United States Patent Office 3,488,138
Patented Jan. 6, 1970

3,488,138

STABILIZED NITRO-AMINOBENZENE DYEING COMPOSITIONS

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No Drawing. Filed Oct. 18, 1962, Ser. No. 231,561
Int. Cl. A61k 7/12
U.S. Cl. 8—10.1 9 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to dyeing living human hair with stabilized nitro-aminobenzene dye compositions. The stabilizers are ascorbic acid, salts thereof and carboxy acid esters thereof of organic acids having up to 20 carbon atoms.

This invention relates to stabilized dyeing compositions. More particularly, this invention relates to various dyes which have been stabilized with ascorbic acid or its derivatives.

Synthetic organic dyes known as oxidation dyes are widely used for dyeing living human hair because they can be easily applied, produce natural looking shades, and have no adverse affect on normal hair. However, dyeing compositions containing an oxidation dye are subject to deterioration when in contact with air. Deterioration can occur when the container for the composition is not air tight or is not completely full and has a large air space in contact with the composition, or when the container for the composition is left open or even when a portion of the composition has been removed and the container immediately resealed. Deterioration of the oxidation dye appears to be due to oxygen from the air reacting with the dye and the rate of deterioration appears to be proportionate to the quantity of air and particularly oxygen which is in contact with the composition. Deterioration of the dyeing composition by this premature oxidation manifests itself by a darkening and by a partial or even complete loss of the dyeing properties of the composition as well as a difference in shade of the hair which has been dyed by such a composition as compared to hair which has been dyed with a composition which has not suffered such deterioration.

Various techniques have been proposed to eliminate deterioration of oxidation dye composition. Thus, it has been proposed to leave as small an air space as possible in the container, to employ containers which have a sufficient amount of dye composition for only one application, and to incorporate certain reducing agents into the composition.

However, the above prior art techniques suffer from various shortcomings. Leaving as small an air space as practicable in the container does reduce deterioration; however, this does not prevent deterioration when the container is opened and only partially used, such as in the blending of shades, which is a very common practice. It does not prevent deterioration when containers having more than one application of the dye are employed and the container is then sealed and again stored. The dye composition which remains in each of the containers is then rapidly deteriorated and must be discarded. Furthermore, even in establishments where large quantities of such dyeing compositions are employed, individual unit applications are generally used to prevent deterioration. Only a relatively few antioxidants or reducing agents are described in the prior art, generally sulfur containing compounds, which have properties sufficiently satisfactory to be used under the conditions required of an oxidation dyeing composition for the hair and even those which have

been described for such use suffer from various shortcomings. Deterioration is particularly evident in toners which are hair dyeing compositions having a relatively low concentration of oxidation dye and which are generally used for light blond shades.

The problem of satisfactorily stabilizing oxidation dye compositions is made even more complex when such compositions also contain a nitro-aminobenzene dye, particularly since many antioxidants or reducing agents in quantities high enough to have some stabilizing effect on the oxidation dye destroy the dyeing properties of the nitro compounds by reduction of the nitro chromophore. Generally a nitro dye is added to oxidation dye compositions to give a more natural tone or shade to the hair.

In addition to oxidation dye compositions and oxidation dye compositions containing nitro-aminobenzene dyes wherein the development of color in either of these compositions is primarily dependent on oxidation with chemical oxidizing agents such as hydrogen peroxide, living human hair is also dyed with nitro-aminobenzene dyes without the use of oxidizing agents. The nitro-aminobenzene dyes are colored compounds having both a chromophore and auxochrome group. They do not require chemical oxidizing agents for color development or substantivity to the hair; consequently they are known as direct dyes. However, residual quantities of chemical agents from previous treatments, for example oxidizing agents such as salts of peracids, may be incompletely removed from the hair because of inefficient shampooing. In those cases the direct dyeing nitro dyes show a lower strength on hair or a different shade or color than when dyed on hair not containing such residual quantities of chemical agents. Repeated or intensive shampooing can remove the residual oxidizing agent, but this can require an inordinately long period of time for the hairdresser, and it is difficult to determine when the residual oxidizing agent has been removed to permit satisfactory direct dyeing. Although contact of nitro dyes with oxidizing agents in an oxidation dyeing system is generally not objectionable, the uncontrolled oxidation from residual chemical agents in the hair produces dyeings which are variable in color or affinity and often unattractive.

It has now been found that ascorbic acid or its derivatives stabilize oxidation dyes, and dyeing compositions containing a nitro-aminobenzene dye in admixture with an oxidation dye; also, ascorbic acid or its derivatives enhance the dye uptake and color development of the hair in direct dyeing with nitro-aminobenzene dyes after bleaching when the hair still contains some of the chemical oxidizing agent. This discovery provides many advantages which are not possessed by reducing agents generally, nor by the prior art techniques. Ascorbic acid or its derivatives can be effectively used even in small concentrations when the oxidation dye has been placed in contact with air such as when a portion of the composition has been removed from the container. Furthermore, ascorbic acid or its derivatives which are employed in the compositions of this invention do not irritate the scalp or damage the hair; and in effective concentrations do not produce excessive heating, or reduction of the nitro chromophore.

Ascorbic acid, its esters and salts are known antioxidants or reducing agents. The term ascorbic stabilizer will be employed herein to embrace ascorbic acid, a salt of ascorbic acid or an ester of ascorbic acid. The ascorbic stabilizers can be used in the form of their various optical isomers such as the levo-form or the dextroform. The levo-form of ascorbic acid is variously known as L-ascorbic acid, L-xyloascorbic acid and Vitamin C. The dextro-form of ascorbic acid is variously known as isoascorbic acid and D-araboascorbic acid. The ascorbic stabilizers can be used either alone or with small quantities

of other reducing agents to stabilize the dyes employed in this invention.

Although the ascorbic stabilizers are known reducing agents and have been used to stabilize certain compositions it was not foreseeable that these materials would be suitable, and particularly so uniquely suitable, for use with compositions for dyeing living human hair on the head. Many exacting requirements must be met for stabilizing such compositions. It is insufficient for proper stabilization and dyeing out on the hair that a material is a known reducing agent or antioxidant. Thus, many reducing agents or commercial antioxidants are not suitable for this use since they suffer from various shortcomings such as: a total or partial inability to prevent unwanted oxidation of the dye; reacting with the dye or conventional dye additives and thus altering the properties of the composition; inhibition of the dyeing action or production of off-shade dyeing, reducing the nitro chromophore when employed in large enough quantities to have effective antioxidant properties on the composition; irritation or damage to the scalp or hair; or liberation of excessive heat when admixed with a peroxide, which can cause irritation or at least an uncomfortable feeling on the user's head.

It has also been found that many materials which are closely related to ascorbic acid suffer from the above shortcomings and are inferior when substituted for the ascorbic stabilizers in the dyeing compositions of this invention. Among related compounds or known antioxidants or reducing agents which have been found to have shortcomings in comparison to the ascorbic stabilizers there can be mentioned: glucose; gluconic acid; sorbic acid; glucuronic acid; sorbitol; citraconic anhydride; citric acid; lactic acid; glucuronic anhydride; tartaric acid; pyruvic acid; glycolic acid; glyoxal; furfural; furoic acid; furfuryl alcohol; crotonaldehyde; salicylaldehyde; thiosalicylic acid; dibutyl thiourea; butylated hydroxytoluene; 2,2'-thiobis-(4-methyl-6-t-butyl phenol); dilauryl thiodipropionate; ferrous ammonium sulfate; and sodium hypophosphite.

Sodium sulfite has long been used as a stabilizer in oxidation dyes. Sodium sulfite in concentrations up to 1%, however, gives inadequate protection of the oxidation dye in partially filled containers. Sodium sulfite concentrations above 1% (i.e. 2%) appear to prevent the darkening of the oxidation dye and eliminate the production of off-shade colors when the dye is applied to hair. However, in these higher concentrations the subsequent addition of peroxide to the composition for development of the color results in an exothermic reaction and the temperature of the composition can be raised by 10° C. or even higher. The heat which is produced on contact of the sulfite and peroxide is sufficient to annoy or irritate a person whose hair is being dyed and can cause damage to the hair or scalp. Furthermore, sodium sulfite, particularly in concentrations above about 1%, reduces or in some other manner affects the nitro dye so that upon subsequent dyeing of the hair undesirable off-shades are developed.

Various thio compounds, particularly thioglycolic acid, have been proposed as stabilizers in oxidation dyeing compositions. The thio compounds, however, at low concentrations such as about 0.2% give little or no protection from deterioration of the oxidation dyes in partially filled containers. In somewhat higher concentrations, such as 0.5% and above, the thio compounds and particularly thioglycolic acid destroy the nitro dyes. Furthermore, since the oxidation dyeing compositions are generally in the alkaline range, such as a pH of 9 or 9.5, concentrations of the thio compounds, particularly thioglycolic acid in ranges of from 0.5% and above, damage the hair under these alkaline conditions. Also the scalp and skin of many persons is irritated by alkaline compositions containing the higher quantities of the thio compounds.

Sodium hydrosulfite has also been suggested as a stabilizer for oxidation dyeing compositions. However, in effective concentrations sodium hydrosulfite irreversibly reduces the nitro dyes causing a loss of color, particularly of the red components used for obtaining red and brown shades.

As mentioned hereinbefore the stabilizing agent can be an ester of ascorbic acid. Illustrative of the esters of ascorbic acid which can be employed in this invention there can be mentioned those wherein the ester is formed by reaction with organic acids having up to 20 carbon atoms, e.g.: ascorbyl palmitate, ascorbyl stearate, ascorbyl myristate, ascorbyl laurate, ascorbyl acetate, ascorbyl propionate, ascorbyl tartrate, ascorbyl citrate, ascorbyl succinate, and ascorbyl benzoate. The preferred ascorbyl esters are those produced from higher fatty acids, e.g. ascorbyl palmitate.

As mentioned hereinbefore salts of ascorbic acid can be employed as the stabilizer and indeed the salt form is often present since the preferred dyeing compositions are alkaline. Alkaline materials whether in the form of free base or alkaline salts which can be either of organic or inorganic bases are conventional constituents of oxidation and direct nitro hair dyeing compositions. These alkalizing agents can form a suitable salt of ascorbic acid. Illustratively, the alkalizing agent for the dyeing compositions or salt forming agents of the stabilizer can be those of an alkali metal, e.g. sodium hydroxide, potassium hydroxide, sodium carbonate, trisodium phosphate and the like. They can be those of ammonium hydroxide or organic amines such as those of the (lower) alkanolamines, e.g. mono-, di-, or triethanolamine, or (lower) alkylamines, such as monoethylamine, diethylamine, propylamine, dipropylamine, N (lower) alkylenediamines such as ethylenediamine, propylenediamine, trimethylenediamine, or heterocyclic amines such as morpholine, or other organic bases such as diethylenetriamine, tetramethylguanidine, cyclohexylguanidine and the like. Also. alkaline earth compounds can be used for alkalizing the composition or forming the salts of ascorbic acid. Illustratively the alkaline earth compound can be calcium or magnesium hydroxide or calcium carbonate. The ammonium or organic amine bases are preferred as the alkalizing agent; whereas the preferred ascorbic stabilizers are L-ascorbic acid, isoascorbic acid, and the ammonium, amine, sodium or potassium salt of these acids.

Oxidation dyes are often referred to as intermediates since their actual dyeing properties are developed only on oxidation. Oxidation dyes for use on living human hair are well known and a number of such dyes are listed in Sagarin, Cosmetic Science and Technology (1957) pages 503–506.

Illustrative of oxidation dyes there can be mentioned the aminodiphenylamines, phenylenediamines, aminophenols, aminophenol ethers, and their acid addition salts. Such dyes also often have lower aliphatic substituents on the aryl nucleus or the amino group.

The aminodiphenylamines have an amino group in one or both of the unsubstituted para positions of the phenyl radicals. Also, the aminodiphenylamines can be sulfonated. Illustrative of aminodiphenylamine oxidation dyes there can be mentioned: p-aminodiphenylamine; p-aminodiphenylamine hydrochloride; p-aminodiphenylamine sulfonic acid; p,p'-diaminodiphenylamine; and the like.

The phenylenediamines are diaminobenzenes which often also have aliphatic, e.g. lower alkyl radicals on the aromatic ring or on the amino groups. Illustrative of phenylenediamines there can be mentioned: o-phenylenediamine; m-phenylenediamine; p-phenylenediamine; p-phenylenediamine hydrochloride; p-phenylenediamine sulfate; N-(p-aminophenyl) glycine; m-tolylenediamine; p-tolylenediamine; and the like.

The aminophenols are also often substituted by an additional amino group or sulfo group on the aromatic nucleus or by an alkyl or carboxyalkyl group on the nitrogen. Illustrative of aminophenols there can be mentioned: o-aminophenol; p-aminophenol; p-aminophenol hydrochloride; p-aminophenol sulfate; 2-aminophenol-4-sul-

fonic acid; 4-aminophenol-2-sulfonic acid; p-methylaminophenol sulfate; 2,4-diamino-phenol; 2,4-diaminophenol hydrochloride; 2,5-diaminophenol-4-sulfonic acid; N-(p-hydroxyphenyl) glycine; and the like.

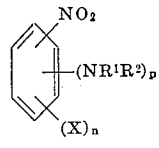
Illustrative of the aminophenol ethers there can be mentioned: o-anisidine; 2,4-diaminoanisole; 2,4-diaminoanisole sulfate; 2,4-diaminophenetole; and the like.

Illustrative of the polyhydroxybenzenes and polyhydroxynaphthalenes that may be incorporated in the compositions of the present invention there can be mentioned: hydroquinone; catechol; resorcinol; pyrogallol; 1,2,4 - trihydroxybenzene; 1,3,5-trihydroxybenzene; 1,5-naphthalenediol; and the like.

Although nitro dyes are often used with oxidation dyes and are included in the lists of oxidation dyes, they are better identified as direct dyes since they do not require the use of chemical oxidizing agents such as various peroxides to develop their color. Thus, the term oxidation dye as employed herein does not include such a dye containing a nitro group.

Nitro aminobenzene dyes and their use in either direct or oxidation dyeing are well known and are particularly described in the following patents: U.S. 2,750,326; U.S. 2,750,327; U.S. 2,983,651; U.S. 3,049,393; German 1,114,775; German 1,087,565; German 1,071,712; German 1,017,750; and British 812,211. Additionally, the hereinabove cited Sagarin reference, page 504 shows various nitro dyes used in oxidation dyeing compositions.

As is evident from the terminology, the nitro-aminobenzene dyes have a benzene nucleus which is substituted by both a nitro and an amino group. The benzene nucleus of such dyes can contain more than one nitro group, such as up to 3 nitro groups, more than one amino group, such as up to 3 amino groups, and can further be substituted with from 1 to 3 hydroxyls and with from 1 to 3 lower aliphatic radicals. Illustrative of the lower aliphatic radicals which can be substituted on the benzene nucleus, there can be mentioned alkyls and hydroxyalkyls. The amino group or groups can be primary or can be substituted with various aliphatic or aryl radicals to form secondary or tertiary amines. Illustrative of the amino substituents there can be mentioned lower aliphatic radicals such as alkyls, hydroxyalkyls, carboxyalkyls, polyalkylene-glycol radicals, aminoalkyls, and the like. The aryl amino substituent can be phenyl or substituted phenyl. The preferred nitro-aminobenzene dyes can be represented by the formula:



wherein each of R^1 and R^2 is hydrogen or a lower aliphatic radical as hereinabove described; p is an integer from 1 to 2; X is the hydroxyl or the primary amino radical; n is an integer from 0 to 1; and n plus p is at least 2.

Illustrative of the nitro-aminobenzene dyes there can be mentioned:

2-nitro-p-phenylenediamine;
4-nitro-o-phenylenediamine;
1-anilino-4-amino-2-nitrobenzene;
1-methylamino-2-amino-4-nitrobenzene;
1-ethylamino-4-amino-2-nitrobenzene;
1-(2'-hydroxyethylamino)-2-amino-4-nitrobenzene;
1-[2'-(2''-hydroxyethoxy)ethylamino]-4-amino-3-nitrobenzene;
1-(2'-hydroxyethylamino)-4-amino-2-nitrobenzene;
1,4-bis-(2'-hydroxyethylamino)-2-nitrobenzene;
1-(2',3'-dihydroxypropylamino)-4-amino-3-nitrobenzene;
1-methylamino-4-amino-2-nitrobenzene;
1-methylamino-4-[2'-(2''-hydroxyethoxy)ethylamino]-2-nitrobenzene;
5-nitro-2-aminophenol;
4-nitro-2-aminophenol;
2-nitro-4-aminophenol;
4,6-dinitro-2-aminophenol;
4-nitro-2-(2'-hydroxyethylamino)phenol;
2,4,6-trinitroaniline;
N-(p-nitrophenyl)glycine;
N-(2-hydroxy-5-nitrophenyl)glycine;

and the like.

In addition to dyeing human hair the stabilized dyeing compositions of this invention can also be used to dye other keratinaceous or proteinaceous fibers, e.g. animal fibers, such as wool, bristles, feathers, silk, and hair. However, the stabilized dyeing compositions of this invention are particularly advantageous for dyeing living human hair on the head.

In addition to the dye and ascorbic stabilizer the compositions of this invention can contain one or more of the various conventional hair dyeing adjuvants such as surfactants, thickening agents, water, solvents, and alkalizing agents. The various ingredients of the composition are intimately dispersed. The more cosmetically elegant compositions contain water, a surfactant and a thickening agent in addition to the dye and ascorbic stabilizer.

The ascorbic stabilizers can be used in the compositions of this invention over a broad range of concentrations such as that of 0.01% to 10%. However, larger or smaller quantities can be employed dependent on the purpose or type of composition, e.g. in a concentrate of the dye compositions which is to be subsequently diluted larger concentrations can be employed. When the composition is intended for oxidation dyeing and contains an oxidation dye or combinations of an oxidation dye and a nitro dye it is preferred that from about 0.01% to about 1% and particularly from about 0.1% to about 1% of an ascorbic stabilizer be employed. However, smaller concentrations of the stabilizer, such as .005% and larger concentrations such as 5% or more can also be employed. When the composition contains nitro dyes for direct dyeing and it is not intended to add an oxidizing agent the quantity of ascorbic stabilizer preferably varies from about 0.5% to about 7% and particularly from about 1% to about 4%.

The quantity of dye in the composition can vary over a wide range such as that of about 0.01% to about 10%. However, as mentioned with the stabilizers larger or smaller concentrations can also be employed. Thus in compositions containing an oxidation dye or combinations thereof with the nitro dye the oxidation dye can vary from about 0.01% to about 10% and preferably from about 0.2% to about 6% whereas the nitro dye when employed in such a composition can vary from about 0.01% to about 6%. In compositions intended for dyeing without chemical oxidizing agents the nitro dye preferably varies from about 0.01% to about 10% and particularly from about 0.1% to about 6%.

Thickening agents when used in the compositions can vary over the broad concentrations used in the hair dyeing art such as from about 1% to about 15% and preferably from about 2 to 10%. Water dispersible surface active agents, including detergents, when used in the compositions can vary over the broad concentrations used in the hair dyeing art such as that of from about 0.5% to about 30% and preferably from about 1 to about 10%.

The quantity of the alkalizing agent, if employed, can vary over a wide range depending on the dye, the particular alkalizing agent, and the desired pH. Thus, the alkalizing agent can vary from less than about 0.1% to over 10% and preferably from about 0.5% to about 3% by weight of the dyeing composition.

The dyeing compositions of this invention generally contain water although they can be formulated with no water present. Generally the compositions can contain from about 5% to 99% water, depending on the contem-

plated particular type of dyeing composition and the physical form of the composition, e.g. paste, slurry, thin liquid, etc. In the oxidation dyeing compositions the water content preferably varies from about 5% to about 80% and particularly from about 10% to about 50%. When the nitro dyes are employed for direct dyeing the water content preferably varies from about 10% to about 99% and particularly from about 70% to about 95%.

The water dispersible surface active agents employed in the compositions of this invention can be anionic, non-ionic or cationic. Illustrative of the various types of water soluble surface active agents there can be mentioned: higher alkyl benzene sulfonates; alkyl naphthalene sulfonates; sulfonated esters of alcohols and polybasic acids; taurates; fatty alcohol sulfates; sulfates of branched chain or secondary alcohols; alkyl dimethyl benzyl ammonium chlorides; polyoxyethylene alkylethers, alkyl phenoxypolyethylene ethanols and the like. Illustrative of specific surfactants there can be mentioned: lauryl sulfate; polyoxyethylene lauryl ester; myristyl sulfate; glyceryl monostearate; sodium salt of palmitic methyl taurine; cetyl pyridinium chloride; lauryl sulfonate; myristyl sulfonate; lauric diethanolamide; polyoxythylene stearate; stearyl dimethyl benzyl ammonium chloride; dodecyl benzene sodium sulfonate; nonyl naphthalene sodium sulfonate; dioctyl sodium sulfosuccinate; sodium n-methyl-n-oleoyl taurate; oleic acid ester of sodium isethionate; sodium dodecyl sulfate; the sodium salt of 3,9-diethyl tridecanol-6-sulfate; and the like.

Illustrative of thickening agents there can be mentioned: sodium alginate vegetable gums such as agar; and synthetic thickeners such as sodium carboxymethylcellulose.

The dyeing compositions of this invention can be formulated to have an acid, neutral or alkaline pH such as that of from a pH of about 3 to about 12. Preferably the pH is about 7.5 to about 11 and particularly from about 8 to about 11.

The dyeing compositions of this invention can be applied to living human hair on the head by the conventional techniques, at the conventional temperatures and for the conventional periods of time. Illustratively, when oxidation dyeing compositions are applied the stabilized composition can be poured on the hair either prior to and preferably after mixing with peroxide and permitted to remain on the hair for about 5 minutes to about 2 hours and preferably about 15 minutes to about 60 minutes at temperatures from about 20° C. to about 40° C. The direct dyeing compositions are applied in the same manner, but of course without the oxidizing agent.

The stabilized dyeing compositions of this invention can be prepared by the conventional methods used in the dyeing art. The ascorbic acid or its derivatives can be simply incorporated into the composition such as by simply adding a sufficiently effective quantity to the water or the dispersion of the dye in the various adjuvants.

The percentage values given herein are on a weight basis. The term "lower" as employed herein to modifyl various radicals such as aliphatic, alkyls or alkanols refers to such radicals having from 1 to 6 carbon atoms. The term dispersion is used herein in its generic sense as embracing true solutions as well as stable homogeneous colloidal solutions. The terms direct dye or direct dyeing refer to dyes or dyeing systems which do not require the addition of oxidizing agents such as peroxides for color development or affinity of the dye to hair.

The following examples are illustrative of the invention:

EXAMPLE 1

Normal oxidation dye formula (dark brown)

	G.
p-Aminodiphenylamine	0.05
4-amino - 2 - nitrophenol	0.10
p-Aminophenol	0.21
2-nitro - p - phenylenediamine	0.20
4-nitro - p - phenylenediamine	0.10
p-Phenylenediamine	1.50
2,4 - diaminoanisole	0.60
Pyrogallol	0.20
Resorcinol	1.50
L - ascorbic acid	0.20
28% ammonia	10.00
Oleic acid	35.00
Isopropanol	12.50
Disodium ethylene diamine tetraacetate	0.25
Lanolin, water soluble	1.80
Polyoxyethylene sorbitan monoleate	10.00
Nonylphenoxypoly (ethyleneoxy) ethanol	5.00
Water to make 100 g.	

pH adjusted between 9 and 9.5.

The composition of the above example was prepared by adding the various ingredients to water and forming a dispersion. The composition did not show deterioration in containers exposed to air and the subsequent dyeing with peroxide on hair did not show evidence of deterioration. In place of the L-ascorbic acid in the above composition, an equal quantity of its sodium salt or its palmitate ester can be employed. An additional antioxidant, such as 0.2% of sodium sulfite can also be added to the composition.

EXAMPLE 2

Normal oxidation dye formula (medium red)

	G.
4 - amino - 2 - nitrophenol	1.5
P - aminophenol	1.0
4 - nitro - o - phenylenediamine	0.5
2 - nitro - p - phenylenediamine	2.5
P - phenylenediamine	0.7
2,4 - diaminoanisole	0.3
Pyrogallol	2.0
Resorcinol	0.3
L - ascorbic acid	0.5
28% ammonia	9.0
Oleic acid	25.0
Sodium lauryl sulfate	1.0
Ethylene diamine tetraacetic acid	0.2
Glycerine	5.0
Water to make 100 g.	

To the above formula solvents such as ethanol, propylene glycol, and ethylene glycol can also be added. Also, there can be added emulsifying agents, thickeners, hair conditioning agents, lanolin derivatives and other additives known to the art. The pH of the above composition is adjusted between 9 and 9.5.

EXAMPLE 3

An ash blond oxidation dye formula toner

	G.
p-Aminodiphenylamine	.003
o-Aminophenol	.06
p-Aminophenol	.015
2-nitro-p-phenylenediamine	.05
4-nitro-o-phenylenediamine	.006
p-Phenylenediamine	.06
2,4-diaminoanisole	.03
Hydroquinone	.004
Pyrogallol	0.3
Resorcinol	0.08
L-ascorbic acid	0.10
28% ammonia	10.00
Oleic acid	35.00
Isopropanol	11.00
Polyoxyethylene sorbitan trioleate	9.00
Polyoxyethylene lauryl ether	5.00
Water to make 100 g.	

pH adjusted between 9 and 9.5.

To the composition of Example 3 an additional antioxidant such as 0.1% of sodium sulfite can also be added. The pH can also be adjusted to neutral or the acid range.

EXAMPLE 4

A platinum toner

	G.
p-Aminophenol	0.09
1,5-dihydroxynaphtalene	0.08
p-Tolylenediamine	0.06
2,4-diaminoanisole sulfate	0.03
Catechol	0.08
Isoascorbic acid	0.25
28% ammonia	9.0
Oleic acid	25.0
Sodium lauryl sulfate	1.0
Ethylenediamine tetraacetic acid	0.2
Glycerine	5.0
Water to make 100 g.	

To the above formula there can be added other solvents such as ethanol, propylene glycol, ethylene glycol, other water soluble surface active agents, thickeners, hair conditioning agents, lanolin derivatives and other additives known to the art. The pH of the composition is preferably adjusted between 9 and 9.5. In place of isoascorbic acid there can be used L-ascorbic acid or a salt or ester of isoascorbic acid, e.g. its sodium salt or its palmitic acid ester.

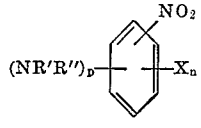
EXAMPLE 5

Hair on the human head is bleached with an aqueous composition containing a mixture of hydrogen peroxide, a detergent, and small quantities of isopropyl alcohol and potassium persulfate. The hair is then shampooed and rinsed. A dyeing composition is then poured on the hair and permitted to impregnate the hair for 20 minutes at room temperature. The dyeing composition contains a dispersion of 1 gram of 2-nitro-p-phenylenediamine, 5 grams of isopropanol, 934 grams of water, 10 grams of monoethanolamine, 30 grams of L-ascorbic acid, and 20 grams of methyl cellulose. The hair is dyed a scarlet color. A salt or ester of L-ascorbic acid or isoascorbic acid or a salt or ester thereof can be substituted as the stabilizer in the above composition. In a similar experiment wherein the dyeing composition did not contain an ascorbic stabilizer the hair was dyed a dull orange shade.

What is claimed is:

1. A stabilized dyeing composition comprising a nitro-amino-benzene dye and an ascorbic stabilizer selected from the group consisting of ascorbic acid, salts thereof and carboxy acid esters thereof of organic acids having up to 20 carbon atoms, said dye being capable of dyeing hair without the use of an oxidizing agent.

2. A stabilized dyeing composition comprising an aqueous dispersion having a pH of about 8 to about 11 containing an ascorbic stabilizer selected from the group consisting of ascorbic acid, salts thereof and carboxy acid esters thereof of organic acids having up to 20 carbon atoms and a nitro-aminobenzene dye capable of dyeing living human hair without the use of an oxidizing agent, of the formula:



wherein X is a member selected from the group consisting of the hydroxyl and the primary amino radical, *n* is an integer from 0 to 1, each of R' and R'' is a member selected from the group consisting of hydrogen and a lower aliphatic radical, *p* is an integer from 1 to 2, and the total of *n* plus *p* is at least 2.

3. The dyeing composition of claim 2 wherein the stabilizer is ascorbic acid.

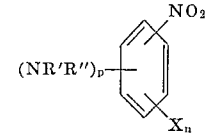
4. The dyeing composition of claim **2** wherein the stabilizer is a salt of ascorbic acid.

5. The dyeing composition of claim **2** wherein the stabilizer is an ester of ascorbic acid.

6. The dyeing composition of claim **2** including a water dispersible surface active agent and a thickening agent.

7. A method for dyeing bleached living human hair on the head containing residual quantities of an oxidizing agent which comprises contacting the hair with an aqueous dispersion containing a nitro-aminobenzene dye capable of dyeing living human hair without the use of an oxidizing agent, and an ascorbic stabilizer selected from the group consisting of ascorbic acid, salts thereof and carboxy acid esters thereof of organic acids having up to 20 carbon atoms.

8. A stabilized dyeing composition comprising a nitro-aminobenzene dye, capable of dyeing living human hair without the use of an oxidizing agent, of the formula:



and an ascorbic stabilizer selected from the group consisting of ascorbic acid, salts thereof and carboxy acid esters thereof of organic acids having up to 20 carbon atoms; wherein X is a member selected from the group consisting of the hydroxyl and the primary amino radical, *n* is an integer from 0 to 1, each of R' and R'' is a member selected from the group consisting of hydrogen and a lower aliphatic radical, *p* is an integer from 1 to 2, and the total of *n* plus *p* is at least 2, said dye being capable of dyeing hair, and said dyeing composition not requiring the addition of oxidizing agents for color development or affinity of dye to the hair.

9. A dyeing composition according to claim **8**, wherein said ascorbic stabilizer is ascorbic acid.

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U.S. Cl. X.R.

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