafter, the method and compositions of the present invention provide solubilities on the order of 10 to 30 times greater than those demonstrated by these prior art methods.

SUMMARY OF THE INVENTION

It has now been discovered that the p-toluene-sulfonic acid salts of p-phenylenediamine color developing agents are unusually soluble in aqueous alkaline solutions of the type used as working solutions in the color development of multilayer color photographic elements and as concentrates for the shipping of such color developers from the chemical manufacturer to the processor.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention the p-toluene-sulfonic acid salts of color developing agents having the formulas:
wherein R₁ and R₂ are alkyl groups having from 1 to 4 carbon atoms i.e. methyl, ethyl, propyl, butyl etc., hydroxy alkyl groups having from 1 to 4 carbon atoms i.e. hydroxy methyl, hydroxy ethyl, etc., or alkoxy alkyl groups having from 2 to 8 carbon atoms i.e. methoxy methyl, methoxy ethyl, ethoxy methyl, ethoxy ethyl etc. and R₃ is an alkyl or alkxy group having from 1 to 4 carbon atoms have been found to have unusually and unexpectedly high solubility in aqueous alkaline solution.

The p-toluene sulfonic acid salts of these developing agents are generally represented by the following generic formula:

\[ \text{R}_1 / Y (II) \text{R}_2 \]

wherein n is either 1 or 2 and R₁, R₂ and R₃ are all as described above.

Specifically preferred among this class of materials are those having the following generic formula:

\[ \text{CH}_2\text{CH}-\text{N}-(\text{CH})_n-\text{O}-(\text{Hso}-(\text{CH})_2) \]

wherein m is an integer of 2 to 4; R is an alkyl group having 1 to 4 carbon atoms, e.g. methyl, ethyl, propyl, butyl, etc. and R¹ is an alkyl group having from 1 to 4 carbon atoms, e.g. methyl, ethyl, propyl, butyl etc., or an alkxy group having from 1 to 4 carbon atoms, e.g. methoxy, ethoxy, propoxy, butoxy. These compounds have been found to be extremely and unexpectedly more soluble in aqueous alkaline solutions that even the toluenesulfonic acid salts of other p-phenylenediamine developers which also demonstrate improved solubility. Thus, the formulation of even more concentrated “concentrates” of these materials in aqueous alkaline solution is possible. This provides working color developer solutions which yield higher development rates due to the higher developing agent levels. Furthermore, color developing agents falling within the aforementioned generic Formula I possess other substantial processing advantages which will be discussed in greater detail hereinafter and which are described in substantial detail in U.S. Pat. application Ser. No. 94,992 filed Dec. 3, 1970 and issued Apr. 25, 1972 as U.S. Pat. No. 3,658,525 and application Ser. No. 94,993 filed Dec. 3, 1970 and issued Apr. 18, 1972 as U.S. Pat. No. 3,656,950. These applications are incorporated herein by reference. Furthermore, the high solubility of these salts permits the use of higher developer concentrations in “PODS” of the type used in the “picture-in-a-minute” photographic system of the type described in U.S. Pat. Nos. 3,537,851 and 3,537,852 to Bloom issued July 1, 1968. The advantages of having high volume of color developer present in an extremely small amount of solvent in these and other photographic systems will of course be readily apparent to those skilled in this art.

Typical representative examples of the preferred color developing agents of Formula I are the following:

1. N-Ethyl-N-methoxymethyl-3-methyl-p-phenylenediamine
2. N-Ethyl-N-methoxybutyl-3-methyl-p-phenylenediamine
3. N-Ethyl-N-ethoxyethyl-3-methyl-p-phenylenediamine
4. N-Ethyl-N-methoxymethyl-3-n-propyl-p-phenylenediamine
5. N-Ethyl-N-methoxyethyl-3-methoxy-p-phenylenediamine
6. N-Ethyl-N-butoxyethyl-3-methyl-p-phenylenediamine

In general, the color developing agents of Formula I are prepared by reacting the appropriate α-alkoxyalkyl chloride or bromide with the appropriate N-ethyl-3-alkyl-aniline or N-ethyl-3-alkoxyaniline. The tertiary anilines formed by this reaction are then either nitrosated or azo-coupled followed by catalytic hydrogenation to give the corresponding p-phenylenediamine. The p-toluenesulfonic acid salts of these materials are generally prepared by forming the 4-(2,5-Dichlorophenylazo) derivative of the p-phenylenediamine derivative of Formula I, reducing the azo dye and adding p-toluenesulfonic acid.

Specifically, the di-p-toluensulfonic acid salt of Preferred Color Developing Agent 3 is advantageously prepared by the following sequence of reactions:

I. N-(β-Ethoxyethyl)-N-ethyl-3-methylaniline
A mixture of 135 g (1 mole) of N-ethyl-3-aniline, 153 g (1 mole) of 2-bromoethyl ethyl ether (purified by treatment with sodium bicarbonate and distillation), 0.8 g (1.05 mole) of sodium bicarbonate, 1,100 ml of ethanol and 290 ml of water are refluxed for a total of 64 hours. The ethanol is removed by distillation and the oil layer is extracted with ether; the ether extracts are dried and concentrated, followed by distillation of the residual oil under reduced pressure. After removal of the lower boiling foreruns, the fraction, b.p. 92°-95°C/1mm (overheats readily) is collected. The yield of I is approximately 70 percent.

II. 4-(2,5-Dichlorophenylazo)-N-(β-ethoxy-ethyl)-N-ethyl-3-methylaniline
A total of 44 g (0.27 mole) of 2,5-dichloroaniline is dissolved in a mixture of 240 ml concentrated hydrochloric acid and 700 ml of water by heating with stirring on a steam bath. When solution is complete, the reaction mixture is cooled with stirring to 5°C, the hydrochloric salt precipitating out. A solution of 19 g (0.275 mole) of sodium nitrite in 75 ml of water is added dropwise with stirring, keeping the temperature at about 5°C. When complete, stirring is continued for another 20 minutes and the excess nitrous acid destroyed by the addition of sulfamic acid. The cold diazonium solution is filtered and at once added to a cold solution of 56 g (0.27 mole) of I in dilute hydrochloric acid. Considerably more water is added and with stirring a total of 250 g of sodium acetate is added to promote the coupling. After standing for a few hours, the azo dye is filtered off and at once recrystallized from approximately 1,000 ml of ethanol. This is followed by
The di-p-toluensulfonic acid salt of Color Developing Agent 2 is made in a manner similar to the synthesis described for the corresponding acid salt of Color Developing Agent 5, excepting that an equimolar amount of 3-bromobutyl methyl ether is used in place of 2-bromoethyl methyl ether.

The di-p-toluensulfonic acid salt of Color Developing Agent 4 is advantageously made in a manner similar to that described for the corresponding acid salt of Color Developing Agent 3, excepting that an equimolar amount of N-ethyl-3-propylaniline is used in place of N-ethyl-3-methylaniline.

Still other color developing agents of Formula I are made using the synthesis illustrated herein using the appropriate starting materials and intermediates.

The following examples are included for a further understanding of our invention and the utility thereof.

EXAMPLE 1

Saturated solutions of various of the color developing agents described herein were obtained by gradually adding small amounts of developer salts to water under nitrogen atmosphere and adjusting the pH with alkali to pH 10.0 after each addition. Saturation was indicated by the initial appearance of turbidity (further addition caused phase separation). The solutions were analyzed for developing agent and the results converted to g/l or mol/l of substance in the saturated solution. The results are tabulated in Table 1.

EXAMPLE 2

The procedure described in Example 1 was repeated with solutions of different pH values. The results are tabulated in Table 2.

EXAMPLE 3

The procedure described in Example 1 was repeated by adding the developer salt to sodium carbonate solutions of 25, 100 or 320 g/l, respectively, to simulate actual color developer solutions. The results are tabulated in Table 3.

EXAMPLE 4

The procedure described in Example 1 was repeated by adding the developer salt to solutions with 50, 100 or 150 g/l NaPTS. The results are summarized in Table 4.

EXAMPLE 5

The procedure described in Example 1 was repeated by adding the developer salt to a solution with 120 g/l NaPTS. The results are given in Table 5.
Table 2: Small changes in pH (pH 10 ± 1 or 2 units) have little influence on the above results.

Table 3: Higher concentrations of inorganic salts in the solution decrease the solubility of p-phenylenediamines substantially, both for the inorganic and the PTS acid salts of the developing agents.

Table 4: The solubility of p-phenylenediamines with inorganic counteracids can be increased by adding Na-PTS to the solution. In the given example this increase is approximately 8 fold when 150 g/l NaPTS have been added to the solution.

Table 5: Addition of NaPTS to solutions which are ready contain the PTS salt of a p-phenylenediamine is undesirable. The solubility decreases. The PTS introduced with the developing agent obviously is sufficient to give the effect of increased solubility.

The following Example 6 will serve to further distinguish the method and compositions of the present invention from those of the prior art.

Example 6

To simulate an actual working developer solution solubility measurements were obtained by adding the developer or salt in weighed portions to a known volume of pH 10 phosphate buffer (μ = 0.75) to which had been added 2 g/l of Na₂SO₄. The mixture was stirred until solution was obtained (absence of scattered light) and the pH adjusted back to 10.0 by addition of NaOH (pellets). This process was repeated until a portion of the compound no longer dissolved. A repeat of the test using smaller portion additions near the solubility limit establishes the solubility of the compound under these 45 conditions. Storage of the solutions for several days at room temperature insures against supersaturation. The data shown in Table 6 represent the average of 3–4 replicates.

Table 6: Solubility in M/L. (of solvent) g/L. (of solvent)

<table>
<thead>
<tr>
<th>Aromatic primary amine</th>
<th>Free base</th>
<th>HCl salt</th>
<th>C₆H₅SO₃H salt</th>
<th>PTS salt</th>
<th>2β-(CH₂)₄C₆H₈SOH salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃C-N-C₂H₅</td>
<td>0.08 (18.9)</td>
<td>0.14 (72)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The foregoing Table 6 clearly demonstrates that in each case the PTS salt of the primary aromatic amine was more soluble than one or more of either the free base, the inorganic acid salt, the benzene sulfonate salt of U.S. Pat. No. 2,618,558 or the closely analogous 2,5-(CH₃)₂C₆H₄SO₃H.

Thus, it should be clear that use of the PTS salts of p-phenylenediamine developing agents, preferably those of the type defined by Formula II, and even more advantageously those of Formula III, above permits dissolution of substantially larger quantities of developing agent in a given amount of solvent than has heretofore been possible.

The utility of the PTS salts described hereinabove and of the aqueous alkaline solutions prepared therefrom in photographic processing systems will be readily recognized by those skilled in the photographic arts, however, concrete examples of this utility as well as the advantages which can be achieved when specific members of the class of p-phenylenediamine are used as developing agents are presented in the aforementioned copending U.S. Pat. Applications Ser. Nos. 94,992 and 94,993 which have been incorporated herein by reference.

Generally, these organic acid salts of p-phenylenediamine developing agents will be used in aqueous alkaline solution at a pH above about 8 and preferably above about 9.5. The concentration of the salt present in the solution will be dependent upon the concentration of developing agent which is required. Generally, this concentration will range from about 0.5 to about 15 g/l in working developer compositions depending upon the particular system to which the developer is to be applied. However, in "concentrates" suitable for shipping and dilution prior to use as working developers, the concentration of PTS salt is limited only by its own solubility and the stability of such a solution under a given set of conditions of storage and shipping. Thus, in working solution the concentration of the PTS salt is limited by the use to which the solution is to be put and hence the amount of developer which it is sought to have present therein. Theoretically, at least as far as the specific color developing agents described in Formula II hereinabove are concerned, the problem of color developer solubility no longer exists since the limits of the solubility of the PTS salts of these materials are generally at or well above the practical concentration limits for those materials in working solutions.

As demonstrated by the foregoing examples the instant invention demonstrates the following distinct advantages:

A. p-phenylenediamines with p-toluenesulfonic acid (PTS) counteracid have a considerably higher solubility than the same compounds as free bases which are highly unstable and dissolve poorly or as salts with other organic or inorganic counteracids which have only slightly improved solubility;

B. the addition of sodium benzene sulfonate at the levels taught in U.S. Pat. No. 2,618,558, i.e. 20–200 g/l increases the solubility of the model compounds from 0.007 mole/l to 0.035 mole/l for the highest concentrations of benzene sulfonate (data derived from U.S. Pat. No. 2,618,558). Using the PTS salt of p-phenylenediamine increases the solubility to more than 1 mole/l implying that together with the developing agent amounts of more than 388 g/l of Na-PTS would have been added in that case.

Thus, it has now been discovered that compositions having the following generic structure:

```
R₁-N-R₂
```

wherein n is either 1 or 2; R₁ and R₂ are lower alkyl, hydroxy lower alkyl, or alkoxy lower alkyl and R₃ is lower alkyl or lower alkoxy have unexpectedly high solubility in aqueous alkaline solutions of the type utilized for the color development of color photographic elements and that hence they possess all of the above-described advantages incident to such unusually high solubility.

Solutions of these materials can of course include all of the addenda incident to developer compositions of the type described including but not limited to color developer stabilizing agents, alkali metal chloride, alkali metal bromide, sulfite ion and the alkali metal salts of weak acids.

Solutions of the PTS salts of the color developers described by Formulas I and II are formed simply by dissolving the same in an aqueous alkaline solution. Generally the working developer solutions can comprise up to about 200 g/l of color developing agent although much lower concentration levels on the order of from about 0.5 to about 15 g/l will provide satisfactory results in conventional photographic processing above.

Concentrations above this level are useful when it is sought to speed up the development rate and/or to increase the throughput capability of the developer bath. Thus, in conventional practice, concentrated aqueous alkaline solutions of the PTS salts of the developing agent, i.e. those solutions having concentrations above about 200 g/l will generally be prepared for shipping and storage. These "concentrates" may contain as much of the salt as tolerable in the particular system so that precipitation or phase separation does not occur. When received by the consumer-processor these "concentrates" will be diluted with water to provide working solutions with color developer agent concentration of up to, for example, perhaps 200 g/l. The concentrate will generally contain a sufficient amount of alkali i.e. sodium, potassium or ammonium hydroxide or sodium or potassium carbonate to provide when dissolved in water to yield the desired developing agent concentration, a solution of the developing agent which has a pH above about 8 and preferably above about 9.5.

Since the active developing agent of working developer solutions prepared from such concentrates are p-phenylenediamine developing agents they will include small amounts of sulfite ion which stabilize the developing agent against aerial oxidation during storage as a concentrate and while in use as a working developer solution.

Furthermore, in addition to the other addenda such as benzy alcohol, (0–15 ml/l) alkali metal chlorides (0–15 g/l), alkali metal bromides (0.1–1.0 g/l), alkali metal or ammonium sulfite (0.1–5.0 g/l) and alkali metal or ammonium salts of weak acids (10.0–50.0 g/l) which are conventionally present in p-phenylenediamine developer solutions of this type in
the concentration ranges shown in parentheses, it is generally desirable to incorporate a stabilizer composition which insures that the developer does not separate into phases at levels of from about 0.1 to about 5.0 g/l. Two such stabilizers are hydroxylamine sulfate and di-
hydroxyacetone.

Once “working” developer solutions of the novel PTS Salts of p-phenylenediamine developing agents described hereinabove are prepared, their use is in the conventional fashion well known to those skilled in the art. In brief the color development of a multilayer silver halide color emulsion layer is accomplished by contacting the silver halide with an aqueous alkaline solution of a p-phenylenediamine developing agent in the presence of a coupler that reacts with oxidized developing agent to form a dye. In accordance with the present invention the improvement in such a process comprises using the p-toluenesulfonic acid salt of the p-
phenylenediamine developing agent as the developing agent to provide higher concentrations of developing agent than would normally otherwise be possible. It is of course possible to use these salts to obtain conventional levels of developer concentrations the advantage in such usage being the ease with which dissolution is achieved and the certainty that these materials will remain in solution at these relatively low concentration levels in view of their extremely high solubility in aqueous alkaline solvent systems.

The invention has been described in detail with specific reference to preferred embodiments thereof; however, it should be understood that variations and modifications can be effected within the spirit and scope of the invention and that the same should not be limited except as specified in the appended claims.

I claim:

1. An aqueous alkaline photographic color developing solution containing, as the color developing agent, a p-toluenesulfonic acid salt which is highly soluble in aqueous alkaline solutions, said p-toluenesulfonic acid salt having the formula:

\[
\text{R}_1\text{N}-\text{R}_2\left(\text{H}_2\text{SO}_3-\text{D-OH}\right)_m\text{R}_3
\]

wherein \( n \) is an integer having a value of from 1 to 2; each of \( \text{R}_1 \) and \( \text{R}_2 \) is a member selected from the group consisting of alkyl groups of 1 to 4 carbon atoms, hydroxyalkyl groups of 1 to 4 carbon atoms, and alkoxyalkyl groups of 2 to 8 carbon atoms; and \( \text{R}_3 \) is a member selected from the group consisting of alkyl groups of 1 to 4 carbon atoms and alkoxy groups of 1 to 4 carbon atoms.

2. The photographic color developing solution of claim 1 wherein said p-toluenesulfonic acid salt has the formula:

\[
\text{R}_1\text{N}-\text{R}_2\left(\text{H}_2\text{SO}_3-\text{D-OH}\right)_m\text{R}_3
\]

wherein \( m \) is an integer having a value of from 2 to 4, \( \text{R}_1 \) is an alkyl group of 1 to 4 carbon atoms and \( \text{R}_2 \) is a member selected from the group consisting of alkyl groups of 1 to 4 carbon atoms and alkoxy groups of 1 to 4 carbon atoms.

3. The photographic color developing solution of claim 1 wherein said p-toluenesulfonic acid salt is a di-p-toluenesulfonic acid salt of a member selected from the group consisting of:

- N-Ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine;
- N-Ethyl-N-methoxybutyl-3-methyl-p-phenylenediamine;
- N-Ethyl-N-ethoxyethyl-3-methyl-p-phenylenediamine;
- N-Ethyl-N-methoxymethyl-3-propyl-p-phenylenediamine;
- N-Ethyl-N-methoxyethyl-3-methoxy-p-phenylenediamine;
- N-Ethyl-N-butoxyethyl-3-methyl-p-phenylenediamine.

4. The photographic color developing solution of claim 1 further including a stabilizing amount of a water-soluble sulfite.

5. An aqueous alkaline photographic color developing solution containing, as the color developing agent, the di-p-toluenesulfonic acid salt of N-ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine.

6. In a process of color developing a photographic element by contacting said element with an aqueous alkaline solution of a salt of a p-phenylenediamine color developing agent in the presence of a coupler that reacts with oxidized color developing agent to form a dye, the improvement wherein said salt is a p-toluenesulfonic acid salt of the formula:

\[
\text{R}_1\text{N}-\text{R}_2\left(\text{H}_2\text{SO}_3-\text{D-OH}\right)_m\text{R}_3
\]

wherein \( n \) is an integer having a value of from 1 to 2; each of \( \text{R}_1 \) and \( \text{R}_2 \) is a member selected from the group consisting of alkyl groups of 1 to 4 carbon atoms, hydroxyalkyl groups of 1 to 4 carbon atoms, and alkoxyalkyl groups of 2 to 8 carbon atoms; and \( \text{R}_3 \) is a member selected from the group consisting of alkyl groups of 1 to 4 carbon atoms and alkoxy groups of 1 to 4 carbon atoms.

7. The process of claim 6 wherein said salt has the formula:

\[
\text{H}_3\text{C}_\text{R}_1-\text{N}-(\text{CH}_2)_m-0-\text{R}_1
\]

wherein \( m \) is an integer having a value of from 2 to 4, \( \text{R}_1 \) is an alkyl group of 1 to 4 carbon atoms and \( \text{R}_2 \) is a member selected from the group consisting of alkyl
groups of 1 to 4 carbon atoms and alkoxy groups of 1 to 4 carbon atoms.
8. The process of claim 6 wherein said salt is a di-p-toluenesulfonic acid salt of a member selected from the group consisting of:
   1. N-Ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine;
   2. N-Ethyl-N-methoxybutyl-3-methyl-p-phenylenediamine;
   3. N-Ethyl-N-ethoxyethyl-3-methyl-p-phenylenediamine;
   4. N-Ethyl-N-methoxyethyl-3-n-propyl-p-phenylenediamine;
   5. N-ethyl-N-methoxyethyl-3-methoxy-p-phenylenediamine;
   and
9. The process of claim 6 wherein said salt is the di-p-toluenesulfonic acid salt of N-ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine.
********
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,816,134  Dated June 11, 1974

Inventor(s)  Dietmar Schellenberg, et al

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

The term of this patent subsequent to April 25, 1989,

has been disclaimed.

Signed and Sealed this

Twenty-fourth Day of August 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks