

OXIDATIVE HAIR DYE COMPOSITION

The present invention relates to aqueous oxidative hair dye compositions with unique rheological properties. The hair dye compositions of the present invention have excellent flow-on and stay-put properties.

The physical properties of oxidative hair dye compositions of the prior art generally represent a compromise between the flow characteristics required at different stages of the dyeing process. When an oxidative hair dye composition is applied to the hair, it should be of a suitably fluid character so that it flows on, and covers, each entire hair shaft within the mass of hair on the head. On the other hand, if the dye remains too fluid after application to the hair, then, the dye will undesirably run and drip off the head. If the latter problem is intended to be avoided by making the dye rather viscous, then it will not flow desirably on to the hair at the time of application of the dye.

We discovered an oxidative hair dye composition which has favorably variable viscosity characteristics, including a low shear rate (8.5 sec^{-1}) viscosity from about 3,200 to about 10,000 centipoises (cps) and a high shear rate ($1,370 \text{ sec}^{-1}$) viscosity from about 70 to about 150 cps and a stay-put flow path of not more than 1" (2.54 cm). A composition of the present invention comprises, based on the weight of the entire composition: from about 5 to about 10 percent of a fatty acid containing between 18 and 22 carbon atoms in the molecule; sufficient alkalizer to neutralize said fatty acid and to establish in the hair dye composition a pH between 8.5 and 11.5; from about 1.25 percent to about 5 percent of a fatty alcohol having between 12 and 22 carbon atoms in the molecule;

preferably from about 1.5 percent to about 6 percent of a hair dye oxidant, expressed as absolute H_2O_2 ; and from about 10 percent to about 15 percent of at least one alkoxyated alkyl phenol having an HLB from about 9 to about 11.5; the composition having the viscosity properties specified at the beginning of this paragraph. All percentages are by weight unless specified otherwise. All chemical names are used in accordance with the nomenclature employed by the CFTA Cosmetic Ingredient Dictionary, published by The Cosmetic Toiletry and Fragrance Association, Inc. in 1982. All parameters are at room temperature.

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Thus, the present invention provides a hair dye composition having marked thixotropic properties, its "viscosity as a function of shear rate" curve having a rather sharp slope. This means that when the hair dye composition containing the base composition of the present invention is subjected to high shear, e.g. when it is agitated, when applied and for a relatively short period thereafter, its viscosity is rather low. This results in it being sufficiently fluid to flow well onto the hair upon application. After being applied to the hair, the composition will become increasingly viscous and will not drip or run off the hair. Comparative tests with a large number of commercial hair dye compositions have proven the superiority of the flow characteristics of hair dye compositions prepared in accordance with the present invention.

The HLB of an emulsifier is determined in accordance with the detailed description contained in the booklet entitled The Atlas HLB System, published by Atlas Chemical Industries, Inc. The letters HLB stand for hydrophile-lipophile balance. This system was introduced by Atlas Chemical Industries in the late 1940's as a systematic scheme for the designation of the emulsifying characteristics of materials. Each emulsifier is assigned a numerical value which is referred to as its HLB. The numerical value refers to the balance of the size and strength of the hydrophilic or polar and the lipophilic or non-polar groups in each emulsifier, since all emulsifiers consist of a molecule that combines both hydrophilic and lipophilic groups. An emulsifier that is lipophilic in character is assigned an HLB below 9 and one that is hydrophilic is assigned an HLB above 11. Those between HLB 9 and HLB 11 are considered intermediate in character.

When a plurality of emulsifiers are mixed, the composite HLB of the mixture is an arithmetic total of the product of the percentage of a given ingredient and its HLB. For example, in the case of a suitable combination of the alkoxyated alkyl phenols
5 nonoxynol-9 (HLB 13), and nonoxynol-4 (HLB 8.8), when both are present in identical concentrations the resulting HLB of the mixture is 10.9. Other suitable alkoxyated alkyl phenols or blends thereof will be readily apparent to those having an average skill in the art of hair dye formulations.

10 Since the oxidizer is an essential ingredient of the compositions of the present invention, and since the oxidizer, or developer composition as it is referred to in the hair dyeing art, has to be maintained apart from the composition containing one or more hair
15 dye intermediates (often referred to as the "tint" in the hair dyeing art), and since both the developer and tint compositions are aqueous solutions, it is preferred that at least a part of the alkoxyated alkyl phenol emulsifier be contained in the developer composition. This will promote the easier blending of the developer
20 composition with the tint composition when both are mixed with each other prior to use.

Illustrative of the C_{18} - C_{22} fatty acids that can be employed with the present invention are stearic acid, behenic acid, arachidic acid, arachidonic acid, oleic acid, linoleic acid or mixtures of
25 acids, such as from natural sources, e.g. tall oil acid. These acids can be saturated or unsaturated.

A variety of C_{12} - C_{22} fatty alcohols can be employed in the invention, such as lauryl, oleyl, stearyl, isostearyl, cetyl, myristyl, behinyl alcohol and the like. These alcohols can have a saturated, unsaturated, straight chain or branched structure.

30 The alkalizer can be any material conventionally employed in hair care compositions, such as ammonium hydroxide, monoethanolamine, and the like, to neutralize the fatty acid and to establish the requisite alkaline pH.

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Although the oxidizer is expressed in terms of hydrogen peroxide, other oxidizers suitable for use in hair treating compositions, such as other peroxides, e.g. urea peroxide, can also be employed. While it is to be understood that even though
5 reference is made throughout the specification in the claims to a hair dye composition, the present invention, as disclosed throughout the specification and the claims is also intended to include mild bleaches which do not necessarily contain hair dye intermediates which produce a color. Normally, however, compositions intended
10 primarily for the bleaching of hair also contain bleach boosters, such as powdered percompounds in addition to an oxidizer, such as hydrogen peroxide. It was found, however, that the beneficial variable viscosity characteristics of the present invention could not be obtained when such bleach boosters were added to the
15 composition.

The flow properties of the composition of the present invention were compared to a relatively large number of commercially available oxidation hair dyes. The data concerning these comparisons are presented herein, following the examples. All of the commercially
20 available compounds exhibited a certain amount of shear rate dependence in their viscosity, however, none of them have demonstrated the high degree of shear rate dependence as those of the present invention. Therefore, it appears that in formulating the commercial compositions of the prior art a tradeoff was
25 necessary either to provide a high viscosity at low shear rates -to assure good stay-put properties-, or to provide sufficiently low viscosities at high shear rates -to provide good flow-on properties-, but not both. With a minor exception, it appears that the formulators of the commercial compositions generally chose to
30 provide low viscosities at high shear rates, at the expense of obtaining insufficiently high viscosities at low shear rates. No such tradeoff is necessary in the case of the compositions of the present invention, because the considerably sharper shear rate dependence of the viscosity values permits the achievement of ideal
35 viscosities at both the high and low ends of the shear rate range.

Following the examples there is a listing given of many of the commercial oxidative hair dye products that were used in this

comparison, on the basis of the ingredient listings on their labels. This information was available only for those commercial hair dyes which are sold in the United States, because no ingredient listing is required in other countries. None of the commercial oxidative hair dyes for which the ingredients are available, contain the unique combination of ingredients of the present invention.

Since the shear rate-dependent viscosity measurements of compositions in accordance with the present invention and of commercial oxidative hair dye compositions indicated that the formulators of the commercial compositions apparently intended primarily to assure good flow-on properties during application of the dyeing composition to the hair, a further series of tests were made. In this series of tests the high viscosity stay-put properties of compositions in accordance with the present invention and of commercial compositions were compared. A dab of each oxidative hair dye composition was placed onto the top of an inclined board and after five minutes the distance that each sample traveled, was measured. The data of these comparative stay-put tests are also provided following the examples. These data show that only one commercial hair dye composition (Polycolor Creme Haircolor 45) had stay-put properties similar to those of the compositions of the present invention. The high shear-rate viscosity data for that same commercial composition indicate, however, a relatively high viscosity value which suggests comparatively unfavorable flow-on properties and, of course, indicates that the tradeoff in the case of this commercial composition was weighted towards providing high viscosity at low shear rates for better stay-put properties. As explained below, the stay-put tests further revealed that high viscosity at low shear rates does not necessarily assure good stay-put properties of a dye composition. Therefore, in addition to the requirement that the composition have a viscosity at a low shear rate of 8.5 sec^{-1} of from about 3,200 to about 10,000cps, it is a further requirement that on the stay-put test it should have a travel distance of not more than 1 inch (2.54 cm).

A number of comparative experiments were carried out for determining the essential ingredients which contribute to the favorable rheological properties in accordance with the present invention. These comparative experiments not only established the essential

ingredients which contribute the desirable properties, but also established that while it might be expected that the low shear viscosity values are somewhat indicative of the stay-put characteristics of the composition, the stay-put flow test on the inclined substrate is at least equally if not more important characteristic. Therefore, a high low shear viscosity does not necessarily result in an acceptable stay-put results on the inclined plate.

A tint base containing the following ingredients, expressed as percent by weight, based on the tint base composition, served as the basis of comparison.

	lauramide DEA	3.0%
	ammonium hydroxide	8.7
	cetyl alcohol	2.5
15	oleic acid	12.0
	laureth-23	0.5
	water to 100	-

An equal volume of the developer of Example 3 was employed in these tests. The base had a low shear (8.5 sec^{-1}) viscosity of 5324 cps and a high shear (1370 sec^{-1}) viscosity of 101 cps, and in the stay-put flow test it did not show any movement.

The following table summarizes the comparative results. The first column of the table indicates the difference between the sample and the above-mentioned tint base-composition.

	<u>Sample</u>	<u>Flow Dist.(in)</u>	<u>Shear Rate (sec⁻¹)</u>	<u>Viscosity (c)</u>
5	oleic acid omitted	9	8.5	1521
			1370	38
	cetyl alcohol omitted	3.5	8.5	1711
			1370	160
	lauramide DEA omitted	1	8.5	3423
			1370	70
	laureth-23 omitted	0	8.5	6465
			1370	101
	lauramide DEA			
10	and laureth-23 omitted	0	8.5	4563
			1370	81
	oleyl alcohol instead			
	of cetyl alcohol	0	8.5	7225
			1370	105
	lauric acid instead			
	of oleic acid	10	8.5	950
			1370	211
15	lauryl alcohol			
	instead of cetyl alc.	0	8.5	6465
			1370	105
	palmitic acid instead			
	of oleic acid	6	8.5	1521
			1370	105
	myristic acid instead			
20	of oleic acid	9	8.5	950
			1370	139
	isostearic alc. instead			
	of cetyl alcohol	1	8.5	3802
			1370	90

A further series of similar comparative tests were made to determine the other essential ingredients which are contributed to the hair dye composition through the developer component. Accordingly, it was found that the oxidizer is an essential ingredient and so is the presence of from about 10% to about 15% by weight, based on the hair dye composition, of an alkoxylated and alkyl phenol having an HLB of from about 9 to about 11.5.

The following illustrative examples demonstrate embodiments of the present invention. All percentages are by weight of the composition of the examples, unless indicated otherwise.

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Example 1

The following composition is a tint component of a oxidative hair dye composition to provide light brown dyeings.

	ammonium hydroxide	8.7%
	cetyl alcohol	1.5
15	stearyl alcohol	1.0
	lauramide DEA3	3.0
	oleic acid	12.0
	fragrance	0.1
	laureth-23	0.5
20	phenylenediamide	0.27
	N,N bis(2-hydroxyethyl)	
	p-phenylenediamine sulfate	0.11
	1-naphthol	0.1
	resorcinol	0.85
25	sodium sulfite	0.1
	erythorbic acid	0.2
	EDTA	0.05
	water to 100	-

The tint composition contains ammonium hydroxide, 2 fatty
30 alcohols (cetyl and stearyl) and oleic acid which are the critical ingredients of the composition of the present invention.

Example 2

The following tint composition was prepared to provide a blonde shade.

	ammonium hydroxide	9.0%
5	cetyl alcohol	4.5
	lauramide DEA3	3.0
	oleic acid	13.0
	fragrance	0.1
	laureth-23	0.5
10	p-phenylenediamine	0.06
	N,N bis(2-hydroxyethyl)	
	p-phenylenediamine sulfate	0.16
	1-naphthol	0.03
	resorcinol	1.0
15	sodium sulfite	0.1
	erythorbic acid	0.2
	EDTA	0.05
	water to 100	-

Example 3

20 The following developer was prepared for use in conjunction with the tint compositions of Example 1 or Example 2.

	nonoxynol-9	10.0%
	nonoxynol-4	10.0
	EDTA	0.02
25	hydrogen peroxide - 50%	12.3
	water to 100	-

30 The hair dyeing composition is formed by mixing equal parts by volume of either of the tint compositions of Example 1 or Example 2 and the developer composition of Example 3. Mixing is accomplished either by shaking the mixture in an applicator bottle from which it can be directly applied through a spout to the hair, or by blending the two compositions in a mixing bowl and then applying the mixture with an applicator brush, as is customary in the hair dyeing art.

The viscosity measurements comparing the commercial oxidative

hair dyes with the compositions prepared in accordance with the present invention, were carried out on the Haake Rotovisco viscometer. The measurements are summarized in the following table, wherein the viscosity in centipoises (cps) is given for each material at a low shear rate of 8.5 sec^{-1} and at $1,370 \text{ sec}^{-1}$ high shear rate. All compositions employed the respective developer compositions of the commercial samples except in the case of the present invention where the developer of Example of 3 was employed.

	<u>sample</u>	<u>shear rate</u>	<u>viscosity</u>
10	Example 1	8.5	4563
		1370	78
	Preference 5	8.5	2282
		1370	93
15	Excellence 6	8.5	3042
		1370	110
	Nice 'n Easy 115	8.5	950
		1370	55
	Miss Clairol Creme Formula 36	8.5	2472
20		1370	105
	Clairette 214	8.5	1711
		1370	63
	Miss Clairol Shampoo Formula 36	8.5	1331
		1370	70
25	Kolestone 1200N	8.5	2472
		1370	89
	Majiblonde 901	8.5	2472
		1370	105
	Example 2	8.5	5894
30		1370	110
	Haute Mode A	8.5	3993
		1370	140
	Polycolor Creme Haircolor 43	8.5	3993
		1370	169
35	Polycolor Tonungs Wasche 18	8.5	951
		1370	80

The stay-put flow test comparisons of the compositions of the present invention with the commercial oxidative hair products were carried out by spotting 0.5g of each hair dye composition, respectively, onto a stiff cardboard which was inclined at an angle of 60° . After five minutes the distance to which each droplet

flowed downward was measured. The distances traveled by the various samples are shown in the following table. In the case of the commercial oxidation dyes the developer of that product was used. In the case of the compositions in accordance with the present invention the developer of Example 3 was employed. The numbers following some commercial samples indicate shade designations.

	<u>Sample</u>	<u>Flow Length</u>	
		<u>Inches</u>	<u>Centimetres</u>
	Example 1	0	0
10	Example 2	0	0
	Nice'n Easy	1.7	4.3
	Preference 9 1/2 BB	2.7	6.9
	Excellence 6	2.8	7.1
	Haute Mode A	2.2	5.6
15	Miss Clairol Shampoo Formula 36	1.7	4.3
	Miss Clairol Creme Formula 36	0.9	2.3
	Clairese 206	4.3	11
	Kolestone 800N	2.6	6.6
	Majiblond	1.8	4.6
20	Polycolor Tonungs Wasche 18	3.3	8.4
	Polycolor Creme Haircolor 45	0	0

In the case of the last commercial sample which demonstrated a good stay-put flow characteristic the high shear viscosity data for this sample show that in formulating this product the flow characteristics were apparently compromised towards higher viscosity.

From the labels of the commercial products sold in the United States and used for comparisons herein, the following compositions could be ascertained.

Preference, tint: ammonia, oleic acid, oleyl alcohol, cocamide DEA, polyglyceryl-4-oleyl ether, polyglyceryl-2-oleyl ether.
Developer: ceteth-2, oleamide DEA.

Nice'n Easy, tint: ammonia, oleic acid, octoxynol-1, nonoxynol-4, cocamide DEA. Developer: nonoxynol-9, nonoxynol-4, cetyl alcohol, stearyl alcohol.

Miss Clairol Shampoo Formula, tint: ammonia, tall oil fatty acid, octoxynol-1, nonoxnol-4, linoleamide DEA. Developer: nonoxynol-9, nonoxynol-4, cetyl alcohol, stearyl alcohol.

Miss Clairol Creme Formula, tint: ammonia, oleic acid
5 nonoxynol-4, octoxynol-1, sodium lauryl sulfate. Developer: water.

Excellence, tint: ammonia, triethanolamine, ammonium laureth sulfate, pareth-15-9, pareth-15-3. Developer: Ceteth-2, oleamide DEA.

10 Clairese, tint: Monoethanolamine, octoxynol-1, nonoxnol-9, linoleamide-DEA. Developer: nonoxynol-9, nonoxynol-9, cetyl alcohol, stearyl alcohol.



CLAIMS:

1. An oxidative hair dye composition which spreads easily when applied to the hair and stays in place once applied to the hair said composition having a viscosity at room temperature of from 3,200 to 10,000 centipoises at a shear rate of 8.5 sec^{-1} , a viscosity of from 70 to 150 centipoises at a shear rate of 1,370 sec^{-1} , and a maximum stay-put flow distance of one inch (2.54 cm).
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2. An oxidative hair dye composition which has an alkaline pH, has the viscosity properties specified in claim 1, contains an oxidizer and water, and comprises: from 5% to 10% by weight of a fatty acid containing from 18 to 22 carbon atoms in the molecule, sufficient alkalizer to neutralize said fatty acid and to establish a pH from 8.5 to 11.5, from 1.25% to 5% of a fatty alcohol having from 12 to 22 carbon atoms in the molecule, and from 10% to 15% of at least one alkoxyated alkyl phenol having an HLB, or a plurality of such phenols having a composite HLB, from 9 to 11.5.
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3. The oxidative hair dye composition of claim 2 wherein the composition comprises from 1.5% to 6% of a hair dye oxidant, expressed as absolute hydrogen peroxide.
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4. The oxidative hair dye composition of claim 2 or 3 wherein the fatty acid is saturated or unsaturated and the fatty alcohol is saturated or unsaturated and has a straight-chain or branched structure and said composition contains at least one oxidative hair dye intermediate.
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5. The oxidative hair dye composition of claim 4, wherein the fatty acid is at least one of stearic, behenic, arachidic, arachidonic, oleic, linoleic and tall oil acid.
6. The oxidative hair dye composition of claim 4/^{or 5} wherein the fatty alcohol is at least one of lauryl, oleyl, stearyl, isostearyl, cetyl, myristyl and behinyl alcohol.
30
7. The oxidative hair dye composition of claim 4/^{5 or 6,} wherein the alkoxyated alkyl phenol is an ethoxyated alkyl phenol.



8. An oxidative hair dye composition in accordance with claim 5 and with claim 6 and with claim 7, wherein the neutralization of the fatty acid and the adjustment of the pH are carried out with ammonium hydroxide.

9. A package including two containers, the contents of which are intended to be combined with each other before use each of said containers containing an aqueous composition, wherein:

- (a) one container contains an oxidative hair dye tint composition which comprises
 - (i) from 5% to 10% by weight, based on the weight of the contents of both containers, of a fatty acid containing from 18 to 22 carbon atoms in the molecule;
 - (ii) sufficient alkalizer to neutralize said fatty acid and to establish a pH from 8.5 to 11.5 in the composition after the contents of the two containers are combined; and
 - (iii) from 1.25% to 5% of a fatty alcohol having from 12 to 22 carbon atoms in the molecule; and
- (b) the other container contains an oxidative hair dye developer composition which comprises
 - (i) from 10 percent to 15%, based on the weight of the contents of the both containers, of at least one alkoxyated alkyl phenol having an HLB, or a plurality of such phenols having a composite HLB, from 9 to 11.5; and
 - (ii) from 1.5% to 6% of a hair dye oxidant, expressed as absolute hydrogen peroxide.



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10. A package as claimed in Claim 9, wherein composition "(a)" is substantially as indicated in Example 1 or 2, and composition "(b)" is substantially as indicated in Example 3.
- 5 11. An oxidative hair dye composition as claimed in Claim 2, comprising a mixture of substantially equal parts of a tint composition substantially as indicated in Example 1 or 2 and a developer composition substantially as indicated in Example 3.
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