

1

3,578,386

DYEING HUMAN HAIR WITH BENZOTHAZOLE AZO COMPOUNDS

Gregoire Kalopissis, Paris, and Andree Bugaut, Boulogne-sur-Seine, France, assignors to L'Oreal, Paris, France
No Drawing. Filed Feb. 16, 1968, Ser. No. 705,925
Claims priority, application Luxembourg, Feb. 22, 1967, 53,050

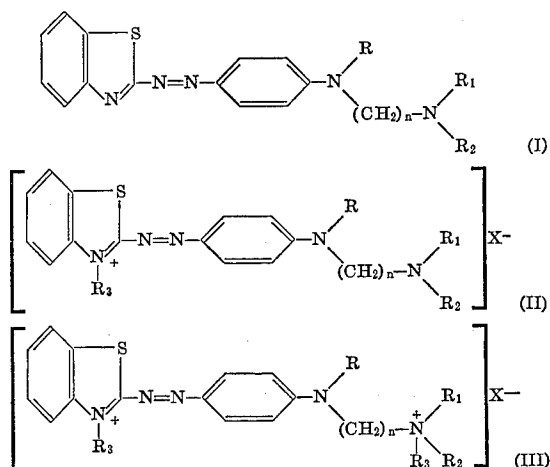
Int. Cl. A61k 7/12

U.S. Cl. 8-10

3 Claims

ABSTRACT OF THE DISCLOSURE

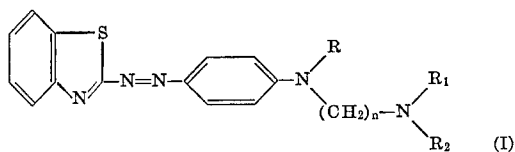
This invention relates to methods of dyeing and dyes for keratinic fibers, especially human hair with benzothiazole compounds corresponding to one of the following formulae:



In each of these formulae R, R₁ and R₂ may be lower alkyl radicals, but in some of the formulae they may be H or acyl radicals instead, as set forth in detail in the specification. Preferably R₁ and R₂ are combined with an adjacent N to form a heterocyclic radical falling within the group consisting of morpholino, piperidino and pyrrolidino radicals.

The object of the present invention is to provide a new dyeing composition for keratinic fibers and more particularly for human hair, essentially characterized by the fact that it contains in solution at least one compound taken from the group consisting of:

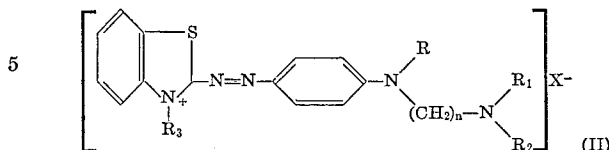
(a) the compounds having the general formula:



in which R represents a lower alkyl radical having from 1 to 4 carbon atoms; n is a number between 2 and 6 inclusive; R₁ represents a hydrogen atom or a lower alkyl radical having from 1 to 4 carbon atoms; R₂ represents a hydrogen atom, a lower alkyl radical having from 1 to 4 carbon atoms or an acyl radical and in which R₁ and R₂ may be included with the nitrogen in a heterocyclic ring falling within the group consisting of morpholino, piperidino and pyrrolidino radicals,

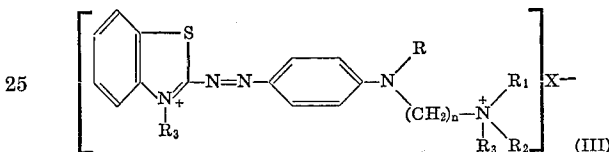
2

(b) the mono-quaternary compounds having the general formula:



in which R, R₁ and n have the significances indicated above, and R₂ represents a lower alkyl radical having from 1 to 4 carbon atoms or an acyl radical but cannot be a lower alkyl radical when R₁ represents a hydrogen atom; R₁ and R₂ may be included with the nitrogen in heterocyclic ring falling within the group consisting of morpholino, piperidino and pyrrolidino radicals, R₃ represents a lower alkyl radical and X a halogen atom or a SO₄CH₃ radical, it being understood that in the latter case R₃ may represent only a methyl group:

(c) the bis-quaternary compounds having the general formula:



in which R, R₃ and X have the significances indicated above, R₁ and R₂ each represent a lower alkyl radical having from 1 to 4 carbon atoms or may constitute part of a heterocyclic ring including nitrogen and falling within the group consisting of morpholino, piperidino and pyrrolidino radicals.

Certain of the compounds described above have already been described in French Pat. No. 1,443,251, in which it was shown that they could be used to dye polyacrylic fibers. The applicants have found that, surprisingly enough, use of the compounds yields particularly worthwhile results in the dyeing of keratinic fibers and, more particularly, for dyeing hair, due to the notable intensity, brilliance and fastness of the desired shades, which range from red to blue black. The blue shades obtained from the quaternary compounds are especially stronger than the blue shades heretofore obtained on hair by means of cationic anthraquinone dyes.

It should be made clear that the dyeing compositions according to the invention may be used in a relatively wide pH range, but that the pH of these compositions should preferably be between 5 and 8.

The length of time that the dyeing compositions according to the invention should be in contact with the hair may vary greatly, but should preferably fall between 5 and 30 minutes. The application temperature of these dyeing compositions may also vary, but in most cases, they should preferably be used at room temperature.

The concentrations of dyes responding to Formulas I, II and III may vary significantly in the dyeing compositions according to the invention, but this concentration is preferably between 0.01% and 3%.

It should be noted that the dyes according to the invention may be mixed with each other or with other dyes normally used in dyeing hair, such as benzene, anthraquinone or azo dyes.

Moreover, the dyeing compositions according to the invention may contain ingredients normally used in cosmetics, such as dispersing or wetting agents, thickeners, detergents, emollients or perfumes.

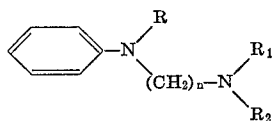
Another object of the present invention is to provide a process for dyeing keratinic fibers and particularly human hair essentially characterized by the fact that the hair is impregnated with a dyeing composition according to the

invention, such as those described above, and that the composition is allowed to act for 5 to 30 minutes after which the hair is shampooed, rinsed and then dried.

Another object of the present invention is to provide the new articles of manufacture consisting of those new chemical compounds having the Formulas I, II and III which are not described in the French Pat. No. 1,443,251, that is to say the new compositions consisting of those chemical compounds having the general Formula I, II or III, in which the radicals R_1 and R_2 form with the adjacent nitrogen atom a heterocyclic ring belonging to the group consisting of piperidino, morpholino and pyrrolidino radicals.

The previously known compounds having the Formulas I, II and III may be prepared as shown in the French Pat. No. 1,443,251.

The new compounds described above may be prepared by condensing a diazonium salt obtained by diazotation of 2-aminobenzothiazole on an N,N-disubstituted aniline having the general formula:



(IV)

in which R and n have the significances hereinbefore indicated; R_1 and R_2 form with the adjacent nitrogen atom a heterocyclic ring belonging to the group consisting of morpholino, piperidino and pyrrolidino radicals; the final mono or bis-quaternization being carried out with methyl sulfate or a halide of a lower alkyl with or without an appropriate solvent.

In order that the invention may be better understood, several examples will now be described, purely by way of illustration.

EXAMPLE 1

Preparation of azo (2-aminobenzothiazole→N-ethyl-N-β-piperidinoethyl-aniline)

0.2 mole (30 g.) of 2-aminobenzothiazole is diazotized in solution in 300 cm.³ of phosphoric acid by the amount of nitrosyl acid sulfate which can be obtained from 0.2 mole (13.8 g.) of sodium nitrite and 115 cm.³ of sulfuric acid (density d.=1.83). To the diazonium salt solution is added 200 cm.³ of ice water and, little by little, at between -5° C. and 0° C., 0.2 mole (46.4 g.) of (N-ethyl-N-β-piperidinoethyl)-aniline in solution is 50 cm.³ of acetic acid and 50 cm.³ of water. The reaction mixture is left for two hours at 0° C. and overnight at the ambient temperature. The mixture is partially neutralized to a pH of 4 to 5 by means of a 3 N sodium hydroxide solution, and cooled overnight at 0° C., after which drying yields the azo compound in the form of a salt. The precipitate is suspended in one liter of water at 80° C.; rendered alkaline by means of a 10 N sodium hydroxide solution; and cooled; after which drying yields 55 g. of the desired azo compound, which, after recrystallization in alcohol melts at 130° C.

Analysis of the product yields the following results:

Product	Analysis (percent)			
	Calculated		Found	
	N	S	N	S
C ₂₂ H ₂₇ N ₅ S.....	17.81	8.14	17.56-17.64	8.04-8.17

EXAMPLE 2

Preparation of the hydrate of [3-methyl-benzothiazolium], 2-azo-4-[N-ethyl-N-(β-methyl-piperidino ammonium) ethyl-1-amino benzene]dimethosulfate

0.01 mole (3.93 g.) of the azo compound prepared in Example 1 is heated in 8 cm.³ of methyl sulfate for five hours at 100° C. The product is dried, finely ground and washed in hot chlorobenzene, 6.1 g. of a bis-quaternary

hydrate are obtained which, after recrystallization in alcohol at 80°, melts with decomposition at between 250 and 255° C.

Analysis of the product yields the following results:

Product	Analysis (percent)			
	Calculated		Found	
	N	S	N	S
C ₂₂ H ₂₇ N ₅ S ₂ O ₄	10.55	14.48	10.27-10.51	14.69-14.83

EXAMPLE 3

The following dyeing composition is prepared:

	G.
Azo (2-aminobenzothiazole→N-ethyl-N-β-amino-ethyl-aniline)	0.15
Iso-octylphenyl-polyethoxy-ethanol	5
20% citric acid solution q.s.p. (pH=8).	
Water q.s.p.	100

This composition is applied to brown hair and left thereon for 15 minutes. The hair is then rinsed and shampooed.

A deep mahogany shade results.

EXAMPLE 4

The following dyeing composition is prepared:

	G.
Dimethosulfate of the bis-quaternary compound corresponding to the azo (2-aminobenzothiazole→N-ethyl-N-piperidinoethyl-aniline)	0.65
Lauric alcohol oxyethylenated with 10.5 moles of ethylene oxide	2
Na ₂ CO ₃ solution at 2 N, q.s.p. (pH=7).	
Water q.s.p.	100

This composition is applied to chestnut hair and left thereon for 15 minutes. The hair is then rinsed and shampooed.

A deep ash brown results.

EXAMPLE 5

The following dyeing composition is prepared:

	G.
Methosulfate of the mono-quaternary compound corresponding to the azo (2-aminobenzothiazole→N-ethyl-N-formamido-ethyl-aniline)	0.48
Lauric alcohol oxyethylenated with 10.5 moles of ethylene oxide	2
Na ₂ CO ₃ solution of 2 N, q.s.p. (pH=7).	
Water q.s.p.	100

This composition is applied to chestnut hair and left thereon for 15 minutes. The hair is then rinsed and shampooed.

A black shade with bluish glints results.

EXAMPLE 6

The following dyeing composition is prepared:

	G.
Methosulfate of the mono-quaternary compound corresponding to the azo (2-aminobenzothiazole→N-ethyl-N-formamido-ethyl-aniline)	0.024
Nitro-meta-phenylene-diamine	0.112
Azo (2-aminobenzothiazole→N-ethyl-N-β-amino-ethyl-aniline)	0.032
Iso-octylphenyl-polyethoxy-ethanol	5
2-butoxyethanol	3
Lauric diethanolamide	2
Monoethanolamine q.s.p. (pH=7.5).	
Water q.s.p.	100

This composition is applied to 90% white hair and left for 15 minutes, after which the hair is rinsed and shampooed.

A dull ash grey shade results.

5 EXAMPLE 7

The following dyeing composition is prepared:

Dimethosulfate of the bis-quaternary compound corresponding to the azo (2-aminobenzothiazole→N-ethyl-N-piperidinoethyl-aniline) -----	0.032	
Nitro-meta-phenylene-diamine -----	0.105	
Azo (2-aminobenzothiazole→N-ethyl-N-β-aminoethyl-aniline) -----	0.040	10
Iso-octylphenyl-polyethoxy-ethanol -----	5	
2-butoxyethanol -----	2.8	
Lauric diethanolamide -----	2	
Monoethanolamine q.s.p. (pH=7.5).		
Water q.s.p. -----	100	15

This composition is applied to 90% white hair and left thereon for 15 minutes. The hair is then rinsed and shampooed.

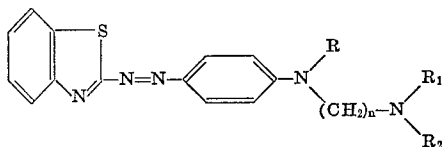
A dull ash chestnut results.

It will be appreciated that the foregoing examples are merely representative of the many possible ways of carrying out the invention, and may be modified as to detail without thereby departing from the basic principles thereof.

What is claimed is:

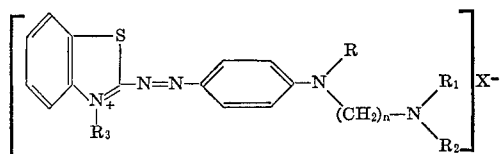
1. A composition for dyeing human hair which comprises an aqueous solution of a compound selected from the group consisting of

(a) a compound having the formula



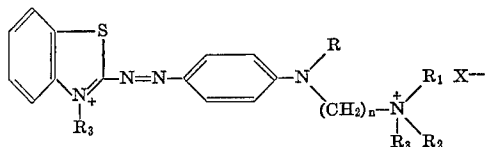
wherein R represents lower alkyl having 1-4 carbon atoms; n is a number between 2-6 inclusive; and R_1 and R_2 form, in combination with the nitrogen atom to which they are attached, piperidino;

(b) a compound having the formula



wherein R, and n have the meanings given above, R_1 and R_2 form, in combination with the nitrogen atom to which they are attached, piperidino; R_3 represents lower alkyl and X represents a member selected from the group consisting of halogen and CH_3SO_4 with the proviso that when X is CH_3SO_4 , R_3 is methyl; and

(c) a compound having the formula



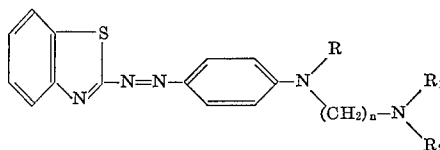
wherein R, R_3 , X and n have the meanings given above, and R_1 and R_2 form, in combination with the nitrogen atom to which they are attached, piperidino, said compound being present in amounts from 0.01-3 weight percent of the total composition.

2. The composition of claim 1 having a pH between 5-8 inclusive.

6

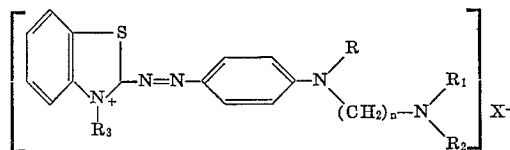
3. A method for dyeing human hair comprising impregnating said hair with a composition comprising an aqueous solution of a compound selected from the group consisting of

(a) a compound having the formula



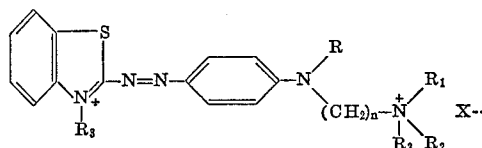
wherein R represents lower alkyl having from 1 to 4 carbon atoms; n is a number between 2 and 6 inclusive, R_1 represents a member selected from the group consisting of hydrogen and lower alkyl having from 1 to 4 carbon atoms, R_2 is selected from the group consisting of hydrogen, lower alkyl having 1 to 4 carbon atoms and formyl, and R_1 and R_2 may form, in combination with the nitrogen, piperidino;

(b) a compound having the formula:



wherein R, R_1 and n have the meanings given above, R_2 represents a member selected from the group consisting of lower alkyl having 1 to 4 carbon atoms and formyl, with the proviso that R_2 is not lower alkyl when R_1 is hydrogen, and R_1 and R_2 may form, in combination with the nitrogen atom to which they are attached, piperidino; R_3 represents lower alkyl and X represents a member selected from the group consisting of halogen and CH_3SO_4 with the proviso that when X is CH_3SO_4 , R_3 is methyl; and

(c) a compound having the formula:



wherein R, R_3 , X and n have the meanings given above; R_1 and R_2 each independently represent lower alkyl having 1 to 4 carbon atoms and may form, in combination with the nitrogen atom to which they are attached, piperidino, said compounds being present in amounts from 0.01 to 3 weight percent of said composition, said composition being applied to the hair in amounts to effectively dye said hair, leaving said composition in contact with the hair for 5 to 30 minutes, and then washing, rinsing and drying said hair.

References Cited

UNITED STATES PATENTS

3,414,559 12/1968 Sartori ----- 260-158

FOREIGN PATENTS

65 1,443,251 5/1966 France ----- 260-158

ALBERT T. MEYERS, Primary Examiner

V. C. CLARKE, Assistant Examiner

U.S. Cl. X.R.

8-10.1, 41; 260-158