

[72] Inventors **Gregoire Kalopissis**
Paris;
Andree Bugaut, Boulogne sur Seine, both of
France
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[73] Assignee **Societe anonyme dite: L'Oreal**
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[54] **1-METHYLAMINO-2-NITRO-4-(2'-**
HYDROXYETHYL)-METHYLAMINO BENZENE
FOR DYEING HUMAN HAIR
8 Claims, No Drawings

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Primary Examiner—Albert T. Meyers

Assistant Examiner—Vera C. Clarke

Attorney—Holcombe, Wetherill & Brisebois

ABSTRACT: An improved dye compound 1-methylamino-2-nitro-4-(2'-hydroxyethyl)-methylaminobenzene and a method of making it. A hair dye composition containing this compound and the method of dyeing hair with this composition.

1-METHYLAMINO-2-NITRO-4-(2'-HYDROXYETHYL)-METHYLAMINO BENZENE FOR DYEING HUMAN HAIR

Nitroparaphenylenediamine is a known active ingredient used in dyes for living hair.

Various substituted products have been proposed in order to produce deeper shades than those produced by nitroparaphenylenediamine itself, and among these are alkyl groups and hydroalkyl groups.

In particular the use of trihydroxyalkylated derivatives of nitroparaphenylenediamine has been suggested, and especially those trihydroxyethyls having a hydroxyethyl radical on the amino group in the ortho position of the nitro group and two hydroxyethyl radicals on the amino group in the meta position of the nitro group.

However, it is very difficult to obtain without tedious purification a commercially satisfactory yield of a trihydroxyethylated derivative of the type in question from nitroparaphenylenediamine, for example, by halohydrin action, for the substitution of the hydroxyethylated groups for the hydrogens of the amine functions leads in practice not to a pure trihydroxyethylated product, but instead to a mixture of mono-, di-, or trisubstituted products, each having a dyeing power of its own, said mixture often comprising also tarry impurities.

Under the operating conditions which prevail during this substitution, the proportions within the resulting mixture vary, and the shades produced when the mixture is used cannot therefore be exactly reproduced.

The object of the present invention is to provide a new nitrated hair dye and the coloring compositions which can be made with this new dye.

The new dye is 1-methylamino-2-nitro-4-(2'-hydroxyethyl)-methylaminobenzene.

The invention also comprises a method of manufacturing this new dye. This process consists in starting with 1-amino-2-nitro-4-methylaminobenzene, transforming this by methylation into 1-methylamino-2-nitro-4-methylaminobenzene, and subjecting the resulting product to hydroxyethylation, using a glycol halohydrin.

In this process the amine function in position 1 is methylated by blocking the position of the hydrogen atom carried by the amine group in position 4 with acetic anhydride, then blocking the position of one of the hydrogen atoms of the amine function in position 1 with paratoluene-sulfochloride, methylating the resulting product with a neutral methyl sulfate, and finally freeing the two previously blocked positions using first sulfuric acid to detach the tosyl group carried by the nitrogen atom in position 1, and then hydrochloric acid to detach the acetyl group carried by the nitrogen atom in position 4.

Applicants have discovered that, under the foregoing conditions, the nitro group is readily hydroxyethylated in the meta position with a commercially satisfactory yield, and without impurities. In this way, since a methyl group on one of the amine groups may be easily substituted on the initial product, after which a hydroxyethyl group is substituted on the other amino group, a product which will produce constant, reproducible, results is obtained, since there is no contamination by any secondary coloring agent.

It has been determined that with 1-methylamino-2-nitro-4-(2'-hydroxyethyl)-methylaminobenzene perfectly uniform deep shades of violet are obtained. It should moreover be noted that this dye has an excellent affinity for the keratinic fibers of human hair and that the hair dyes made with it are especially resistant to shampooing, yet have no coloring effect on the scalp.

The hair dyes comprising the composition according to the invention are simple aqueous solutions containing the composition, preferably having an alkaline pH. No oxidizing agent is required to develop the color. Various additives known in the hair-coloring art may be included, such as organic solvents, thickening agents, detergents, and lacquers.

The time during which the hair-coloring solutions should be kept in contact with the hair varies within broad limits, but is preferably between 5 and 30 minutes.

The temperature of application may also be varied, but in most cases the dye is applied at room temperature. The pH of these solutions is usually between 7 and 10 and preferably between 8 and 9.5. Among the alkaline products which may be used to adjust the pH are ammonia, any organic base, for example and alkylamine, an alkanolamine, or a heterocyclic amine. The concentration of the dye may be varied over a wide range, but this concentration is preferably between 0.1 and 3 percent.

It should be noted that the dye according to the invention may be mixed with other dyes, whether nitrated, azo, anthraquinone, or of any other type conventionally used for dyeing hair.

The process of preparing 1-methylamino-2-nitro-4-(2'-hydroxyethyl)-methylaminobenzene in accordance with the invention will now be described, but it will be appreciated that not only bromohydrin, but any other halohydrin of ethanediol, can be used for the hydroxyethylation.

Preparation of 7-amino-2-nitro-4-methylacetaminobenzene.

0.258 moles of 1-amino-2-nitro-4-methylaminobenzene (i.e. 43.2 g.) are dissolved in 85 cm.³ of dioxane and 0.266 moles (25.2 cm.³) of acetic anhydride are added little by little, while maintaining the temperature at 70° C. After cooling 44.9 g. of an acetylated derivative which melts at 165° C. are obtained by drying.

Preparation of paratoluene-1-sulfonylamino-2-nitro-4-methylacetaminobenzene.

0.43 moles (82 g.) of paratoluene-sulfochloride is added to a solution of 0.287 moles (60 g.) of 1-amino-2-nitro-4-methylacetaminobenzene at a temperature of 40° to 45° C., little by little, while stirring the mixture. After the addition has been completed, the mixture is kept at 45° C. for 2 hours, emptied into a liter of cold water, after which soda is added to yield the desired product in the form of sodium tosylate. Any of the starting composition which remains untransformed is extracted using methyl isobutyl ketone. The aqueous phase is acidified with hydrochloric acid and, after cooling for several hours, 72 g. of paratoluene-1-sulfonylamino-2-nitro-4-methylacetaminobenzene is removed by drying. After recrystallization, this product melts at 120° C.

Analysis of the End Product

	Calculated	Found
C%	52.89	53.03-52.82
H%	4.68	4.55-4.59
N%	11.57	11.53-11.70

Preparation of methyl-paratoluene-1-sulfonylamino-2-nitro-4-methylacetaminobenzene.

0.16 moles (15.7 cm.³) of methyl sulfate are added to a solution of 0.110 moles (40 g.) of paratoluene-1-sulfonylamino-2-nitro-4-methylacetaminobenzene in normal soda, while stirring and keeping the temperature between 40° and 45° C. After cooling, the mixture is dried and the resulting 40.5 g. of methyl-para-toluene-1-sulfonylamino-2-nitro-4-methylacetaminobenzene is washed with water. After recrystallization in acetic acid this product melts at 225° C.

Analysis of End Product

	Calculated	Found
C%	54.11	54.08-54.04
H%	5.04	5.06-4.92
N%	11.14	11.35-11.30

Preparation of 1-methylamino-2-nitro-4-methylacetaminobenzene.

0.08 moles (33.35 g.) of methyl-paratoluene-1-sulfonylamino-2-nitro-4-methylacetaminobenzene, are added little by little, while stirring, to 62 cm.³ of sulfuric acid cooled in ice. When the addition has been completed the mixture is left for 4 hours at 15° C. It is then poured over cracked ice and dried. The resulting 16 g. of 1-methylamino-2-nitro-4-methylacetaminobenzene is washed with water and, when recrystallized in ethyl acetate, melts at 158° C.

Analysis of End Product

	Calculated	Found
C%	53.81	53.56-53.75
H%	5.83	5.70-5.69
N%	18.83	19.17-19.05

Preparation of 1-methylamino-2-nitro-4-methylaminobenzene.

0.05 moles (11.2 g.) of 1-methylamino-2-nitro-4-methylacetaminobenzene are heated to reflux in 26 cm.³ of concentrated hydrochloric acid in 26 cm.³ of water. After cooling, the end product is obtained by drying in the form of a hydrochlorate. The hydrochlorate is dissolved in water and ammonia added to render the pH alkaline. Drying, after cooling, yields 8 g. of 1-methylamino-2-nitro-4-methylaminobenzene which melts at 114° C.

Analysis of End Product

	Calculated	Found
C%	53.00	52.67-52.52
H%	6.07	6.05-6.09
N%	23.21	23.32-23.36

Preparation of 1-methylamino-2-nitro-4-(2'-hydroxyethyl)-methylaminobenzene.

0.033 moles (6 g.) of 1-methylamino-2-nitro, 4-methylamino-benzene are mixed with 50 cm.³ of water and 3.5 g. of sodium carbonate, and boiled to reflux. 0.0695 moles (4.9 cm.³) of glycol bromohydrin is then added drop by drop. After 3 hours of reflux the mixture is cooled, acidified with 20 cm.³ of concentrated hydrochloric acid and the end product extracted using ethyl acetate to eliminate impurities. Ammonia is added in the aqueous phase to bring it to an alkaline pH and drying yields 5.7 g. of 1-methylamino-2-nitro-4-(2'-hydroxyethyl)-methylaminobenzene in a practically pure state. This melts at 92.5° C.

Analysis of End Product

	Calculated	Found
C%	53.33	53.21-53.24
H%	6.66	6.97-6.85
N%	18.66	18.90-18.66

Two examples will now be given, showing how the dyes according to the invention may be used in a preparation for dyeing the hair.

EXAMPLE 1

The following solution is prepared:

1-methylamino-2-nitro-4-(2'-hydroxyethyl)-methylaminobenzene	1 g.
oxyethylated lauric alcohol having 10.5 molecules of ethylene oxide	5 g.
ammonia q.s.p.	pH 7
water q.s.p.	100 g.

This solution is applied to completely white hair for 10 minutes. After the waiting period is over, the hair is rinsed, washed, and dried. An intense mauve shade results.

EXAMPLE 2

1-methylamino-2-nitro-4-(2'-hydroxyethyl)-methylaminobenzene	0.46 g.
1-amino-2-nitro-4-methylaminobenzene	0.06 g.
nitro-metaphenylenediamine	0.05 g.
nitro-paraphenylenediamine	0.02 g.
oxyethylated lauric alcohol having nine molecules of ethylene oxide	5 g.
ammonia q.s.p.	pH 9
water q.s.p.	100 g.

This solution is applied to completely white hair. It is left for 15 to 20 minutes, after which the hair is rinsed, shampooed, and dried. A clear copperish chestnut shade is obtained.

It will of course be appreciated that the processes of preparing the dye and the methods of applying it which have just been described may be modified as to detail without thereby departing from the basic principles of the invention.

What we claim is:

1. 1-methylamino-2-nitro-4-(2'-hydroxyethyl)-methylaminobenzene.
2. A composition for dyeing hair comprising an aqueous solution containing hair-dyeing amounts of the compound of claim 1.
3. A hair-dyeing composition as claimed in claim 2 having a pH between 7 and 10.
4. A hair-dyeing composition as claimed in claim 2 having a pH between 8 and 9.5.
5. A hair-dyeing composition as claimed in claim 2 in which the concentration of said compound lies between 0.1 and 3 percent.
6. The method of preparing 1-methylamino-2-nitro-4-(2'-hydroxyethyl)-methylaminobenzene comprising blocking the position of the hydrogen atom carried by the amine group in position 4 of 1-amino-2-nitro-4-methylaminobenzene by reacting it with acetic anhydride, and blocking the position occupied by one of the hydrogen atoms of the amine function in position 1 by reacting it with paratoluene-sulfochloride, methylating the resulting product with methyl sulfate, freeing the two blocked positions by reacting the methylated compound first with sulfuric acid and then hydrochloric acid, then reacting the resulting compound with glycol halohydrin to hydroxyethylate the nitrogen atom in position 4.
7. The method claimed in claim 6 in which the halohydrin is glycol bromohydrin.
8. The method of dyeing human hair which comprises the step of applying thereto a composition containing dyeing amounts of 1-methylamino-2-nitro-4-(2'-hydroxyethyl)-methylaminobenzene.

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