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[54] **OXIDATIVE HAIR-COLORING MIXTURES CONTAINING A CONDITIONING AGENT**

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[63] Continuation-in-part of Ser. No. 152,404, June 11, 1971, abandoned.

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[58] **Field of Search** 8/10.2, 11, 32; 424/70

[56] **References Cited**

UNITED STATES PATENTS

2,149,319	3/1939	Soussa	424/62
3,011,858	12/1961	Lantz et al.	8/10.2 X
3,167,478	1/1965	Charle et al.	8/10.2
3,194,734	7/1965	Seemuller et al.	8/10.2
3,210,252	10/1965	Blanke et al.	8/10.2
3,359,168	12/1967	Brechner et al.	8/10.2
3,582,253	6/1971	Berth et al.	8/10.1
3,649,159	3/1972	Cohen et al.	8/10.2
R24,373	10/1957	Eckardt et al.	8/10.2

FOREIGN PATENTS OR APPLICATIONS

224,135	11/1924	United Kingdom	424/62
1,347,285	11/1963	France	424/62
2,013,762	10/1971	Germany	424/62
298,719	10/1965	Netherlands	424/62

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[57] **ABSTRACT**

The intermixture of milk or beer with an oxidizing agent and an oxidative hair-dye composition provides a greatly improved hair-coloring mixture which conditions damaged hair, and provides uniform coloring throughout the entire hair. While any oxidizing agent can be successfully employed in the hair-coloring mixture of this invention, in the preferred embodiment the oxidizing agent comprises a solution of a hydrogen peroxide-yielding compound in a polyhydroxy alcohol. The use of the preferred oxidizing agent increases the conditioning effect of the hair-coloring mixture and also substantially reduces the annoying effects inherent in the prior art agents.

11 Claims, No Drawings

OXIDATIVE HAIR-COLORING MIXTURES CONTAINING A CONDITIONING AGENT

RELATED INVENTION

This application is a continuation-in-part of our previous application, Ser. No. 152,404, filed June 11, 1971, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the coloring of hair on the human head, and more particularly to hair-coloring mixtures employing oxidizing agents and commercially-available dyeing or tinting compositions generally comprising para-benzenoid-diamines, couplers, wetting and foaming agents, viscosity controlling agents, antioxidants, ammonia, isopropyl and/or ethyl alcohol, and water, hereinafter referred to as oxidative hair-dye compositions or "dye intermediate" compositions.

During the last 25 years, the polularity of hair-coloring has continually increased to afford both men and women the opportunity to maintain a youthful appearance by coloring their graying hair. Oxidative permanent dye mixtures have been employed to color hair regardless of the percentage of gray hairs that an individual had. These permanent dye mixtures employ a specific dye composition which is oxidized by an oxidizing agent while applied to one's hair to impart a particular color thereto. On hair that is less than 75% gray, these permanent dye mixtures are not particularly useful, since the coverage result is an undesirable darker shade and/or the oxidation reaction is so great that it actually lightens the naturally colored hair by bleaching and damages the naturally colored hair.

Another difficulty encountered with the use of the permanent dye mixtures is the take of the dye on damaged hair. The hair on the head of a modern woman is repeatedly shampooed, treated with a wide assortment of cosmetics from aerosol hair sprays and setting solutions to permanent waving products. This causes the ends of the hair, which are the older hair, to become "damaged," since they are more porous and absorptive, possess less luster, and are inclined to tangle. This damaged condition is further accentuated by exposure to sunlight, especially if the hair has been treated with an oxidizing agent through such treatments as blecahing, dyeing or permanent waving. Since the porosity of each strand of damaged hair varies throughout the length of the strand, portions of each strand of hair will absorb larger amounts of dye and will possess an entirely different color than the less absorptive portions of the hair strand. This produces color streaks and an unnatural appearance unless special methods are used.

In order to cause the oxidative hair-dye composition to react and impart color to the hair, an oxidizing agent must be present. Generally, a 6 percent solution of hydrogen peroxide in water is employed. This hydrogen peroxide solution is difficult to handle since it may react with the skin of the individual applying the hair-coloring mixture. Generally, the hydrogen peroxide solution will cause a whitening or blanching of the skin which is also accompanied by a painful, stinging sensation which persists for several minutes. This undesirable blanching and painful stinging sensation are associated by the hairdresser or user with hair damage.

Women who are in the transition stage, whose naturally colored hair is gradually acquiring gray strands, have sought other methods of coloring their hair to avoid the inherent difficulties encountered with the permanent dye mixtures. The products employed by most women who desire coverae of a few gray strands are hair coloring rinses. While these products do provide sufficient coloring for the few gray strands in an individual's head of hair, the color is relatively easily washed out with normal shampooing. Furthermore, the desired coverage is not achieved when the quantity of gray hair exceeds 10%.

In order to satisfy the requirements for women who have 10 to 75 percent gray hairs, a "semi-permanent" dye product has been developed. Generally, these semi-permanent products comprise aqueous solutions of nitrophenylene diamines or similar nitro benzenoid amines or nitro aminó phenols, together with dispersed colors. The major faults of these products are that the color does not remain true, and undesirable shades develop in sunlight or even with repeated shampoos. Also, the color tends to fade rapidly. The most objectionable problem that exists with these semi-permanent dyes is the fact that porous hair and hair that has been permanently waved will accept the colors very rapidly and/or will preferentially select one of the coloring ingredients. Consequently, unnaturally streaked or colored hair sections frequently occur.

OBJECTS OF THE INVENTION

It is an object of this invention to provide a hair-coloring mixture which is capable of conditioning the hair as well as coloring it.

Another object of this invention is to provide a hair-coloring mixture of the above character that substantially reduces or eliminates skin discomfort during application.

Another object of this invention is to provide a hair-coloring mixture of the above character that imparts unfading natural colors which are highly resistant to light and shampoo, even with prolonged wear and repeated shampoos.

A further object of this invention is to provide a hair-coloring mixture of the above character that does not produce off shades or streaky color sections, either during or after application thereof.

Another object of this invention is to provide an oxidizing agent that does not produce the blanching or stinging effects of hydrogen peroxide.

Another object of this invention is to provide a hair-coloring mixture of the above character which will not damage the hair to which it is applied, while imparting a high gloss and smooth feel thereto.

Another object of this invention is to provide a hair-coloring mixture of the above character which provides excellent uniformly leveled color throughout the hair regardless of the damaged character or porosity of the hair.

Other and more specific objects will be apparent from the features, elements, combinations and operating procedures disclosed in the following detailed description.

SUMMARY OF THE INVENTION

The hair-coloring mixtures of this invention substantially reduce or completely eliminate the inherent problems associated with prior art hair-coloring mixtures by employing one or more of the hair-coloring mixture additives that we have developed. By adding milk or beer as a partial substitute for a portion of the oxidizing

agent employed in the hair-coloring mixture, distinct and unexpected advantages are produced. Additional partial substitutes or additives for the oxidizing agent which substantially improve prior art hair-coloring mixtures are viscosity-imparting ingredients. The inclusion of viscosity-imparting ingredients in the oxidizing agent provides conditioning to the hair while also producing an oxidizing agent that is more easily handled and applied. The inclusion of milk or beer in the hair-coloring mixture also conditions the hair and thereby allows the coloring to take more uniformly throughout.

As a substitute for the commonly used oxidizing agents, we have developed a new oxidizing agent for use in hair-coloring. This oxidizing agent comprises a hydrogen/ peroxide yielding compound in solution with a polyhydroxy alcohol. Preferably, an aqueous solution of hydrogen peroxide or solid urea peroxide is dissolved in a polyhydroxy alcohol, such as glycerine and-/or propylene glycol, in sufficient percentages to provide an available hydrogen/peroxide yeilding compound concentration of about 8 percent by weight. This oxidizing agent has been found to be completely safe and more easily handled by the user, since skin blanching and stinging are substantially reduced. Since the annoying, undesirable effects of normally used hydrogen peroxide yielding solution are substantially reduced or eliminated, the hairdresser or user finds the oxidizing agent of this invention much more desirable to use, and does not associate hair damage with this oxidizing agent.

The various hair-coloring mixture additives of this invention can be employed separately with prior art hair-coloring mixtures or as individual or multiple substitutes for some of the ingredients of the prior art hair-coloring mixtures without departing from the scope of the invention.

The invention accordingly comprises the features, elements, combinations and operating procedures hereinafter disclosed, and the scope of the invention will be indicated in the claims.

DETAILED DESCRIPTION

The hair-coloring mixture of this invention prevents the normal damaging action of dyeing hair with oxidative hair-dye compositions and oxidizing agents while also improving the condition of the hair by substituting milk or beer for part of the conventional water solution of the oxidizing agent. Although milk is being used broadly to include all natural and synthetic liquids which resemble milk, whole fresh milk is the preferred additive. It is believed that the high protein content of these liquids provides an excellent protective and remedial action upon hair, since hair is also a protein. Whole milk is the preferred liquid for use in the hair-coloring mixture of this invention due to the fact that whole milk contains suspended lipoidal ingredients, making it similar to the surface of the hair, which is believed to consist of lipo-proteins.

In most hair coloring applications, the oxidizing agent employed is a solution of hydrogen peroxide or urea peroxide in water. The hydrogen/peroxide-yielding compound concentration usually comprises 6 percent by weight of the solution or, as is known in the art, "20 volume peroxide." The term "20 volume peroxide" indicates the quantity of peroxide in solution, which will produce a quantity of oxygen that is twenty times greater in volume than the volume of the peroxide solution. Throughout this disclosure, all percentages relating to the hair color mixture and its constituents are weight percentages.

We have found that the beneficial action provided by the incorporation of milk or beer is present even when the concentration of the hydrogen peroxide or urea peroxide is substantially increased above the level usually used in commercial practice. To substantiate this point, a 12 percent aqueous solution of hydrogen peroxide or 40 volume peroxide, instead of the usual 6 percent hydrogen peroxide, was prepared and used for dyeing. The hair coloring was excellent and the conditioning action was clearly evident.

We have also found that even at peroxide concentrations substantially lower than commercial levels, the presence of the milk or beer provides a leveling and protective effect and allows the dye to provide a very natural hair color, substantially reducing or eliminating damaged and porous sections of the hair from "grabbing" the dye and thereby developing more intense and darker colors. Furthermore, the surface of the hair is more lustrous, smoother to the touch, and easier to comb and arrange into a coiffure. More importantly, a significant stiffness is imparted to the hair so that the dry coiffure has more "body," especially when whole milk is employed.

Virtually any commercially available oxidative hair-dye composition can be successfully employed in the hair-coloring mixture of this invention. Such oxidative hair-dye compositions generally comprise para-benzenoid-diamines, couplers, wetting and foaming agents, viscosity-controlling agents, antioxidants, ammonia, isopropyl and/or ethyl alcohol, and water. Some typical oxidation dye formulations are shown below in TABLES I and II, and were obtained from the American Perfumer and Cosmetics magazine, page 61, Vol. 83, October 1968.

TABLE I.

OXIDATION DYE FORMULATIONS

Intermediates & Chemicals	Black	Dark Brown	Light Brown	Auburn	Blond	Grey
para-phenylenediamine	2.70	0.80	0.56	0.08	0.15	0.15
resorcinol	0.50	1.60	0.80	0.10	1.00	0.80
para-aminophenol		0.20	0.20		0.20	0.15
ortho-aminophenol	0.20	1.00	0.28	0.04	0.20	
2, 4-diaminoanisol sulfate	0.40				0.01	0.07
nitropara-phenylene-diamine			0.04	0.40	0.04	
2-nitro-4-aminophenol				0.40		
oleic acid	20.0	20.0	20.0	20.0	20.0	20.0
oleyl alcohol	15.0	15.0	15.0	15.0	15.0	15.0
Solulan 5*	3.0	3.0	3.0	3.0	3.0	3.0

TABLE I. -Continued

Intermediates & Chemicals	OXIDATION DYE FORMULATIONS Black	Dark Brown	Light Brown	Auburn	Blond	Grey
propylene glycol	12.0	12.0	12.0	12.0	12.0	12.0
isopropyl alcohol	10.0	10.0	10.0	10.0	10.0	10.0
Hampene 100**	0.5	0.5	0.5	0.5	0.5	0.5
sodium sulfate	0.5	0.5	0.5	0.5	0.5	0.5
ammonium hydroxide (28%)	10.0	10.0	10.0	10.0	10.0	10.0
water (de-ionized)	19.0	19.0	19.0	19.0	19.0	19.0

*Solulan 5 — 5 mole ethyoxylated lanolin alcohols (American Cholesterol, Edison, N.J.)
**Hampene 100 — Ethylene diamine tetracetic acid Na_2 (New Hampshire Chem. Div., W. R. Grace, Nashua, N.H.) All weights are given in grams. The correct amount of dye is dissolved in the propylene glycol by heating. The oleic acid and Solulan 5 are mixed together and the dye solution added to this mixture with stirring. The oleyl alcohol is dissolved in the isopropyl alcohol and added to the mixture with stirring. Next, the ammonium hydroxide is added followed by the Hampene and sodium sulfate dissolved in the water.

TABLE II

Intermediates & Chemicals	OXIDATION DYE FORMULATIONS — TONERS Platinum	Silver	Smoke	Platinum Blond	Ash Blond	Gold Blond	Red Blond
para-phenylenediamine	0.08		0.06		0.10	0.05	0.06
para-toluylenediamine sulfate		0.10	0.04	0.08			
resorcinol	0.50	0.02	0.08	0.08	0.70	0.40	
pyrogallic acid			0.04				0.40
para-aminophenol	0.08			0.04			
2, 4-diaminoanisol sulfate	0.04	0.05	0.04	0.02	0.01		
2-nitro-4-aminophenol		0.002		0.02	0.04	0.20	
nitropara-phenylene-diamine			0.02			0.008	0.02
6-chloro-4-nitro-2-aminophenol						0.04	
4-nitroortho-phenylene-diamine							0.03
oleic acid	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Ethomeen S—12*	9.0	9.0	9.0	9.0	9.0	9.0	9.0
Cerasynt 303**	6.0	6.0	6.0	6.0	6.0	6.0	6.0
propylene glycol	12.0	12.0	12.0	12.0	12.0	12.0	12.0
isopropyl alcohol	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Hampene 100***	0.5	0.5	0.5	0.5	0.5	0.5	0.5
sodium sulfate	0.5	0.5	0.5	0.5	0.5	0.5	0.5
ammonium hydroxide (28%)	10.0	10.0	10.0	10.0	10.0	10.0	10.0
water (de-ionized)	22.0	22.0	22.0	22.0	22.0	22.0	22.0

*Ethomeen S—12 — Bis-2-hydroxyethyl soybean amine (Armour Industrial Chemical Co., Chicago, Ill.)
**Cerasynt 303 — Hydroxyethyl stearyl amide (Van Dyk, Belleville, N.J.)
***Hampene — Ethylene diamine tetracetic acid Na_2 (New Hampshire Chemical Company, Nashua, N.H.) All weights are given in grams. The method of dissolving is the same as in Table I, except that the oleic acid, Ethomeen S—12, and Cerasynt 303 are melted together until uniform, and then the propylene glycol solution of the dye is added.

Oxidation dye compositions of this type are already known to the experts. Typical formulas which can be used are disclosed in U.S. Pat. No. 3,561,912, issued to Boosen et al., and U.S. Pat. No. 3,563,684, issued to Charle et al. Other typical formulas are listed in Sagarin's "Cosmetics, Science and Technology," Interscience Publishers, Inc., New York 1957, on pages 503–512. Other typical oxidative dye compositions are described in a series of articles titled "Technology of Modern Oxidation Hair Dyes" by Gus S. Kass in the American Perfumer, see particularly Part I, July 1956, pages 27 and 28, and Part III, September 1956, pages 48 and 49. Some well-known commercial dye compositions which are representative of this type of oxidative hair-dye compositions and can be employed in the hair-coloring mixtures of this invention are "Vitacolor," manufactured by Zotos International, Inc.; "Miss Clairol," manufactured by Clairol, Inc.; "Color Charm" manufactured by Wella, Inc.; and similar dyes manufactured by Revlon and L'Oreal.

When the white hair of a particular individual is at least three times the number of naturally colored hair, generally referred to in the trade as 75% gray, complete dye coverage is required and the hydrogen peroxide concentration generally used in the trade is 6% or higher, provided substantially equal quantities of oxidative hair-dye compositions and oxidizing agents are intermixed.

In order to compare the hair-coloring mixture of this invention with the hair-coloring mixtures normally used for coverage of a 75% gray head of hair, the following experiment was performed. One ounce of Zotos "Vitacolor" V-51 Raven Black, an oxidative hair-dye composition, and one ounce of a 6 percent solution of hydrogen peroxide in water (20 volume hydrogen peroxide) were intermixed and applied to half the head of hair. The other half of the head of hair was dyed with a hair-coloring mixture comprising one ounce of the same oxidative hair-dye composition, one half ounce of whole milk, and one half ounce of a 12 percent solution

of hydrogen peroxide in water (40 volume hydrogen peroxide). The two sides of the head were equally intense in color, but the side dyed with the hair-coloring mixture containing the milk was more evenly colored from the scalp to the ends of the hair, while also being more lustrous, easier to comb, and the set coiffure when dry had more body.

Similarly, experiments involving other dye intermediate compositions, shown in Table III below, produced substantially identical results. Regardless of the particular coloring shade desired or the oxidative hair-dye composition employed, more desirable hair coloring was provided when the hair coloring mixture contained the milk.

TABLE III

COMMERCIALLY AVAILABLE OXIDATIVE HAIR-DYE COMPOSITIONS

Shade Groupings	Vitacolor	Miss Clairol Hair Color Bath	L'Oreal Imedia Par Excellence	Wella Color Charm	Roux Fanci-Tone Creme Tint	Helene Curtis Color-essence	Revlon Soft Tint
Ash Blondes	V42 August Moon	42 Moongold	6 Lt. Brown	542 Ash Blonde	16 Hidden Honey	23 Lt. Brown	15 Ultra Ash Med. Blonde
Reds	V45 Russet	45 Sparkling Sherry	66 Lt. Auburn	445 Lt. Auburn	31 Dark Blaze	44 Lt. Auburn	7 Cherry
Warm Browns	V57 Cafe Brown	57 Coffee Brown		257 Dark Golden Brown		31 Dark Warm Brown	8A Chestnut
Black	V51 Raven Black	51 Black Velvet	1 Blue Black	051 Black	12 Black Rage	20 Deep Black	12 Ebony

Semi-Permanent Hair Coloring

For women who are going gray and have less than 75 percent gray hairs and preferably less than 50 percent, our semi-permanent dyeing composition provides beautifully natural, non-fading colors which are highly resistant to light and shampoo, and do not develop off shades or streaky color sections even with prolonged wear and repeated shampooing. We have also found that on women who are going gray a much more natural appearance is achieved if complete coverage is avoided. The natural appearance desired can be achieved by maintaining the hydrogen peroxide-yielding compound concentration in the mixture applied to the hair between 0.2 and 1 percent by weight. The results, however, are generally improved when milk or beer is incorporated into the hair-coloring mixture.

By applying a hair-coloring mixture with substantially lower peroxide levels than normally employed in the trade, either with or without the use of milk or beer, a unique hair-coloring mixture is provided for the coloring of hair on heads which are merely going gray. The lower peroxide level substantially eliminates bleaching of the naturally colored hair while providing sufficient oxidation of the oxidative hair-dye composition and coloring only the graying hairs. Consequently, the advantages of a permanent dye — such as its resistance to repeated shampooing, prolonged wear, and stability to light — are provided in a semi-permanent hair-coloring mixture while avoiding the disadvantages of permanent and semi-permanent hair-coloring mixtures — such as streaky color sections, off shades, and hair bleaching. By incorporating milk or beer into the semi-permanent hair-coloring mixture of this invention, more natural and lustrous colors and more manageable hair are achieved.

The preferred hydrogen peroxide-yielding compound concentration in the semi-permanent hair-coloring mixture to be applied to the hair is about 0.35 percent by weight. This concentration of the available hydrogen peroxide-yielding compound is the same whether an aqueous solution of hydrogen peroxide or powdered urea peroxide is employed. We have found that at concentration levels below 0.2 percent by weight, the color development is too slow to be effective, and with hydrogen peroxide-yielding compound concentrations greater than 1 percent by weight, the coverage becomes too great to adhieve naturalness and the natural colored hair is lightened as well as damaged. By preventing damage to the hair's "natural appearance" and substantially reducing or eliminating areas where deeper color formation occurs, the new growth of the natural colored hair will not result in color variations. This reduces the rapidity with which touch-up applications are required, depending upon the relative amount of gray hairs.

In the final hair-coloring mixture to be applied to the hair comprising the oxidative hair-dye composition, the milk or beer and the oxidizing agent, the concentration of the milk or beer preferably ranges from about 25 to 75 percent by weight. If the concentration is greater than 75 percent by weight, the color imparted to the hair will tend to be too light; and if the concentration is less than 25 percent by weight, the improved even color, luster and body are not obviously present. Also, when low concentrations of milk or beer are employed, it is desirable to reduce the concentration of the oxidative hair-dye composition in the final hair coloring mixture to approximately 50 percent in order to prevent the developed hair color from becoming too dark. This concentration reduction is best achieved by merely adding a required amount of water to the hair-coloring mixture. In the preferred embodiment, whole fresh milk is used. However, skimmed milk, evaporated or dried milk powder, or synthetic milk-like products can be used with equal efficacy as long as their approximate solid content is substantially the same as whole fresh milk.

Once the hair-coloring mixture has been prepared, the mixture is preferably poured into a clean plastic applied bottle and immediately applied to the hair. Preferably, the mixture is first applied to the hair closest to the scalp without sectioning the hair. Then, the mixture is applied to the rest of the hair and worked throughout the hair as a shampoo, without massaging the mixture into the scalp.

A sufficient amount of time is then allowed to elapse until proper color development is achieved. Generally, from 20 to 35 minutes will be required for proper color development; however, various conditions and/or the use of well known methods can substantially alter the required time. When the desired color is achieved, water is added to the hair in sufficient quantity to work the hair-coloring mixture into a lather. The lather is spread throughout all the hair and then rinsed out with water immediately.

When previously colored hair is being retouched, the hair-coloring mixture is applied generously to the new growth only. If the hair shafts and ends have enough color from previous treatments, the hair-coloring mixture is not applied thereto. If the previously colored hair is faded, dry, porous or permanently waved, the remaining hair-coloring mixture should be diluted with an equal amount of shampoo and then blended throughout all the hair.

Oxidizing Agent

One of the major difficulties encountered with all hair coloring mixtures that require a source of oxidation is the inherent problems associated with hydrogen peroxide and urea peroxide. These two compounds have been found to be the best source of oxidation for hair-coloring purposes, but do possess well known stability and handling problems, and have characteristics that are distinguished by the hairdresser or the user as damaging to the hair. We have found that virtually all the difficulties and undesirable characteristics encountered with the use of hydrogen peroxide and urea peroxide are substantially reduced or eliminated by providing a solution of hydrogen peroxide or urea peroxide in a polyhydroxy alcohol, such as glycerine and/or propylene glycol. The hydrogen peroxide-yielding compounds have been found to be sufficiently stable in the presence of the polyhydroxy alcohols, and the presence of a polyhydroxy alcohol in the hair-coloring mixture has been found not to interfere with the reaction of the hydrogen peroxide-yielding compound and the oxidative hair-dye composition, but instead supplements the hair-coloring operation by providing a further conditioning action.

The solution of urea peroxide in an anhydrous polyhydroxy alcohol is particularly advantageous because of the difficulties involved with the use of urea peroxide. When the powdered form of urea peroxide is added directly to the oxidative hair-dye composition, complete mixture is difficult to obtain and oxidation of the dye composition begins immediately, before all the urea peroxide powder has been dissolved. Furthermore, solid crystals may fall to the bottom of the hair-coloring mixture, thus becoming inactive or if shaken may plug the nozle of the applicator. Also, sloid urea peroxide is not always sufficiently stable for a commercial product when subjected to the wide variations in temperature and humidity found in warehouses and the market shelves. The water solution of urea peroxide has been found to be even less stable than the powdered form and is avoided in the trade.

The solution of urea peroxide in the anhydrous polyhydroxy alcohol has been found to be completely stable and fully employable in all oxidizing hair-coloring mixtures. The only limitation found with urea peroxide is its upper solubility limit, such as 17 percent in propylene glycol at room temperature.

A solution of hydrogen peroxide in a polyhydroxy alcohol has the advantage of achieving higher concentrations than is possible with urea peroxide. This advantage is important when equal amounts of the oxidative hair-dye composition and milk or beer are used, since the hydrogen peroxide-yielding compound concentration in the polyhydroxy alcohol must be sufficiently high to assure proper oxidation of the oxidative hair-dye composition to achieve the desired intensity of the developed color.

Solutions of hydrogen peroxide in polyhydroxy alcohols have been found to be sufficiently stable, with the undesirable characteristics and properties of aqueous solutions of hydrogen peroxide substantially reduced or completely eliminated. One of the most important advantages of these polyhydroxy alcohol solutions is the elimination of whitening or blanching action on many skins. An 8 percent solution of hydrogen peroxide in a polyhydroxy alcohol did not produce a whitening or blanching action on most skins, while a 6 percent aqueous solution of hydrogen peroxide did produce a whitening or blanching action on most skins. Even on skins where a blanching reaction did occur with the hydrogen peroxide-polyhydroxy alcohol solutions, the time before skin blanching occurred was substantially increased. In most hair treatment operations, the hydrogen peroxide-polyhydroxy alcohol solutions will have been diluted or removed before the more sensitive skins will be blanched.

The substantial reduction or elimination of skin blanching is extremely important since a painful stinging sensation which persists for several minutes accompanies the skin blanching. To the hairdresser or user, the elimination of painful stinging and blanching is an important advantage since hair damage is associated therewith. Consequently, an oxidizing agent which comprises a solution of a hydrogen peroxide-yielding compound in a polyhydroxy alcohol represents a unique advancement in the hair treatment field and possesses great marketing potential.

In our preferred embodiment for the oxidizing agent, the concentration of the polyhydroxy alcohol is maximized, since the polyhydroxy alcohol does impart a conditioning action to the hair while also being a humectant. The fact that the polyhydroxy alcohol is a humectant is extremely important since this property slows or prevents water evaporation on the skin, thereby preventing the hydrogen peroxide from becoming concentrated thereon. Consequently, blanching and stinging does not occur on most skins.

These solutions of either urea peroxide or hydrogen peroxide in the polyhydroxy alcohol have the added desirable characteristic of being oily and viscous. This oily, viscous characteristic provides the user of the hair-coloring mixture with a feeling of increased conditioning.

The lower the water content, the more oily and viscous the solution will be. However, normally aqueous hair-coloring mixtures can be made more viscous by

incorporating viscosity-imparting materials in the aqueous oxidizing agents. However, most viscosity-imparting material will make the hydrogen peroxide-yielding compound in the aqueous oxidizing agent less stable, unless the viscosity-imparting material is one selected from the group consisting of carboxy methyl cellulose, methyl cellulose, hydroxyethyl cellulose, and polyvinylpyrrolidone. The incorporation of a viscosity-imparting material in the oxidizing agent substantially improves the handling characteristics of the oxidizing agent while conditioning the hair to obtain more natural colors.

Some persons skilled in the art may believe that an oxidizing agent such as hydrogen peroxide when dissolved in an organic liquid such as a polyhydroxy alcohol would be hazardous. However, independent tests were performed and it was discovered that a saturated sollution of urea peroxide and propylene glycol and a 24 percent solution of hydrogen peroxide in propylene glycol were not explosively hazardous. The hydrogen peroxide solution tested was prepared by dissolving a 35 percent aqueous solution of hydrogen peroxide in propylene glycol.

The preferred oxidizing agent compositions of this invention comprises a hydrogen peroxide composition prepared by dissolving a sufficient quantity of a 35 percent aqueous solution of hydrogen peroxide in propylene glycol to provide an 8 percent available hydrogen peroxide concentration. Generally, 23.3 kilograms of a 35 percent aqueous solution of hydrogen peroxide is dissolved in sufficient propylene glycol to obtain a final volume of 100 litres. In Table IV the compositions of the two preferred oxidizing agents are presented. Hydrogen peroxide stabilizers, well known in the art, may be added to these solutions of hydrogen peroxide-yielding compounds in the polyhydroxy alcohol to improve the hydrogen peroxide-yielding compound's stability in storage. We have also found that these solutions may be stored in glass; however, plastic containers are preferred. In summary, Table V presents various hair-coloring mixtures of this invention; and, in the examples that follow, the many distinct advantages of some of these mixtures are states.

TABLE IV

PREFERRED OXIDIZING AGENTS

Composition	Relative Weight Percent Formula No.1	Formula No.2
hydrogen peroxide	7–9	—
urea peroxide	—	15–17
water	14–16	—
propylene glycol	75–79	83–85

TABLE V

HAIR-COLORING MIXTURES

	A		B		C		D		E	
	Quantity (oz.)	% Wgt/Vol.	Quantity (oz.)	% Wgt/Vol.	Quantity (oz.)	% Wgt/Vol.	Quantity (oz.)	% Wgt/Vol.	Quantity (oz.)	% Wgt/Vol.
Oxidative hair dye composition	2	50	2	50	2	50	2	50	2	50
Oxidizing agent available hydrogen peroxide-yielding compound	1/6	.34	2	.35	2/3	1.0	1/6	.25	1/6	.34
water		.68		49.65		15.6		—		3.82
polyhydroxy alcohol		3.22		—				3.85		—
viscosity-imparting material		—		—		—				0.08
Milk	1–5/6	45.8	—	—	1–1/3	33.4	1–5/6	45.8	1–5/6	45.8

In Mixture A, the oxidizing agent is an 8% solution of H_2O_2 in propylene glycol.
In Mixture B, the oxidizing agent is an 0.7% solution of H_2O_2 in water.
In Mixture C, the oxidizing agent is a 6% solution of H_2O_2 in water.
In Mixture D, the oxidizing agent is a 17% solution of urea peroxide in propylene glycol (equivalent to 6.1% H_2O_2)
In Mixture E, the oxidizing agent is an 8% solution of H_2O_2 & 2% hydroxy methyl cellulose aqueous vehicle.

EXAMPLES

The following examples of our invention in use are presented for illustrative purposes only, and are not intended to be used in a limiting sense.

1a. A hair-coloring mixture of the following:
2 oz. Ash Blonde shade of "VitaColor V-42 August Moon," a trademarked dye produced by Zotos International, Inc., and
2 oz. of a 0.7 percent aqueous solution of hydrogen peroxide
was applied for 30 minutes to a head of clean brown hair that was "25 percent gray," and then shampooed out and dried. The hair appeared natural, since the pigmented hair was not lightened and the white hair was colored to the natural brown color. Also, the hair was not damaged, as indicated by a high 20 percent index of 0.95–1, using an Instron Tensile Tester. This test for hair damage is well known in the art and indicates the comparative strength of the treated hair with untreated hair when stretched 20% of its initial length

1b. By comparison, when the same "25 percent gray" head of hair was treated in the same way for the same time with a hair-coloring mixture comprising:
2 oz. of Vitacolor V-42 August Moon, and
2 oz. of a 6 percent aqueous solution of hydrogen peroxide,
the natural pigmented hair was bleached and resulted in an overall unnatural appearance. Also, the hair was damgaged, as indicated by the 20 percent index being 0.70–0.80, using an Instron Tensile Tester.

1c. A hair-coloring mixture comprising:
1-5/6 oz. of whole milk,
1/6 oz. of an 8 percent aqueous solution of hydrogen peroxide, and

2 oz. of Vitacolor V-42 August Moon

was applied in the manner described above in Example 1(a). The hair showed a higher gloss and smoother feel to the touch than was evident in Examples 1(a) and 1(b). These effects were easily observed by one skilled in the art. Furthermore, there was no damage to the hair, as indicated by a high 20 percent index of 0.95 using an Instron Tensile Tester.

1d. Ash Blond hair such as in the above examples was permanently waved and then two months later was colored by half-head techniques with the Semi-Permanent hair-coloring Loving Care Ash Blonde No. 73, marketed by Clairol, and the other half with the hair-coloring mixture employed in Example 1(c). Part of the hair was non-porous new growth and part was porous from the permanent wave. The results showed that the hair-coloring mixture of Example 1(c) produced excellent, leveled coloring with the color on the new growth (non-porous hair) substantially identical to the color on the porous section of hair. The Loving Care side was unevenly colored, with the porous (permanently waved) area having a different shade than the non-porous area.

2a. A hair-coloring mixture of the following:

2 oz. of the same Vitacolor Ash Blonde shade as used in Example 1 above,

1-5/6 oz. of milk, and

1/6 oz. of 8 percent hydrogen peroxide in propylene glycol (made by dissolving 23.3 Kg. of 35 percent hydrogen peroxide in sufficient propylene glycol to made 100 litres).

The hair-coloring mixture was applied on the same type of hair as in Example 1(a) above. The results in all respects were similar to those obtained in Example 1(c) above, but the hairdresser preferred to use this mixture and stated that she experienced no blanching or tingling action from contact with the propylene glycol solution, and liked its conditioning effect on the hair.

In place of the Viatcolor 42 August Moon, which is an Ash blonde shade, we have also done the same experiments on graying heads having naturally different colored hair. For example, we have used "Vitacolor V-45 Russet" for a head containing 65 percent natural red colored hair, and "Vitacolor V-57 Cafe Brown" for a head containing 75 percent warm brown natural colored hair, and "Vitacolor V-51 Raven Black" on a head having 80 percent natural black colored hair. The results were the same except for the shades of color produced.

The same superior results were obtained with the hair coloring mixture of our invention when we used dyes or tints from other commercial sources. In Table I above, the trade marked items from other commercial sources similar to the four Vitacolor shades noted above are presented.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative so as to obtain the benefit of all equivalents to which the invention is fairly entitled.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A hair-coloring mixture comprising:

A. between about 25 and 75 percent by weight of an aqueous oxidative hair-dye composition;

B. between about 0.1 and 50 percent by weight of an oxidizing agent comprising a hydrogen peroxide-yielding compound selected from the group consisting of hydrogen peroxide and urea peroxide and an aqueous carrier; and

C. between about 25 and 75 percent by weight of a conditioning agent selected from the group consisting of milk and beer.

2. The hair-coloring mixture as defined in claim **1** wherein said aqueous carrier further includes a viscosity-imparting ingredient selected from the group consisting of methyl cellulose, hydroxyethyl cellulose, carboxy methyl cellulose, and polyvinylpyrrolidone.

3. The hair-coloring mixture as defined in claim **1**, wherein the hydrogen peroxide-yielding compound of said oxidizing agent has a concentration between about 0.2 and 1 percent by weight of the total hair-coloring mixture.

4. The hair-coloring mixture as defined in claim **1** wherein the hydrogen peroxide-yielding compound of said oxidizing agent has a concentration of about 0.35 percent by weight of the total hair-coloring mixture.

5. The hair-coloring mixture as defined in claim **1**, wherein the aqueous carrier further includes a polyhydroxy alcohol selected from the group consisting of glycerine and propylene glycol.

6. A hair-coloring mixture comprising:

A. between about 25 and 75 percent by weight of an aqueous oxidative hair-dye composition; and

B. between about 25 and 75 percent by weight of an oxidizing agent comprising a hydrogen peroxide-yielding compound selected from the group consisting of urea peroxide and hydrogen peroxide and an aqueous carrier containing a polyhydroxy alcohol selected from the group consisting of glycerine and propylene glycol.

7. The hair-coloring mixture as defined in claim **6**, wherein the hydrogen peroxide-yielding compound of said oxidizing agent has a concentration between about 0.2 and 1 percent by weight of the total hair-coloring mixture.

8. The hair-coloring mixture as defined in claim **6**, wherein the hydrogen peroxide-yielding compound of said oxidizing agent has a concentration of about 0.3 percent by weight of the total hair-coloring mixture.

9. A method for coloring the hair on a human head comprising the steps of

A. applying a hair-coloring mixture comprising between about 25 and 75 percent by weight of an aqueous oxidative hair-dye composition; between about 0.1 and 50 percent by weight of an oxidizing agent comprising a hydrogen peroxide-yielding compound selected from the group consisting of hydrogen peroxide and urea peroxide and an aqueous carrier; and between about 25 and 75 percent by weight of a conditioning agent selected from the group consisting of milk and beer to the hair; and

B. allowing sufficient time for color development.

10. A method for coloring hair on a human head comprising the steps of:

A. applying a hair-coloring mixture comprising between about 25 and 75 percent by weight of an aqueous oxidative hair-dye composition; between about 0.1 and 50 percent by weight of an oxidizing agent comprising a hydrogen peroxide-yielding compound selected from the group consisting of hydrogen peroxide and urea peroxide and an aqueous carrier containing a viscosity imparting ingredient selected from the group consisting of methyl cellulose, hydroxyethyl cellulose, carboxy methyl cellulose, and polyvinylpyrrolidone, and between about 25 and 75 percent by weight of a conditioning agent selected from the group consisting of milk and beer to the hair; and

B. allowing sufficient time for color development.

11. A method for coloring the hair on a human head comprising the steps of:

A. applying a hair-coloring mixture comprising between about 25 and 75 percent by weight of an aqueous oxidative hair-dye composition; and between about 25 and 75 percent by weight of an oxidizing agent selected from the group consisting of urea peroxide and hydrogen peroxide and an aqueous carrier containing a polyhydroxy alcohol selected from the group consisting of glycerine and propylene glycol to the hair; and

B. allowing sufficient time for color development.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,898,032 Dated August 5, 1975

Inventor(s) Walter W. Edman and Ralph L. Evans, Jr.

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

Column 1, Line 45, "blecahing" should be -- bleaching --

Column 2, Line 3, "coverae" should be -- coverage --

Column 3, Line 15, "hydrogen/peroxide yielding" should be -- hydrogen peroxide-yielding --

Column 3, Line 20, "hydrogen/peroxide yeilding" should be --hydrogen peroxide-yielding --

Column 4, Line 9, "hydrogen/peroxide yielding" should be -- hydrogen peroxide-yielding --

Column 8, Line 36, "adhieve" should be -- achieve --

Column 9, Line 2, "applied" should be -- applier --

Column 9, Line 64, "nozle" should be -- nozzle --

"sloid" should be -- solid --

Column 12, Line 39, "1a." should be -- 1(a) --

Column 12, Line 55, "1b." should be -- 1(b) --

Column 12, Line 65, "1c." should be -- 1(c) --

Column 13, Line 9, "1d." should be -- 1(d) --

Column 13, Line 24, "2a." should be -- 2(a) --

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,898,032 Dated August 5, 1975

Inventor(s) Walter W. Edman and Ralph L. Evans, Jr.

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

Column 13, Line 39, "Viatcolor" should be -- Vitacolor --

Column 14, Line 53, "0.3" should be -- 0.35 --

Signed and Sealed this

twenty-first Day of *October 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks