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(54) **METHOD OF PROTECTING DYED HAIR
COLOR FROM FADING OR WASH-OUT**

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(57) **ABSTRACT**

A method of protecting dyed hair color from fading or wash-out during exposure to air and/or shampooing is described. In accordance with one aspect the method includes treating dyed hair with a composition containing (i) a hydrophobically modified quaternary polymer, (ii) a hydrophobically modified polymer plus a cationic surfactant, (iii) a polymer containing diethylaminopropyl methacrylamide (DMAPMA), dimethylaminoethyl methacrylamide (DMAEMA) or diethylaminoethyl methacrylamide (DEAEMA) or (iv) a combination thereof.

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METHOD OF PROTECTING DYED HAIR COLOR FROM FADING OR WASH-OUT

FIELD OF THE INVENTION

[0001] This invention relates to a method of protecting dyed hair color from fading or wash-out, and more particularly, to the use of particular polymers, such as hydrophobically modified polymers, for dyed hair color protection against shampoo treatments.

BACKGROUND OF THE INVENTION

[0002] The coloring of hair has become increasingly popular in recent years. However, fading of artificial hair color has become a common problem and a frequent complaint by consumers. Fading can occur during the shampoo washing treatment as color wash-out, or can be initiated by environmental circumstances, such as by exposure to UV radiation. The washing process is the most significant factor in the removal of hair color, while UV exposure had a significant impact only after 90 hours of intense irradiation. S. Marchiorretto, "The Use of Silicones as a Color Lock Aid in Rinse-Off Hair Conditioners", J. of Cosmetic Science, 2003 Annual Scientific Meeting, pp. 130-131. Furthermore, the surfactants present in shampoo formulations provide a wetting function which brings moisture into the hair shaft, thus facilitating the removal of the dye molecules to exit during the water rinsing process.

[0003] Maintaining hair color and minimizing hair color fading is highly desirable in the hair care market. Several anti-fading products exist in the market including anti-fading shampoos and conditioners. Some products contain silicones such as dimethicone and amodimethicone, which are believed to effect color retention. See A. Schlosser, "Silicones Used in Permanent and Semi-Permanent Hair Dyes to Reduce the Fading and Color Change Process of Dyed Hair Occurring by Wash-Out or UV Radiation", J. Cosmetic Sci., 55 (Supplement), pp. 123-131, 2004.

[0004] An article published in 2004 in *HAPPI*, relating to the permanency of Level 2 (a.k.a. demi-permanent) and Level 3 (a.k.a. oxidative or permanent) hair dyes, described an olefin graft conditioner ethylene/acrylate copolymer and acrylates amino methacrylate copolymer, at a 2-5% use-level improved color retention (vs. no treatment) by 15% for Level 2 dyes and by 5% for Level 3 dyes when incorporated into a two-part dye rather than applied as a post-dye conditioner. The proposed mechanism for this function is the formation of an occlusive olefin barrier on the surface of the hair. Martin, T., and Burns, T., "Novel Graft Polymers Boost Hair Color Retention", *HAPPI*, pp. 92-95, October 2004.

[0005] U.S. Pat. Nos. 7,066,966 and 7,147,672 disclose an oxidation dyeing composition for keratin fibers comprising a cationic poly (vinylactam).

[0006] In accordance with certain aspects of the present invention, hydrophobically modified cationic polymers or hydrophobically modified polymers plus a quaternizing agent are effective in protecting dyed hair color from color erosion induced by daily shampooing. The hydrophobically modified cationic polymers or hydrophobically modified polymers plus a quaternizing agent have both hydrophobic moieties and sufficient cationic charge density to maintain substantivity to hair while providing a hydrophobic barrier to "lock-in" hair dye from washing out during daily shampoo washing.

[0007] The present invention provides compositions containing particular polymers that protect dyed hair color

against shampoo washings. Preferred polymers include one or more polymers selected from the following groups of polymers:

[0008] 1. Hydrophobically modified quaternary polymers

[0009] or

[0010] 2. Hydrophobically modified polymers plus a cationic surfactant

[0011] or

[0012] 3. Polymers containing diethylaminopropyl methacrylamide (DMAPMA) or dimethylaminoethyl methacrylamide (DMAEMA) or diethylaminoethyl methacrylamide (DEAEMA)

[0013] Hydrophobically modified quaternary polymers that can be used in the present invention include quaternized polymers containing an alkyl substitution with a carbon number above three. The alkyl substitution can be either attached to the quaternary unit or to any other locations of the polymer. The preferred hydrophobically modified quaternary polymers in accordance with the present invention include the quaternary polymers of general formula $(R,R',R'',N-)^+X^-$, wherein R, R', are identical or different. They can be aliphatic or carry additional substituents. R" is an alkyl chain with a carbon number above 3, preferably from 8 to 22. X⁻ represents an anion, for example, chloride, bromide, etc., and N can be part of a heterocyclic or aromatic ring.

[0014] Examples of the hydrophobically modified cationic polymers include, but are not limited to, terpolymer of vinylpyrrolidone (VP), dimethylaminopropyl methacrylamide (DMAPMA), and methacryloylaminopropyl lauryldimmonium chloride (MAPLDAC) with a trade name of Styleze W-20®; alkyl substituted quaternized cellulose polymers such as those with trade names of Quatrisoft polymer LM-200 (Polyquaternium 24) and SoftCAT™ Polymers such as quaternized hydroxyethyl cellulose polymers with cationic substitution of trimethyl ammonium and dimethyldodecyl ammonium and stearyldimmonium hydroxyethyl or propyl cellulose (Crodacel QS) and Cocodimmonium hydroxypropyl oxyethyl cellulose (Crodacel QM); alkyl substituted quaternary dimethicone copolymers such as Polyquaternium-41 or 42.

[0015] Hydrophobically modified polymers that can be used in the present invention include polymers containing an alkyl moiety with a carbon number of at least 3. Examples of hydrophobically modified polymers include, but are not limited to nonionic hydrophobically modified polymers such as the copolymer of PEG-150, decyl alcohol and saturated methylene diphenyldiisocyanate with a trade name of Aculyn 44; nonionic guar gum with alkyl groups such as those with trade names of Jaguar HP-60, N-Hance® hydroxypropyl Guar; PVP/Eicosene copolymer; Nonoxynyl hydroxylcellulose with a trade name of Amercell Polymer HM-1500; cetyl hydroxyethyl cellulose (Natrosol Plus); hydroxy propyl cellulose; hydroxyl propylmethyl cellulose.

[0016] Examples of polymers containing dimethylaminopropyl methacrylamide (DMAPMA) or dimethylaminoethyl methacrylamide (DMAEMA) include poly(vinylpyrrolidone/dimethylaminopropyl methacrylamide) with a trade name of Styleze CC-10 and poly(vinylpyrrolidone/dimethylaminoethyl methacrylate) with a trade name of Copolymer 937 or 845.

[0017] The amount of polymer used in the compositions described herein depends upon the particular composition and usage of the composition. Typically, the amount of polymer in accordance with certain aspects of the present invention ranges from about 0.1 to about 10%, preferably from

about 0.5 to about 5.0%, and more preferably from about 1.0 to about 3.0% by weight, based on the total weight of the composition.

[0018] The cationic surfactants that can be used in the practice of the present invention include quaternized surfactants. The preferred quaternized cationic surfactants in accordance with certain aspects of the present invention are the quaternary ammonium compounds of general formula (R,R',R'',R''')⁺X⁻, wherein R, R', R'' and R''' are identical or different, are aliphatic or carry additional substituents, X⁻ represents an anion, for example, chloride, bromide, sulfate, etc., and N can be part of a heterocyclic or aromatic ring.

[0019] In particularly useful quaternized surfactants, R and R' are CH₃, and R'' and R''' are aliphatic or aromatic chains, for example, hydroxy ethyl cetearamidopropyltrimonium chloride.

[0020] A suitable amount of cationic surfactant in accordance with certain aspects of the present invention ranges from about 0.01 to about 30%, preferably from about 0.01 to about 25%, and more preferably from about 0.2 to about 20% by weight, based on the total weight of the composition.

[0021] The color protection treatment herein can be delivered by a post-color treatment (after dyeing of hair), either from a leave-in product or a rinse-off product or a combination thereof to provide at least 10% color protection against the untreated control after 10 time washes.

[0022] For optimum performance, the new hair color should be treated with the leave-in treatment formula and dried before the first shampoo wash and treated with the leave-in formula again after each shampoo and conditioner use.

[0023] The post color leave-in treatment formulations preferably may be in the form of a gel or cream or mousse or spray. The post color rinse off treatment typically can be in the form of shampoos, conditioners or other rinse off product forms.

[0024] Test Methods for Evaluating Hair Color Changes for Anti-Fading Effect

[0025] Polymer Screening Test—Soaking Test of Dyed Hair

1. Hair dye dissolution in water was determined by soaking fixed amount of dyed hair sample (0.5 g) in water containing 1% polymer (as solid). The soaking liquor was sampled after fixed hours of soaking and read for L, a and b values on HunterLab colorimeter (t=0 values were read before adding hair into a soaking liquor). Color changes generated by hair dye dissolution in soaking liquor were determined as dE calculated from L, a, b values of the soaking liquor before and after soaking.

$$dE = ((L_t - L_o)^2 + (a_t - a_o)^2 + (b_t - b_o)^2)^{1/2}$$

Where L_o, a_o, b_o; and L_t, a_t, b_t are measured Hunter L, a, b color parameters before and after soaking at certain time period, respectively.

A larger value of dE reflects greater change of color.

Fading Index = dE of polymer solution / dE of water. Maximum Fading index is 1, indicating no protection at all.

Polymers showing reduced dye dissolution or with a Fading Index less than 0.5 are further tested by multiple shampoo washing tests.

2. Multiple Shampoo Washing Test of Dyed Hair Tresses—Color Fastness Test

[0026] Polymers which show effectiveness in reducing hair dye dissolution in the soaking tests were selected to test in a full hair cream or gel formulations in multiple shampoo washing test. These polymers were formulated into hair care formulations as either a leave in treatment or rinse off formulations.

[0027] Hair Samples

[0028] Bleached hair was purchased from International Hair Importers. Each hair tress weighs 3.5 g and has a 1.5" width and a 6.5" length. It was split into halves for color fastness test, one half for the treatment test and the other half served as a non-treated control.

[0029] Hair Dyes

[0030] The bleached hairs were dyed using commercially available hair coloring products. The hair dye product tested in accordance with the certain examples were ones from red shade containing -Hydroxyethyl 4,5-Diamino Pyrazole Sulfate, which is thought to be the most delicate dye. One is intense dark red and the other is radiant Ruby. Intense dark red is used in most tested hair samples unless specified. In addition, a dark brown color of commercial hair coloring product was also used in some tests.

[0031] 10× Washing and Treatment Procedures

[0032] The wax tab of a hair tress was cut into two separate parts. One half was used as the control test, non-treatment tress. The other half was used for treatment test. The control half was washed with 0.75 g 12% SLES solution for 2 min., with one minute shampooing with rubbing and one minute rinse under running warm tap water. Then the hair tress was dried with a cold air hair blow dryer. The wash cycle was repeated for 10 times. Three different treatment procedures were used, leave-in treatment, rinse off treatment and the combination of leave-in and rinse off treatment. For a leave-in treatment test, 0.30 g product was applied to a damp, one half of dyed hair tress before the first shampoo, massaged gently through the tress and dried with cold air hair drier, followed by washing with 12% SLES then treated again with the leave-in formulation and cold air blow dried. Then the SLES wash and treatment and blow dry cycle were repeated 10 times. For a rinse off treatment, hair tress was washed by the treatment shampoo and/or treatment conditioners, cold air blow dried and repeated 10 cycles against 12% SLES as a control. For the combination of leave-in and rinse off treatment, the damp hair tress was treated with 0.30 g product, massaged gently through the tress and dried with cold air hair drier, followed with wash by the treatment shampoo and/or treatment conditioners. The cycle was repeated 10 times.

[0033] At the end of 3×, 5×, 8× and 10× washes, the dried hair tresses were measured for L, a, values using a HunterLab colorimeter and dE was calculated as color changes after washes.

[0034] Color Analysis of Hair Tresses Before and after Multiple Shampoo Washes:

[0035] Hair color changes before and after washes were determined by dE.

[0036] Color changes were measured by measuring Hunter L, a and b values on a HunterLab colorimeter. dE was calculated using the following equations to evaluate color change before and after washes.

$$dE = ((L_t - L_o)^2 + (a_t - a_o)^2 + (b_t - b_o)^2)^{1/2}$$

[0037] Where L_o, a_o, b_o; and L_t, a_t, b_t are measured Hunter L, a, b color parameters before and after washing, respectively.

[0038] The larger value of dE reflects greater change of color. It is reported that color difference with dE greater than 1 are generally perceptible by eye.

$$\% \text{ Color Protection} = \% \text{ dE improvement} = \frac{(dE \text{ treatment} - dE \text{ control}) \times 100}{dE \text{ control}}$$

[0039] A % dE improvement or % Color Protection over 10-15% is perceivable by eye.

EXAMPLE 1

[0040] Table 1 shows the results of color change of soaking liquor from dyed hair samples soaked in different polymer aqueous solutions (1% active), expressed as a Fading Index.

TABLE 1

Polymer No.	Polymer trade name	INCI name	Soaking test Fading index* 30 min.	Soaking test Fading index* 90 min.
1	Styleze W-20	Terpolymer of vinylpyrrolidone(VP), dimethylaminopropyl methacrylamide (DMAPMA), and methacryloylaminopropyl lauryldimonium chloride (MAPLDAC)	0.11	0.35
2	Styleze CC-10	Poly(vinylpyrrolidone/dimethylaminopropyl methacrylamide)(DMAPMA)	0.33	0.31
3	Conditioneze NT-20	Polyquaternium-28, Polyvinyl pyrrolidone and methacrylamidopropyl trimethylammonium chloride (MAPTAC)	0.71	0.84
4	Copolymer 937	Poly(vinylpyrrolidone/dimethylaminoethyl methacrylate)(DMAEMA)	0.34	0.46
5	Gafquat 755N	Quaternized copolymers of vinylpyrrolidone and dimethylaminoethyl methacrylate	0.73	0.94
6	Aquaflax FX-64	Isobutylene/ethylmaleimide/hydroxyethylmaleimide	0.63	1

FI = Fading Index = dEpolymer/dEwater, maximum = 1 = maximum fading.

*A Fading Index less than 0.5 for a polymer is considered to be project grant effective and is as supported also by multiple data in a shampoo wash test.

[0041] The results in Table 1 show that polymer #1 within the scope of this invention containing both a hydrophobic chain and a quaternary unit is the most effective in reducing hair dye dissolution in the critical first 30 min. soaking time. Polymers # 2 & #4 containing dimethylaminopropyl methacrylamide (DMAPMA) and dimethylaminoethyl methacrylate(DMAEMA) are within the scope of this invention and are effective as well. By contrast, comparative examples with polymers #3, 5, 6, are ineffective in reducing hair dye dissolution.

[0042] Table 1a provides results of a soaking test with hydrophilic polymers (PVP) which also fail to provide the fade resistance obtainable with certain aspects of the present invention. The results indicate the ineffectiveness of these polymers in reducing hair dye dissolution in water.

TABLE 1a

Hydrophilic polymers	FI @ 30 min.	FI @ 90 min.
PVP K 90	0.89	0.95
PVP K 120	0.71	0.99
PVP K 15	1.03	
PVP K30	1.03	
PVP K 60	1.01	
PVP/VA	1.03	

[0043] As comparative examples, other polymers were tested in both the soaking test and multiple shampoo washes. The results are given in Table 1b. Both the soaking and multiple shampoo wash tests demonstrate the ineffectiveness of these polymers.

TABLE 1b

Polymers	INCI name	FI 30 min.	FI 90 min	10x wash test
Cotton bloom	Oligosaccharides	1.14	1.57	negative
Aquaflax XL-30	Copolymer of Isobutylene/dimethylaminopropyl maleimide/ethoxylated maleimide/maleic acid copolymer	1.27	1.13	no effect
Styleze 2000, pH7, anionic polymer	Copolymer of vinyl pyrrolidone (VP)/Acrylates/Lauryl Methacrylate	0.82	0.80	negligible effect,
Chitosan	Chitosan			negative
PVA/VAM	Copolymer of vinyl alcohol and vinyl amide	1.01	1.32	
PVA MW 85K	Poly vinyl alcohol	0.94	1.23	
PVA MW 31K	Poly vinyl alcohol	1.15	1.41	
Aquaflax XL-30 + Ultrathix P 100	Ultrathix P 100 is cross linked acrylate polymer			negligible effect
XL-30 + Gantrez P 904	Copolymer of vinyl pyrrolidone and long chain a-olefin			ineffective
Hydroxypropyl quar (without a quaternizing agent)	Hydroxypropyl quar gum			no effect

EXAMPLES 2-9

[0044] Polymer Nos. 1, 2 and 4 from Example 1, which showed effectiveness in reducing hair dye dissolution in water, were tested in a clear gel formulation in a multiple shampoo washing test following the procedure described in the test method section. The hair tresses were treated with the anti-fading gel first, cold air blow dried and then washed with 12% SLES. The treatment and wash cycle was repeated 10x. As a control, the hair tress was treated with the same formulation without the polymer, 11506-85, then blow dried and washed with SLES. The test results are shown in Table 3.

TABLE 2

Gel formulation containing test polymers for leave in treatment in a 10x washing test.		
Ingredient	Test formula 11506-85A-F; 56B, 102-111; 10748-67 wt %	Control formula 11506-85 wt %
Jaquar HP-60, Hydroxy propyl Guar gum (as a thickner)	1.5	1.5
Test polymer (Nos. 1, 2, or 4)	2.0% (active)	0
Glycerin	1.0	1.0
Liquid Germal Plus	0.5	0.5
Water	To 100	To 100

TABLE 3

Hair color fastness test results, % Protection = % dE = (dE treatment - dEcontrol) x 100/dEcontrol							
Example #	Testing polymer/ Formula#	Structure unit	Tress#	3x wash % dE	5x wash % dE	8x wash % dE	10x wash % dE
2	Copolymer 937/11506-85A	VP-DMAEMA	58H	19			7
3	Styleze CC- 10/11506-56B	VP-DMAPMA	53H	18	7	5	14
4	Styleze W-20/ 10748-67	VP-DMAPMA - C12 quat	35H	27	21	24	38
5	Conditioneze NT-20/85B	VP- MAPTAC(quat)	59H	6	9	-5	-6

[0045] The multiple shampoo washing test results in Table 3 demonstrate that polymers within the scope of this invention contain both a hydrophobic chain and a quaternary unit. Styleze W-20 (Example 4) provides the best color protection benefit. Consistent with the soaking test result in Table 1, a quaternary polymer, Conditioneze NT-20 (Example 5)(comparative), containing no hydrophobic chain and no DMAPMA or DMAEMA unit is ineffective.

[0046] Another chemical class of polymer, hydroxyethyl cellulose (HEC) modified with either an alkyl chain (hydrophobicity) and/or quaternization, was tested for anti-fading effect in the multiple shampoo washing tests. These polymers were formulated into the same test formula as specified in Table 2, except Natrosol Plus (alkyl hydroxyl cellulose) in which Jaguar HP-60, Hydroxy propyl Guar gum, was not added. The multiple shampoo washing test results are given in Table 4 below.

TABLE 4

Hair color fastness test results, % Protection (% dE) = (dB treatment - dEcontrol) x 100/dEcontrol							
Example #	Testing polymer/ Formula#	Structure unit	Tress#	3x wash % dE	5x wash % dE	8x wash % dE	10x wash % dE
6	Cetyl-Hydroxy Ethyl Cellulose (HEC), Natrosol Plus/11506-106	Hydrophobic modified cellulose	78H	0	13	9	15
7	Quaternary salt of HEC, Polyquaternium - 10, Ritaquta 400LR/11506405	Quaternized HEC	77H	5	5	19	16

TABLE 4-continued

Hair color fastness test results, % Protection (% dE) = (dB treatment - dEcontrol) × 100/dEcontrol							
Example #	Testing polymer/ Formula#	Structure unit	Tress#	3× wash % dE	5× wash % dE	8× wash % dE	10× wash % dE
8	C12-HEC quaternary, Polyquaternium -24, Quatrisoft polymer LM-200/11506-102	C12-HEC quat	76H	11	22	25	21
9	Steardimonium Hydroxyethyl Cellulose, Crodacel QS/11506-111	C18-HEC quat	95H	18	17	19	31

[0047] The results in Table 4 demonstrate that the HEC derivatives containing both hydrophobic and quaternary units (Examples 8 and 9) provide acceptable levels of hair color fastness, especially in the important early washing stages.

EXAMPLE 10

[0048] A comparative composition containing an anionic polymer with a hydrophobic chain was tested. The anionic polymer was Styleze 2000, a copolymer of vinyl pyrrolidone (VP)/Acrylates/Lauryl Methacrylate, neutralized and formulated into the same test formulation and tested using the procedure specified in Examples 2-9. The results of the color fading test of this anionic hydrophobic polymer are given in Table 5 which shows that its effect on anti-fading is negligible or minor (<10%). The result from the soaking test is also listed in Table 5. Test results for the cationic hydrophobic polymer, Styleze W-20 is also listed showing the improved results obtained with the present invention.

TABLE 5

Hair color fastness test results, % Protection, % dE = (dE treatment - dEcontrol) × 100/dEcontrol							
Hydrophobic polymer/ Formula#	FI@ 30 m	FI@ 90 m	Tress#	3× wash % dE	5× wash % dE	8× wash % dE	10× wash % dE
Styleze 2000 (anionic & C12 chain polymer)/11506-110	0.82	0.80	79H	14	15	7.8	7.2
Styleze W-20 (W-DMAPMA - C12 quat)/10748-67	0.11	0.35	35H	>50	38	15	37

EXAMPLE 11

[0049] This example shows the anti-fading effect of hydrophobically modified polymers plus a quaternizing agent. Aculyn 44 is a hydrophobically modified nonionic polymer and was formulated into a hair care leave in treatment together with a cationic surfactant, Hydroxyethyl Cetearamidopropyl-dimonium Chloride in a raw material with a trade name of Prolipid 161®. The leave in treatment formulation is listed in Table 6. The color fading test results are listed in Table 7.

TABLE 6

Formulation of leave in hair treatment, 11337-82B			
Item#	Ingredients (Trade)/Supplier	INCI	Wt. %
Phase A			
1	Water	Water	84.56
2	Dissolvane NA-2 Hampshire	Disodium EDTA	0.20
3	Propylene Glycol	Propylene Glycol	1.00
4	Aculyn 44 (@ 1% active) Rohm & Haas	PEG-150 Decyl Alcohol/ SMDI Copolymer (34.85% actives)	2.87
Phase B			
5	Prolipid ® 161 (0.86% active) ISP	Hydroxyethyl Cetearamidopropyl-dimonium Chloride (and) Behenyl Alcohol (and) Cetearyl Alcohol	2.87

TABLE 6-continued

Formulation of leave in hair treatment, 11337-82B			
Item#	Ingredients (Trade)/Supplier	INCI	Wt. %
6	Jeecol-20 Jeen	Steareth-20 (HLB 15.3)	0.40
7	Jeecol-2 Jeen	steareth-2 (HLB 4.9)	0.60

TABLE 6-continued

Formulation of leave in hair treatment, 11337-82B			
Item#	Ingredients (Trade)/Supplier	INCI	Wt. %
10	Lanette O Wax Cognis Care	Cetyl Stearyl Alcohol	2.00
Phase C			
11	Water	Water	5.00
12	Liquid Germall Plus ISP	Propylene Glycol (and) Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	.50

[0050] Color fastness test results in Table 7 demonstrate that nonionic hydrophobically modified polymer plus cationic surfactant in Prolipid 161 provided significant benefit for anti-fading of hair color while either of them alone is ineffective by comparing test# 11-2 (inventive) to test# 11-1 and 11-3 (comparative).

TABLE 7

Hair color fading test results, % Protection = % dE = (dE treatment - dEcontrol) x 100/dEcontrol							
Test #	Testing polymer/ Formula#	INCI name	Tress#	3x wash % dE	5x wash % dE	8x wash % dE	10x wash % dE
11-1	Aculyns 44 in Jaquar HP-60 gel/11506-85C	PEG-150 Decyl Alcohol/SMDI Copolymer	67H	5	0	0	2
11-2	Aculyn 44 in Prolipid 161 cream/11337-82B		26H		36	41	48
11-3	Prolipid 161 in water	Hydroxyethyl Cetearamido- propyldimonium Chloride (and) Behenyl Alcohol (and) Cetearyl Alcohol	7H				0

[0051] Color fastness test results in Table 8 further prove that the anti-fading effect in the leave in treatment formula, 11337-82B, is attributable to the synergistic effect of hydrophobic polymer, Aculyn 44 and the quaternizing agent content in Prolipid 161.

TABLE 8

Color fading test results after 10x washes, % Protection = % dE = (dE treatment - dEcontrol) x 100/dEcontrol				
Test #	11-4	11-5	11-6	11-7
Tress#	4H, 8H, 26H	7H	5H	3H
Formula Discription	Original 11337-82B	Prolipid + Jeecols 11337-87A	Aculyn 44 + Jeecols 11337-84	Aculyn 44 + water 11337-86
Ingredients				
Water	84.56	87.43	92.43	96.43
Disodium EDTA	0.20	0.20	0.20	0.20
Propylene Glycol	1.00	1.00	1.00	0.00

TABLE 8-continued

Color fading test results after 10x washes, % Protection = % dE = (dE treatment - dEcontrol) x 100/dEcontrol				
Test #	11-4	11-5	11-6	11-7
Aculyn 44	2.87	0.00	2.87	2.87
Prolipid 161	2.87	2.87	0.00	0.00
Jeecol-20	0.40	0.40	0.40	0.00
Steareth-20				
Jeecol-2	0.60	0.60	0.60	0.00
steareth-2				
Cetyl Stearyl Alcohol	2.00	2.00	2.00	0.00
Water	5.00	5.00	0.00	0.00
Liquid Germall Plus	0.50	0.50	0.50	0.50
Color fastness test results, % dE improvement	20%, 25%, 48%	0%	0%	0%

EXAMPLE 12

[0052] Table 10 shows the color fastness results of a leave in treatment formula containing hydrophobic polymer, Aculyn 44, quaternizing agent content from Prolipid 161 and hydrophobic quaternary polymer, Styleze W-20. The formula ingredients are listed in Table 9. The daily leave in treatment formula provides 37% and 44% color protection with the two types of dye tested.

TABLE 9

Formulation of Leave in treatment cream, 11261-20			
Item#	Ingredients (Trade)/Supplier	INCI	Wt. %
Phase A			
1	Water	Water	79.62
2	Dissolvane NA-2 Hampshire	Disodium EDTA	0.20
3	Propylene Glycol	Propylene Glycol	1.00
4	Aculyn 44 (use @ 1% active) Rhom & Haas	PEG-150 Decyl Alcohol/ SMDI Copolymer (34.85% actives)	2.87

TABLE 9-continued

Formulation of Leave in treatment cream, 11261-20			
Item#	Ingredients (Trade)/Supplier	INCI	Wt. %
Phase B			
5	Prolipid ® 161 (using 0.86% active)ISP	Hydroxyethyl Cetearamidopropylidimonium Chloride (and) Behenyl Alcohol (and) Cetearyl Alcohol	2.87
6	Jeecol-20 Jeen	Steareth-20	0.40
7	Jeecol-2 Jeen	steareth-2	0.60
8	Ceraphyl SLK ISP	Isodecyl Neopentanoate	2.00
9	Beauty Butter ISP	Shea Butter	0.50
10	Lanette O Wax Cognis Care	Cetyl Stearyl Alcohol	2.00
Phase C			
12	Water	Water	5.00
	Styleze W-20 (20.5% active - use @ 0.5%)ISP	Polyquaternium-55	2.44
13	Liquid Germall Plus ISP	Propylene Glycol (and) Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.50

TABLE 10

Hair color fading test results of formula 11261-20, % Protection = % dE = (dE treatment - dEcontrol) × 100/dEcontrol						
Test #	Testing dye	Tress#	3x wash % dE	5x wash % dE	8x wash % dE	10x wash % dE
12-1	Intense dark red	21H	11	20	32	37
12-2	Radiant Ruby	20H	32	42	39	44

EXAMPLE 13

[0053] To further demonstrate the synergistic effect of polymer with a hydrophobic unit and a quat, hydroxypropyl guar gum which contains propyl unit was tested together with Prolipid 161 in color fastness test. Table 11 listed the test formula and the control test formula.

TABLE 11

Gel formula containing testing polymers for leave in treatment in 10x washing test.			
Ingredient	Test formula 11506-317 wt %	Control formula 11506-117a wt %	Test formula 11506-48 wt %
Jaquar HP-60, Hydroxy propyl Guar gum (as a thickener)	2.0	0	1.5
Prolipid 161, Hydroxyethyl Cetearamidopropylidimonium Chloride (and) Behenyl Alcohol (and) Cetearyl Alcohol	3.0	3.0	0
Liquid Germall Plus	0.5	0.5	0.5
Water	To 100	To 100	To 100

[0054] The color fastness results of the test formula and the control formula in Table 11 are shown in Table 12. Treatment with formula 11506-117 containing hydroxy propyl guar and Prolipid 161 which is within the scope of this invention provides 19% color protection after 10x washes (test# 13-2) while the guar gum alone (Test# 13-1) and Prolipid 161 alone (Test# 13-3) are ineffective after 10x washes.

TABLE 12

Hair color fading test results of formula 11506-117, % Protection = (dE = (dE treatment - dEcontrol) × 100/dEcontrol							
Test #	Testing formula	Tress#	3x wash % dE	5x wash % dE	8x wash % dE	10x wash % dE	
13-1	11506-48 vs untreated	34H	17	13	1	0	
13-2	11506-117 vs 117a	91H		20	21	19	
13-3	11337-117 vs untreated	7H				0	

EXAMPLE 14

[0055] The polymer within the scope of this invention contain both a hydrophobic chain and a quaternary unit, Styleze W-20® was formulated into a rinse off formula, a 2-in-1 shampoo formulation and a conditioner formulation to test its color fastness effect. The 2-in-1 shampoo and conditioner formulations are listed in Table 13 & 14. The rinse off formulations were either tested alone or together with a leave in gel formulation (Table 15) as specified below.

1. Styleze W-20® 2-in-1 shampoo wash versus 12% SLES wash as a control, 10 cycles
2. Styleze W-20® 2-in-1 shampoo wash versus the control with the 2-in-1 shampoo wash without Styleze W-20® in it, 10 cycles
3. First treatment to the hair with the leave in treatment formula, 10748-67, blow dried, followed by Styleze W-20® 2-in-1 shampoo wash vs the control with no Styleze W-20® in the leave in gel treatment, 11506-85 and SLES washes, 10 cycles.
4. First treatment to the hair with the leave in treatment formula, 10748-67, blow dried, followed by Styleze W-20® 2-in-1 shampoo wash and using Styleze W-20 conditioner and rinse vs the control with treatment containing no Styleze W-20® leave in gel treatment, 11506-85 and SLES washes, followed with application of no Styleze W-20® conditioner and rinse, 10 cycles.

TABLE 13

2-in-1 Shampoo formula, Pearlescent Bodifying Shampoo		
Ingredients	10906-131A, wt %	Control, 11571-7, wt %
Wafer	55.73	58.23
Styleze W20 (20% active)	2.5	0
Cocamphodiacetate(Miranol C2M NP)	15.0	15.0
Cocamidopropyl Betaine (Miratain CB)	3.52	3.52
Ammonium Lauryl Sulfate (Standapol A)	6.0	6.0
Sodium Lauroyl Sarcosinate(Maprosyl 30)	12.0	12.0
C12-C15 Alkyl Lactate (Ceraphyl 41)	0.50	0.50

TABLE 13-continued

2-in-1 Shampoo formula, Pearlescent Bodifying Shampoo		
Ingredients	10906-131A, wt %	Control, 11571-7, wt %
Glycol Stearate(Cerasynt IP)	0.25	0.25
Liquid Germal Plus	0.30	0.30
Sodium Chloride(25% solution)	2.00	2.00
Citric acid(25% solution)	2.20	2.20

TABLE 14

Conditioner formula			
Ingredients	11571-6A wt %	11571-6B wt %	Supplier
Water	89.90	92.90	
Disodium EDTA (Versene NA2)	0.10	0.10	
Prolipid ®161	2.50	0	ISP
Cetearyl Alcohol (Lanette O)	3.00	3.00	Care Chemicals
Glyceryl Stearate (and) PEG-100 Stearate (Arlacel 165)	1.50	1.50	Uniqema/ICI
Polyquaternium-55 (Styleze ® W-20), 20% active	2.50	2.50	ISP
Propylene Glycol (and) Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate (Liquid Gemmal ® Plus)	0.50	0.50	ISP
Citric Acid (50% aqueous solution)	0.35	0.35	

TABLE 15

Leave in gel formula containing Styleze W-20		
Ingredient	Test formula 10748-67 wt %	Control formula 11506-85 wt %
Jaquar HP-60, Hydroxy propyl Guar gum (as a thickner)	1.5	1.5
Testing polymer	2.0% (active)	0
Glycerin	1.0	1.0
Liquid Gemmal Plus	0.5	0.5

[0056] Table 16 shows the color fastness test results of dyed hair treated with Styleze W-20 rinse off, leave in treatment or combination of both. Three commercial products were also tested using the same test procedure for comparison. The results in Table 15 demonstrate that Styleze W-20 in the 2-in-1 shampoo formula (10906-131A) provides 22% protection at the end of 10 washes (compare test# 14-1a, 14-1b with 14-1c), which is much better than the two commercial products (test # 14-6 & 14-7). The combination treatment from the leave in gel, 10748-67, and the 2-in-1 shampoo provides the highest color protection, 45% to 51% at the end of 10 washes (test# 14-2a and 14-2b), which is better than the commercial product 1 (test# 14-5) and significantly more effective than commercial product 2 & 3 (test # 14-6 & 14-7). Test 14-7 and 14-8 are the tests of W-20 leave in gel, 2-in-1 shampoo and conditioner against commercial color lock product 2 as the control using red hair color samples and dark brown dyed hair respectively. Both results show the W-20 leave in and rinse off treatment are about 40% superior than the commercial product.

TABLE 16

color fading test results, % Protection = % dE = (dE treatment - dEcontrol) × 100/dEcontrol							
Test #	Formula#	Treatment types	Tress#	3× wash % dE	5× wash % dE	8× wash % dE	10× wash % dE
14-1a	10906-131A vs SLES	W-20 2-in-1 Shampoo	56H	29	9.7	33	22
14-1b	10906-131A vs SLES	W-20 2-in-1 Shampoo	75H	15	15	31	20
14-1c	10906-131A vs 11571-7	W-20 2-in-1 Shampoo vs no W 20 shampoo	63H	9	15	30	20
14-2a	10748-67 + 10906-131 vs 11506-85 & SLES	Leave in gel + W-20 2-in-1 Shampoo	73H	36	40	44	45
14-2b	10748-67 + 10906-131a vs 11506-85 & SLES	Leave in gel + W-20 2-in-1 Shampoo	81H	44	49	45	51
14-3	11571-6a vs 11571-6b	W-20 conditioner vs no W-20 cond.	57H	11	9	12	7
14-4	SLES washes 0748-67 + 0906-131a & 11571-6a	Leave in gel + W-20 2-in-1 Shampoo + W 20 conditioner	74H	0	8	17	24
14-5	Commercial color lock product 1 vs SLES washes	Leave in cream + shampoo + conditioner	83H	19	20	35	39

TABLE 16-continued

color fading test results, % Protection = % dE = (dE treatment - dEcontrol) × 100/dEcontrol							
Test #	Formula#	Treatment types	Tress#	3x wash % dE	5x wash % dE	8x wash % dE	10x wash % dE
14-6	Commercial color lock product 2 vs SLES washes	Shampoo + conditioner	89H	0	5	8	11
14-7	Commercial color lock product 3 vs SLES washes	Shampoo + conditioner	90H	41	24	3	12
14-8*	10748-67 + 10906-131a & 11571-6a against commercial color lock product 2	Leave in gel + W-20 2-in-1 Shampoo + W 20 conditioner	96H		26	36	40
14-9**	10748-67 + 10906-131a & 11571-6a against commercial color lock product 2	Leave in gel + W-20 2-in-1 Shampoo + W 20 conditioner	100H	14	27	20	38

*Hair tress was dyed with intense dark red color

**Hair tress was dyed with dark brown color

EXAMPLE 15

[0057] This example demonstrates the importance of applying leave in treatment to the new hair color before first shampoo washes. Two different tests were conducted. First, newly dyed hair samples were treated with leave in formula, 10748-67, blow dried with cold air, followed by 12% SLES wash. The treatment, dry and wash cycle was repeated 10 time. In another test, newly dyed hair sample was washed with SLES first then treated with formula 10748-67, dried. This cycle was repeated by 10x. The results in Table 17 indicate that applying a leave in treatment before the first shampoo wash of new color is important, providing important color protection during early washes (compare test#15-1 & 2 with test#15-3).

TABLE 17

Hair color fading test results of formula 10748-67 vs control formula 11506-85, SLES washes, % Protection = % dE = (dE treatment - dEcontrol) × 100/dEcontrol							
Test #	Formula#	Treatment types	Tress#	3x wash % dE	5x wash % dE	8x wash % dE	10x wash % dE
15-1	10748-67 vs 11506-85	Leave in gel before 1 st SLES wash	33H	>50	38	15	37
15-2	10748-67 vs 11506-85	Leave in gel before 1 st SLES wash	35H	26	20	34	38
15-3	10748-67 vs 11506-85	SLES wash first then leave in treatment	72H	0	19	30	39

[0058] Changes may be made by persons skilled in the art in the compositions and/or in the steps or the sequence of steps

of the method of manufacture described herein without departing from the spirit and scope of the invention as defined in the following claims.

What is claimed is:

1. A method of protecting dyed hair color from fading or wash-out during exposure to air and/or shampooing which comprises treating said dyed hair with a composition which comprises a polymer selected from the group consisting of:

- hydrophobically modified quaternary polymers wherein the polymer contains an alkyl moiety with more than 3 carbon atoms;
- hydrophobically modified polymers plus a cationic surfactant wherein the polymer contains an alkyl moiety with at least 3 carbon atoms;
- polymers containing diethylaminopropyl methacrylamide (DMAPMA) or dimethylaminoethyl methacrylamide (DMAEMA) or diethylaminoethyl methacrylamide (DEAEMA); and
- combinations thereof.

2. A method according to claim 1 wherein said polymer is a cationic polymer.

3. A method according to claim 1 wherein said polymer is a quaternized polymer wherein the alkyl moiety is either attached to the quaternary unit or to another location of the polymer.

4. A method according to claim 3 wherein said polymer has the general formula (R,R',R'', N-)*X⁻, wherein R, R', are identical or different and can be aliphatic or carry additional substituents; R'' is an alkyl chain with a carbon atom number above 3, X⁻ represents an anion and N can be part of a heterocyclic or aromatic ring.

5. A method according to claim 4 wherein R'' contains from 5 to 22 carbon atoms.

6. A method according to claim 1 wherein said composition is applied to the dyed hair in a leave-in manner prior to first shampooing or rinsing and the leave-in treatment is repeated after each shampoo or rinsing.

7. A method according to claim 1 wherein said polymer has both hydrophobic moieties and sufficient cationic charge density to maintain substantivity to hair while providing a hydrophobic barrier to lock-in hair dye.

8. A method according to claim 1 wherein said composition comprises a hydrophobically modified polymer plus a cationic surfactant.

9. A method according to claim 8 characterized in that the cationic surfactant is a quaternized surfactant selected from the group consisting of quaternary ammonium compounds of the general formula $(R,R',R'',R''')N^+X^-$, wherein R, R', R'' and R''' can be identical or different, aliphatic or carry additional substituents, X⁻ represents an anion and N is part of a heterocyclic or aromatic ring.

10. A method according to claim 1 wherein said polymer is selected from the group consisting of a terpolymer of vinylpyrrolidone (VP), dimethylaminopropyl methacrylamide (DMAPMA), and methacryloylaminopropyl lauryldimmonium chloride (MAPLDAC); alkyl substituted quaternized cellulose polymers; quaternized hydroxyethyl cellulose polymers with cationic substitution of trimethyl ammonium and dimethyldodecyl ammonium; stearyldimmonium hydroxyethyl or propyl cellulose; Cocodimonium hydroxypropyl oxyethyl cellulose; Polyquaternium-24, -41 or 42; nonionic hydrophobically modified polymers, copolymers of PEG-150, decyl alcohol and saturated methylene

diphenyldiisocyanate; nonionic guar gum with alkyl groups; hydroxypropyl Guar; PVP/Eicosene copolymer; Nonoxynyl hydroxylcellulose; cetyl hydroxyethyl cellulose; hydroxypropylcellulose; hydroxypropylmethyl cellulose and combinations thereof.

11. A method according to claim 1 wherein said polymer comprises about 0.1-10% by weight of said composition.

12. A method according to claim 1 wherein said dye is retained in an amount of at least 10% after multiple shampoo treatments.

13. A method according to claim 1 wherein the polymer is included in the shampoo or conditioner used in the subsequent shampoo treatment.

14. A method according to claim 1 wherein said composition does not contain a dye.

15. A method according to claim 1 wherein said polymer is applied in a leave-in treatment formulation.

16. A method according to claim 16 wherein said leave in treatment formulation is a gel, cream, mousse or spray.

17. A method according to claim 1 wherein said shampoo includes conditioner.

18. A method of protecting dyed hair color from fading which comprises applying a composition comprising a terpolymer of VP-DMAPMA-C12quat, in a leave-in manner in an amount of 0.1-3% by weight, optionally in a 2-in-1 shampoo, to provide at least 10% dye color protection measured as dE change after 10 washes.

19. A method according to claim 11 wherein said polymer comprises about 0.1-3% of said composition.

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