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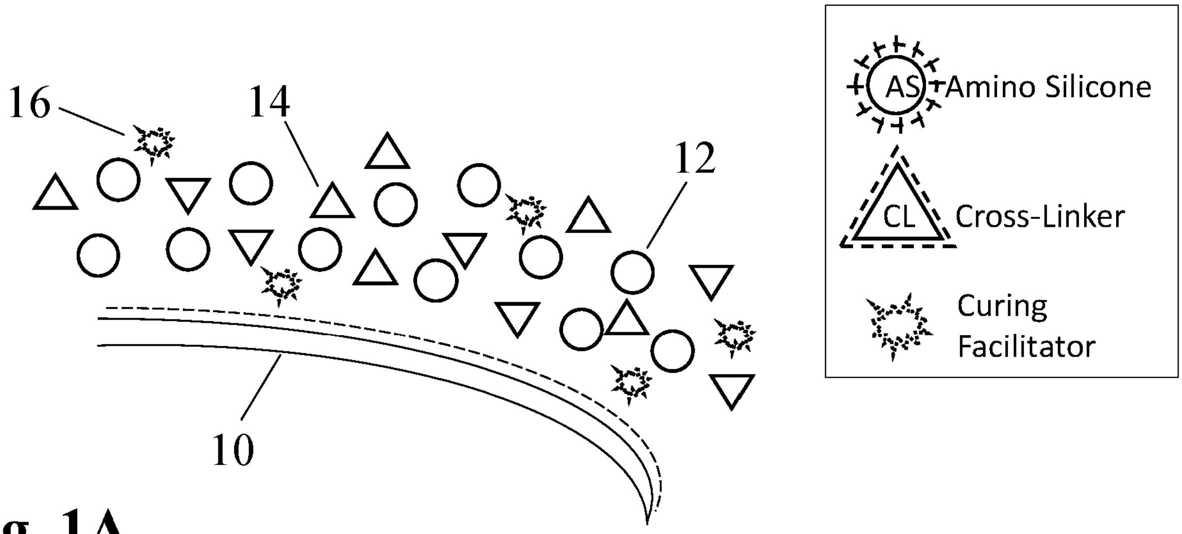


Fig. 1A

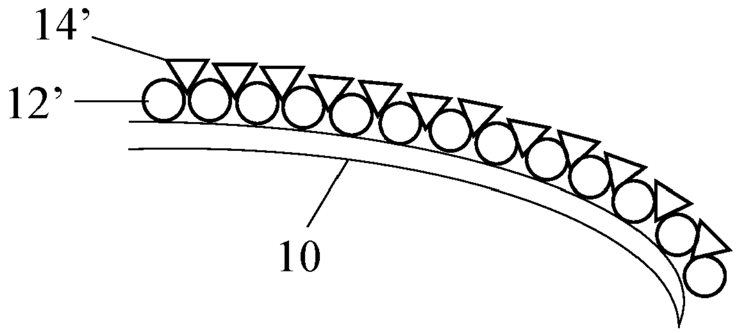


Fig. 1B

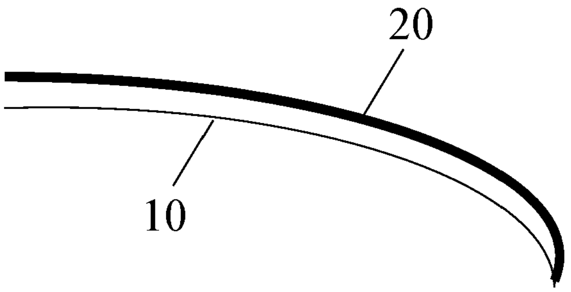


Fig. 1C

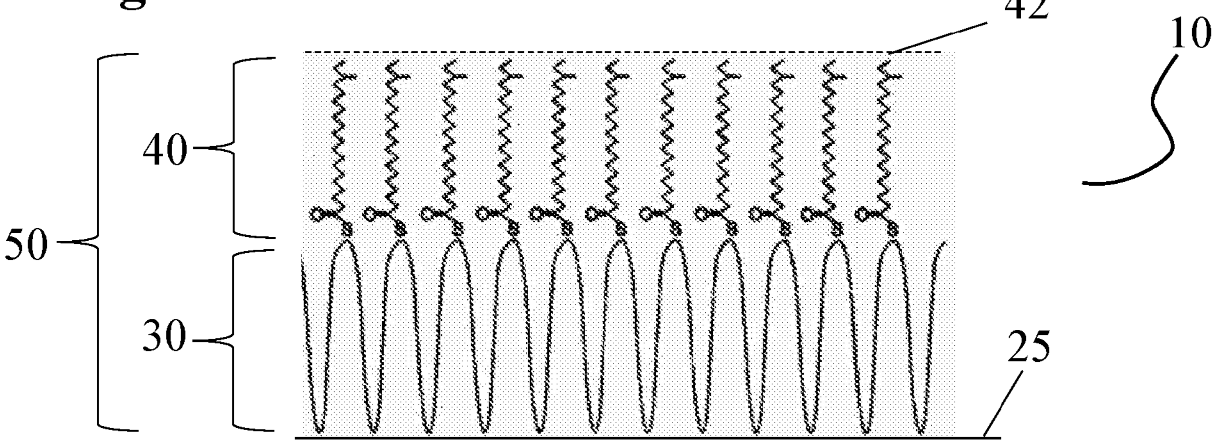
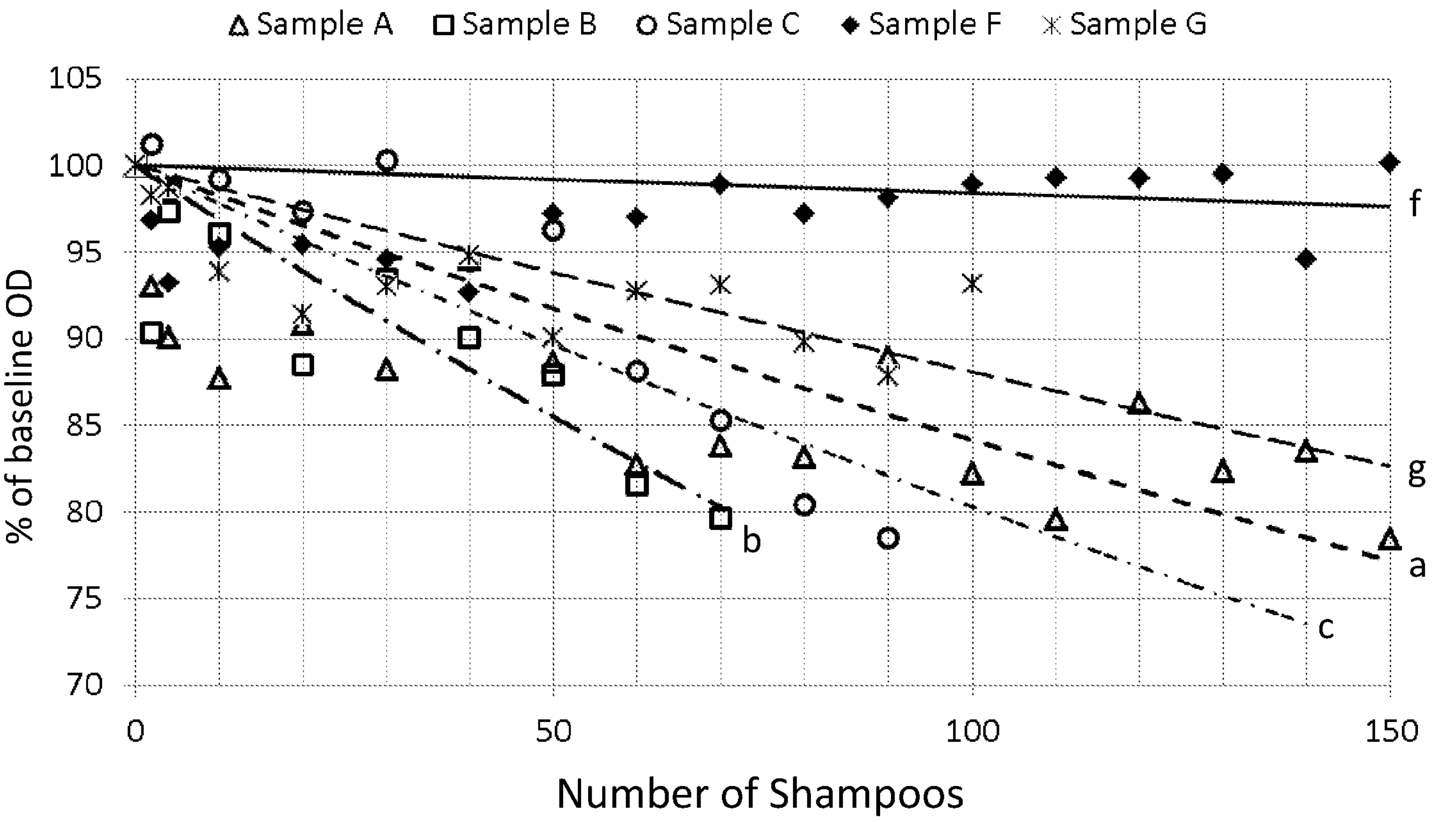


Fig. 1D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95
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% of baseline OD
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Fig. 2A

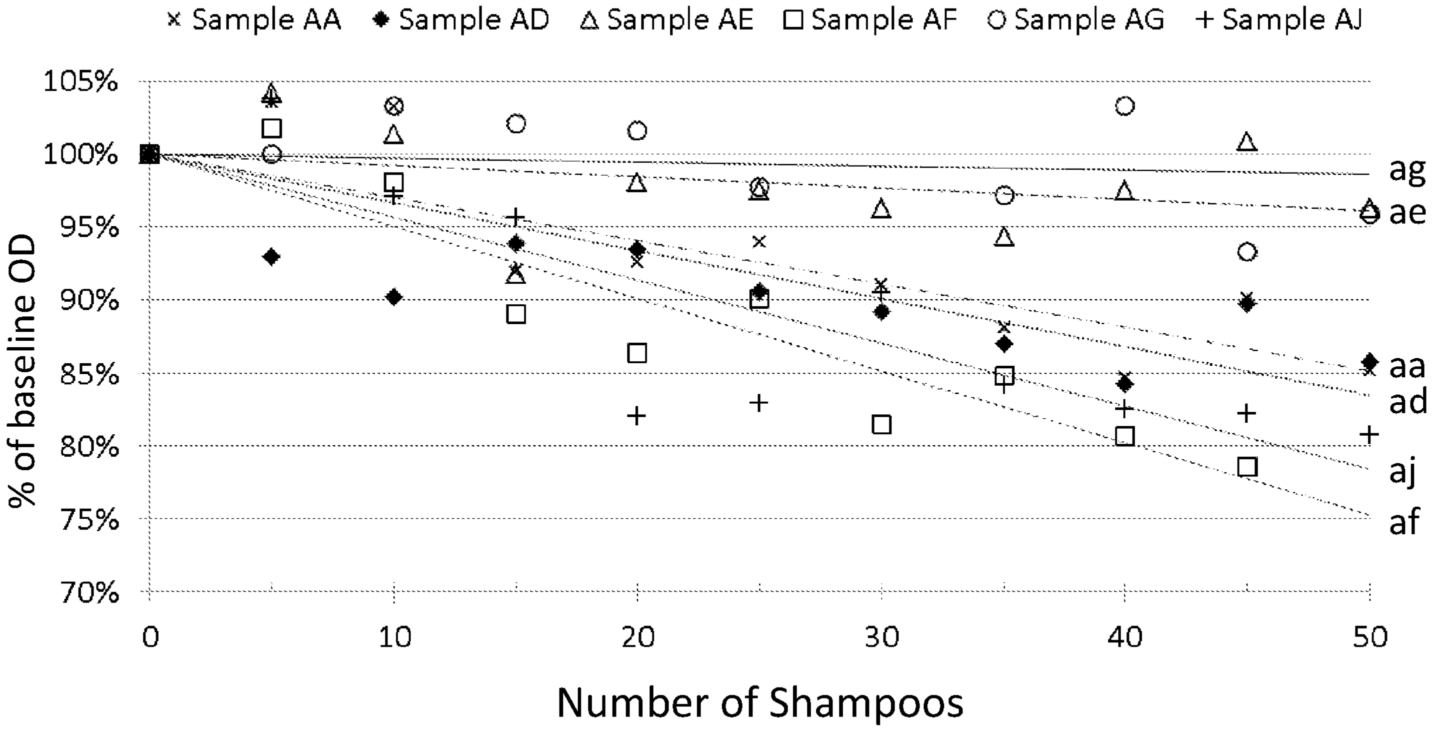
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Fig. 2B

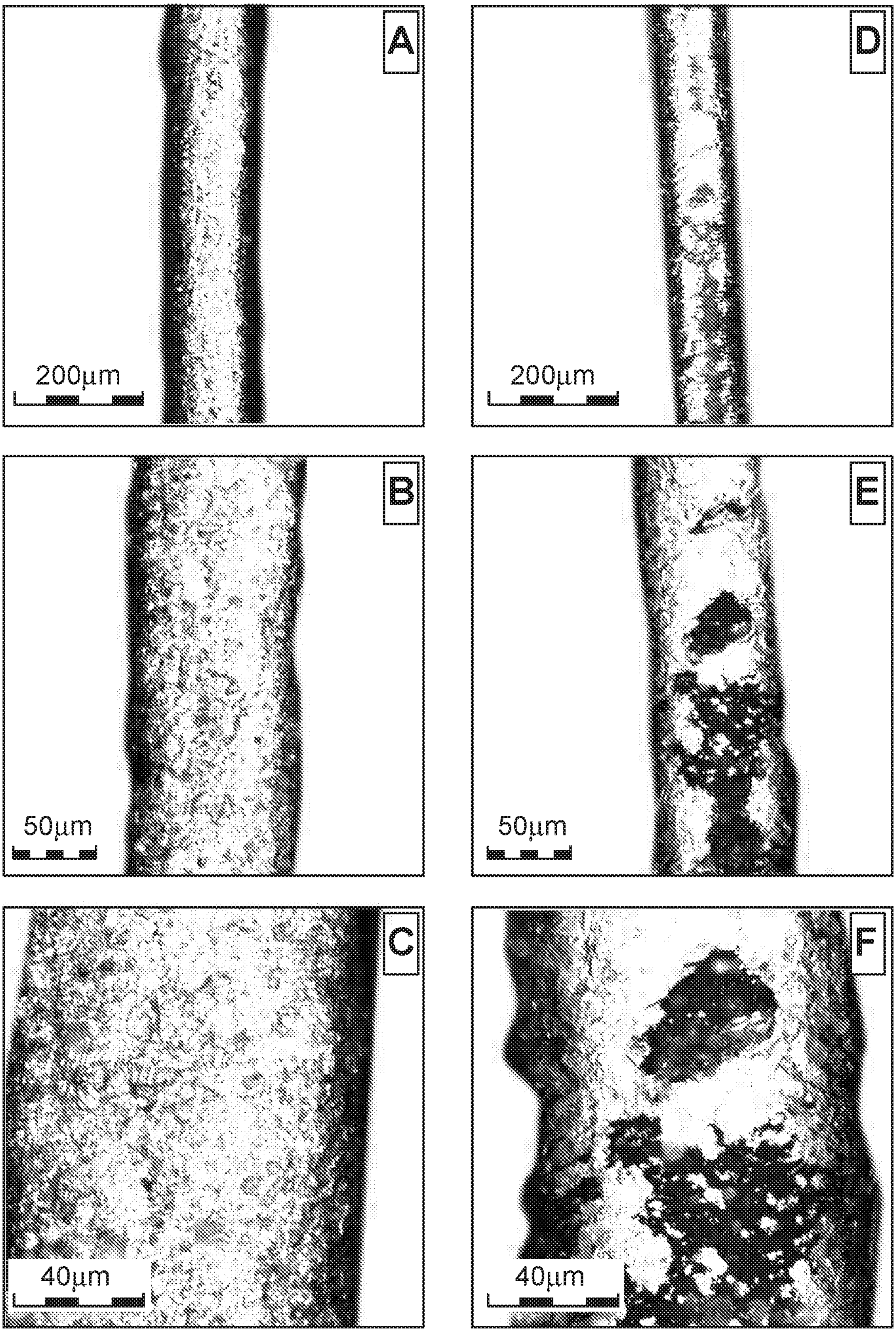

Fig. 3

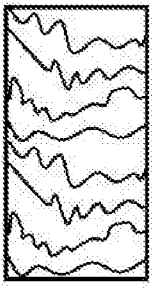

Fig. 4A

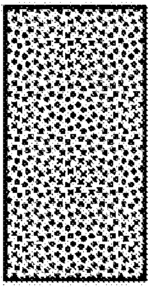

Fig. 4B

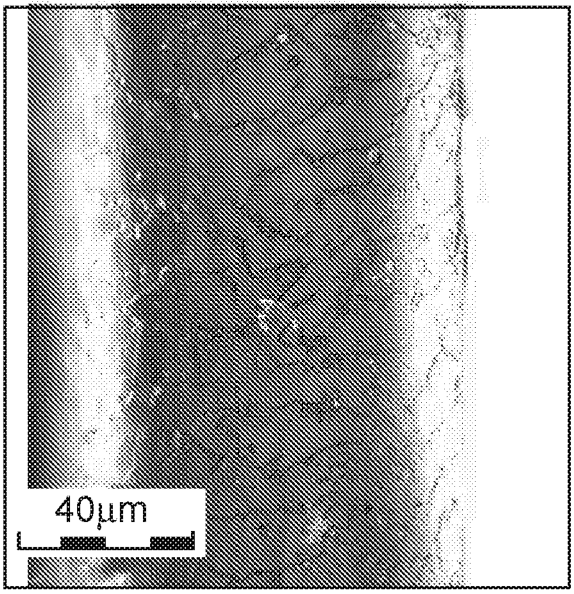

Fig. 4C

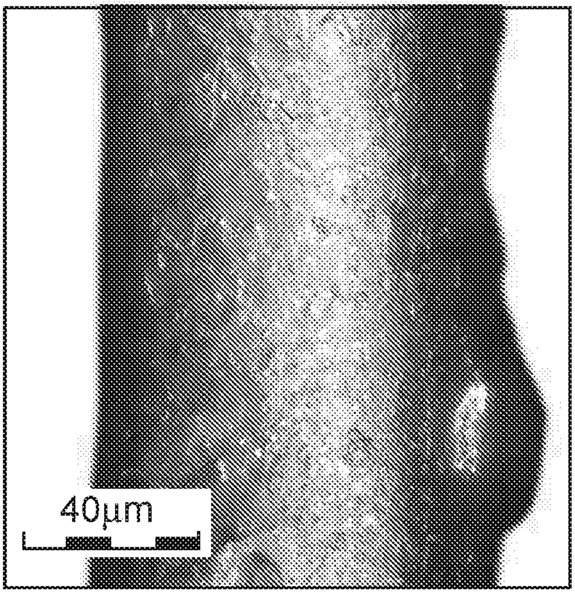

Fig. 4D

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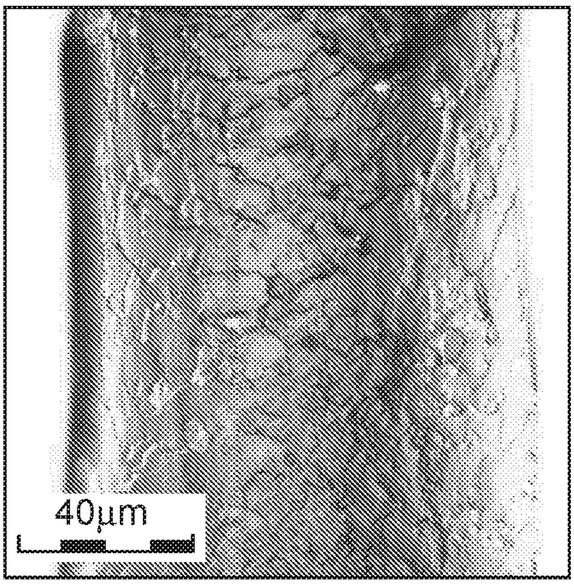

Fig. 4E

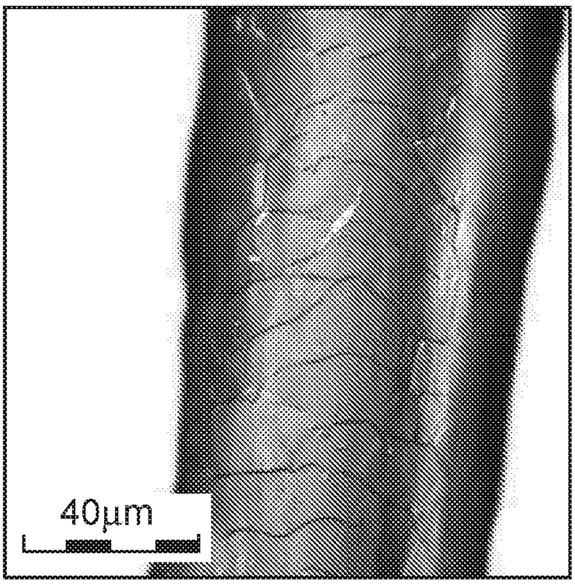

Fig. 4F

COMPOSITION, KIT AND METHOD FOR COLORING KERATINOUS FIBERS

FIELD

The present disclosure relates to compositions and kits for coloring keratinous fibers, such as hair. Methods for preparing and using the same are also disclosed.

BACKGROUND

Natural hair color is the pigmentation of hair follicles due to two types of melanin: eumelanin and pheomelanin. Generally, if more eumelanin is present, the color of the hair is darker; if less eumelanin is present, the hair is lighter. Levels of melanin can vary over time causing hair color to change.

Melanin production decreases in the hair roots of humans with ageing, causing lightening of the hair, and finally ceases. Once melanin production ceases, new hairs grow out gray or white when light reflects through them.

Hair coloring is the practice of changing the color of hair. The main reasons for this practice are cosmetic (*e.g.*, to cover gray hair, to change to a color regarded as more fashionable or desirable, or to restore the original hair color after it has been discolored, for instance by hairdressing processes or sun bleaching). Hair coloring is achieved by use of coloring compositions comprising chemical, organic, herbal or natural coloring agents. The coloring agents generally fall into two categories, a) soluble dyes that may penetrate the hair (but can also remain external) and may be reacted to induce the desired coloring effect, and b) water-insoluble pigments, which in view of their dimensions are typically restricted to external coloring of hair fibers.

Based on how long the effect lasts, coloring may be permanent, demi-permanent, semi-permanent or temporary.

Permanent hair coloring typically involves penetration of direct dye or oxidation dye precursor deep into the hair shaft, generally preceded by the removal of any existing melanin, requiring bleaching, and sealing of the coloring agent into the hair cortex. Permanent coloring further requires an oxidizing agent or coupler in order for the color to fully develop. The color does not wash out with shampoo for at least 30 shampoo washes. However, such permanent coloration may severely damage the hair.

Demi-permanent hair coloring compositions are also known as deposit-only hair colors. These are chemically milder than permanent hair coloring compositions, penetrate only partially into the hair shaft, and typically do not remove the hair's natural pigment. Demi-permanent hair color washes out after about 10-30 shampoo washes.

Semi-permanent hair coloring compositions are chemically milder than either permanent or demi-permanent coloring compositions, involving only a small extent of penetration into the hair shaft. Semi-permanent coloring compositions remain on the hair for only 4-10 shampoo washes.

Permanent, demi-permanent or semi-permanent coloring processes are known to damage keratin fibers. Moreover, certain processes raise health concerns, some compositions being possibly carcinogenic.

Temporary hair coloring compositions do not penetrate into the hair shaft, but remain on the outer surface of the hair shaft. Such coloring compositions may easily be washed out by a single shampoo, resisting at most 2-3 shampoos under favorable circumstances.

There remains a need for coloring compositions for coloring keratin fibers, such as hair, which exhibit reduced penetration and impact on the integrity of the fibers being colored as compared to known coloring compositions, while providing long-lasting coloration of the fibers.

There further remains a need for coloring compositions for dark-colored keratin fibers, wherein such coloring compositions provide a lighter color than that of the native keratin fiber, wherein such coloring compositions are used without the need for bleaching of the keratin fiber.

SUMMARY

The present disclosure relates to compositions for coloring keratinous fibers, such as human hair, and more particularly to compositions comprising a reactive, condensation-curable amino functional silicone pre-polymer and a pigment, in an aqueous medium.

Pre-polymers generally refer to materials (*e.g.*, uncured/curable monomers, oligomers and/or polymers) that can be cross-linked to form larger macro molecules through cross-linkable groups, also termed reactive groups, by techniques known as curing processes. A variety of curing processes exist depending on the chemical composition of the pre-polymers to be cross-linked, their reactive groups and the curing auxiliary factors (cross-linkers, curing accelerators or catalysts, and the like). The present disclosure is concerned with silicone pre-polymers being condensation-curable, namely bearing cross-linkable groups able to react with one another so as to form by condensation a siloxane bond, while liberating in the process a molecule of alcohol, oxime or water. Condensation-curable amino functional silicones are further characterized by the presence of amino groups attached via carbon atoms to the backbone of the silicone pre-polymers. These amino groups or side chains are further capable of attaching other molecules through nucleophilic reaction (for example, but not limited, on carboxylic or epoxy functional molecules or substrates). Therefore, while the silicone pre-polymers disclosed herein are termed "reactive" or "condensation-curable" amino functional silicones, this terminology is not intended to be limiting the curing process exclusively through condensation of the reactive groups, the amino groups being capable of curing also through "non-condensation" processes, such as resulting in the formation of nitrogen-carbon bonding. The products of such curing processes are networks of cross-linked oligomers or polymers termed elastomers or elastomeric networks (rubber like), in reference to their viscoelastic properties. As such cured networks may form a film, the pre-polymers can also be termed film-forming.

Such amino functional silicones (alternatively referred to as amino-silicones or amine-silicones), may be considered as positively charged or positively chargeable under suitable chemical environment (*e.g.*, relatively low pH). Such materials can in part be characterized by their Amine Number. In some embodiments, the condensation-curable amino-silicone pre-polymer is insoluble or substantially insoluble in water. In some embodiments, the solubility of the pre-polymer is of 5wt.% or less, 2wt.% or less, 1wt.% or less, 0.5wt.% or less, or 0.1wt.% or less, with respect to the weight of the aqueous composition wherein it is disposed. Solubility can be assessed by the naked eye, the composition being typically at 23°C. A material is water-soluble at or below a threshold concentration, if forming a clear solution in water. Conversely, the material is insoluble if not water-soluble (*e.g.*, forming a visually detectable dispersion). Typically, the condensation-curable amino-silicone reactants form a phase separate from water, being substantially non-miscible therewith. Such a distinct phase may also be referred to as an "oil phase" or the like.

In some embodiments, wherein a condensation-curable amino-silicone pre-polymer is relatively soluble in water (or becomes so, as a result of hydrolysis), it may be rendered relatively less soluble and even substantially insoluble in water. For instance, a hydrophilic siloxane can be rendered relatively insoluble by reacting it with a different second material (*e.g.*, a hydrophobic silane) capable of modifying its tendency to solubilize in water, the reaction product of the two resulting in a third material being less soluble ("desolubilized") or substantially insoluble ("insolubilized"). This process, which for simplicity may be termed of "desolubilization" or "insolubilization" of a desired reactant, can be carried out prior to the emulsification of the amino-silicone reactant rendered less soluble with the additional constituents of a condensation-curable amino-silicone formulation according to the present teachings.

While at least partially cured pre-polymers can also be non-tacky (*e.g.*, if cross-likers and/or curing accelerators are used), the lack of tackiness to the touch is more generally associated with fully cured polymers. Compositions as used in the present methods, advantageously, are rapidly non-tacky to the touch to increase compliance when coloring is performed on a living subject.

According to an aspect of some embodiments disclosed herein, there is provided a method of coloring or cosmetically treating an external surface of mammalian hair, the method comprising:

(a) applying, on the external surface of individual hairs of the mammalian hair, a formulation comprising:

(i) water;

(ii) at least one reactive condensation-curable film-forming amino-silicone pre-polymer that, subsequent to condensation curing, forms an elastomer;

(iii) a plurality of sub-micronic organic or inorganic pigment particles;

(iv) at least one dispersant for dispersing the sub-micronic pigment particles in the formulation; and optionally,

(v) at least one cross-linking agent adapted to cure the at least one pre-polymer;

(b) effecting partial condensation curing of the at least one pre-polymer at a temperature of up to 45°C, to form a pigmented, at least partially cured film on the external surface of the individual hairs; and

(c) after enabling the partial condensation curing to ensue, washing the hair with a rinsing liquid to leave the pigmented, at least partially cured film on the external surface of the individual hairs.

In some embodiments, wherein the amino-silicone pre-polymer(s) of (ii) is/are condensation-curable oligomers or polymers, the cross-linking agent of (v) can be an amino-silicone monomer.

In some embodiments, the amino-silicone pre-polymer(s) consists or consists essentially of amino-silicone monomer(s).

In some embodiments, the amino-silicone pre-polymer(s) consists or consists essentially of amino-silicone oligomer(s).

In some embodiments, the amino-silicone pre-polymer(s) consists or consists essentially of amino-silicone polymer(s).

In some embodiments, the formulation further comprises a condensation-cure auxiliary, such as a condensation-cure accelerator or catalyst adapted to cure the pre-polymer.

According to some embodiments, the pigment particles are dispersed in the condensation-curable film-forming amino-silicone pre-polymer and/or in the water.

According to some embodiments, the method further comprises, subsequent to step (b), further curing the at least partially cured film for a period of at least 4 hours, at least 6 hours, at least 12 hours, or at least 24 hours at a temperature of at least 15°C and of at most 38°C, at most 36°C, at most 34°C, or at most 32°C, so as to obtain full curing of the film, the period optionally being at most 3 weeks, at most 2 weeks, at most 10 days, at most 7 days, at most 5 days, at most 3 days, or at most 2 days. In various embodiments, the period may be within a range of 6 to 36 hours, 6 to 24 hours, 6 to 18 hours, or 6 to 12 hours.

According to some such embodiments, further curing over the specified period (for the duration of the period) is effected solely by or substantially solely by humidity or ambient humidity. According to alternative embodiments, further curing over the specified period is effected in the absence of any added non-cationic surfactant. In some embodiments, shampooing of the hair during the period of the further curing is effected with a cationic shampoo.

According to some embodiments, the reactive condensation-curable amino-silicone pre-polymer, the cross-linking agent and the optional catalyst are present in a same formulation each separately dispersed in the carrier in the form of emulsion droplets. Emulsions are known two-phase systems, and in some embodiments oil-in-water emulsions are preferred.

Emulsions typically requires emulsifiers (when the constituents lack self emulsifying properties), which can be ionic or non-ionic.

According to some embodiments, the method further comprises combining at least first and second sub-formulations to produce the formulation, the first sub-formulation including water, the pre-polymer, the plurality of sub-micronic pigment particles and the dispersant; and the second sub-formulation including the cross-linking agent. In particular embodiments, the cross-linking agent, if consisting for instance of non-amino condensation-curable monomers or oligomers, may be disposed in the second sub-formulation as a negatively-charged emulsion in water.

In some embodiments, the method further comprises combining with at least one of the afore-said sub-formulations, a third sub-formulation comprising a 3D network former, which in one embodiment can be a hydrophobic fumed silica, having an amorphous structure.

The combination of the at least two sub-formulations can result in an emulsion, typically an oil-in-water emulsion. The hydrophobic fumed silica, if present, is typically disposed within the oil phase of the oil-in-water emulsion.

According to some such embodiments, the method further comprises mixing together the at least first and second sub-formulations at most 4 hours, at most 2 hours, at most 60 minutes, at most 45 minutes, at most 30 minutes, at most 20 minutes, or at most 10 minutes prior to applying. In some such embodiments, the at least two distinct sub-formulations, when provided in a kit of individual compartments according to other aspects of the invention, are separately packaged.

According to some embodiments, the pre-polymer is dispersed in the form of an emulsion.

According to some embodiments, the formulation or sub-formulation further comprises a non-ionic or an anionic emulsifier.

According to some embodiments, the formulation is charged and has a positive surface zeta potential of at least 10 mV, at least 20 mV, at least 40 mV, or at least 60 mV; and of no more than 100 mV, or no more than 80 mV.

According to some embodiments, the first sub-formulation containing the pre-polymer is charged and has a positive surface zeta potential of at least 10 mV, at least 20 mV, at least 40 mV, or at least 60 mV; and at most 100 mV, or at most 80 mV.

According to some embodiments, the second sub-formulation includes the cross-linking agent is charged and has a negative surface zeta potential whose negativity is at least -10 mV, at least -20 mV, at least -40 mV, or at least -60 mV; and whose negativity is at most -100 mV, or at most -80 mV.

In some embodiments, the zeta potential can be measured at a pH of at least 8.0 and at most 12.0, said measurement being optionally performed at a pH of 10.0. Conveniently, the measurement of the zeta potential of a material or of a composition can be performed at low concentration of the material in an appropriate carrier or on a diluted form of the composition. For instance, a test sample may comprise 2wt.% or less of solid material or composition ingredients, 1wt.% or less, or 0.1wt.% or less.

According to some embodiments, the sub-micronic pigment particles have a D_V90 of at most 250 nm, at most 150 nm, or at most 100 nm, and optionally, a D_V50 of at most 150 nm, at most 100 nm, or at most 75 nm.

According to some embodiments, the reactive condensation-curable amino-silicone pre-polymer satisfies at least one of the following structural properties:

a) the pre-polymer includes terminal amino-moieties;

b) the pre-polymer has a viscosity in the range of 10-20,000 milliPascal-second (mPa•s, also referred to as cps), such as 10-15,000 mPa•s, 20-15,000 mPa•s, 30-15,000 mPa•s, 40-10,000 mPa•s or 50-10,000 mPa•s as measured at 25°C;

c) the pre-polymer has an Amine Number in the range of 3-200;

d) the pre-polymer has a ratio of Amine Number (AN) to viscosity (Visc.) in mPa•s, which when multiplied by 1000, is of at least 40, at least 100, at least 200, or at least 500, which can be mathematically expressed as $1000*(AN/Visc.) \geq 40$, and so on;

e) the pre-polymer is devoid of cyclic moieties;

f) the pre-polymer is hydrophobic;

g) the pre-polymer has a solubility in water at 25°C of less than 5% by weight, less than 2% by weight, or less than 1% by weight;

h) the pre-polymer is capable of wetting said hair;

i) the pre-polymer includes reactive groups selected from the group consisting of alkoxy-silane reactive groups, silanol reactive groups and combinations thereof;

j) the pre-polymer is a linear or a branched polymer;

k) the pre-polymer is a linear or a branched oligomer; and

l) the pre-polymer is a monomer.

According to some embodiments, the formulation or sub-formulation further comprises a cosmetically acceptable oil, miscible with the at least one pre-polymer, and/or miscible with the cross-linking agent, and/or miscible with the condensation-cure accelerator or catalyst, the cosmetically acceptable oil including, but not limited to, a silicone oil.

A cosmetically acceptable oil and more generally any cosmetically acceptable ingredient, and similarly cosmetically acceptable compositions or formulations, refer to the suitability of such materials for use in contact with keratinous fibers, in particular human hair, without undue toxicity, instability, allergic response, and the like.

According to some embodiments, the formulation or sub-formulation, has a pH of at least 4.0, at least 5.5, at least 7, at least 8.5, at least 10.0; and of at most 11.0.

According to some embodiments, the duration of time enabling the partial curing is between 5 seconds and 30 minutes, or between 1 minute and 15 minutes.

According to some embodiments, the rinsing liquid is (i) water, or (ii) a cationic rinsing liquid, or (iii) a rinsing liquid devoid of non-cationic surfactants, degreasing agents and/or swelling agents, the degreasing and swelling agent respectively able to degrease and swell the at least partially cured pigmented film. In some embodiments, the rinsing liquid has a pH of at least 6, at least 7, at least 8, or at least 9.

According to some embodiments, the cationic shampoo or the cationic rinsing liquid includes a cosmetically-acceptable primary, secondary, tertiary, or quaternary ammonium compound or polymer.

According to some embodiments, the cationic shampoo or the cationic rinsing liquid includes a polyquaternium polycationic polymer having a quaternary ammonium function.

According to some embodiments, the dispersant is present in the formulation or sub-formulation in an amount ranging from 25% to 400% by weight of the sub-micronic organic or inorganic pigment particles. In some embodiments, the dispersant and the pigment particles are present at a relative weight per weight ratio in the range of 0.5:1 to 2:1, 0.75:1 to 1.5:1, or 0.8:1 to 1.2:1.

According to some embodiments, the dispersant adapted to disperse the pigments are compatible with the condensation-curable formulation. Such dispersant can have a silicone backbone, such as silicone polyether and silicone amine dispersants.

Generally, a material used in the compositions according to the present teachings is said to be compatible with another, if it does not prevent its activity or does not reduce it to an extent that would significantly affect the intended purpose. For instance, a pigment dispersant would not be compatible if, among other things, preventing the curing of the condensation-curable amino-silicone pre-polymers, or reducing or retarding curing to an extent that the amino-silicone film would not sufficiently and/or rapidly attach to a target fiber, or would be deleterious to the pigments, and any like undesired effects. In some embodiments, compatibility may additionally mean that the materials deemed compatible share a common property, such as a common silicon-based chemistry or a similar physical parameter. For instance, materials having a similar refractive index (RI; within ±10% from one another) are believed to yield clearer cured films, as compared to materials having relatively dissimilar RI that may appear more turbid.

The silicone amine dispersants are positively charged and can be advantageous in some embodiments according to the present teachings.

According to some embodiments, the plurality of sub-micronic organic or inorganic pigment particles provide a first color, the method further comprising subsequent to step (c) leaving on the individual hairs an at least partially cured film pigmented with the first color, repeating steps (a) to (c) the sub-micronic organic or inorganic pigment particles of repeated step (b) providing a second color, the second color being same or different from the first color.

According to some embodiments, the method further comprises, prior to step (a), or prior to a first step (a) if repeated, applying a degreasing agent to effect degreasing of the external surface of the hair without effecting degreasing of an inner surface of the hair/without penetration of the degreasing agent within the hair/without bleaching the hair.

According to some embodiments, the method further comprises, prior to step (a), or prior to a first step (a) if repeated, and optionally following a degreasing step, if performed, applying, on the external surface of the individual hairs, a film-forming hair masking binder formulation so as to produce a polymeric film on the hair.

According to some embodiments, the film-forming hair masking binder formulation further includes (i) a plurality of sub-micronic organic or inorganic pigment particles, and/or (ii) metallic-looking particles and/or flakes, so as to produce a tinted binder polymeric film on the external surface of the individual hairs or on top of a previously laid-down film on the hair.

According to some embodiments, the film-forming hair masking binder formulation comprise at least one reactive condensation-curable amino-silicone elastomer, at least one cross-linking agent, at least one emulsifier and optionally, at least one catalyst emulsified in an aqueous carrier.

According to some embodiments, the method further comprises, after a) applying the film-forming hair masking binder formulation:

b) allowing the film-forming binder to preliminarily cure;

c) washing the hair with a rinsing liquid to leave a preliminarily cured polymeric film on the external surface of the individual hairs, the film being optionally tinted;

d) applying to the preliminarily cured film a flake dispersion including of a plurality of metallic-looking pigment flakes, a dispersant and an aqueous carrier;

e) washing the fibers with a rinsing liquid to leave a layer of metallic-looking pigment flakes on and adhering to the preliminarily cured film.

According to a further aspect, there is provided a method for masking keratinous fibers or color thereof, the method comprising

a) applying to an external surface of individual fibers a film-forming hair masking binder formulation, the formulation including at least one reactive condensation-curable amino-silicone elastomer, at least one cross-linking agent, at least one emulsifier and optionally, at least one catalyst emulsified in an aqueous carrier; the formulation optionally further including pigments;

b) allowing the film-forming binder to preliminarily cure;

c) washing the hair with a rinsing liquid to leave a preliminarily cured polymeric film on the external surface of the individual hairs, the film being optionally tinted;

d) applying to the preliminarily cured film a flake dispersion including of a plurality of metallic-looking pigment flakes, a dispersant and an aqueous carrier;

e) washing the fibers with a rinsing liquid to leave a layer of metallic-looking pigment flakes on and adhering to the preliminarily cured film.

According to some embodiments, the pigment flakes have an average longest dimension in the range of 2 μm to 20 μm and an average thickness in the range of 50 nm to 500 nm.

According to some embodiments, the pigment flakes are metallic pigment flakes containing, coated with, consisting essentially of, or made of metals, alloys and oxides thereof, said flakes being selected from the group comprising aluminum flakes, brass flakes, bronze flakes, copper flakes, gold flakes, mica coated flakes, silica coated flakes and silver flakes.

According to some embodiments, the metallic-looking pigment flakes are further coated with a least one coupling agent capable of covalently binding the reactive amino-silicone elastomer of the film-forming hair masking binder formulation.

According to some embodiments, the at least one coupling agent is a cosmetically acceptable coupling agent selected from the group consisting of acrylate coupling agents, thiol coupling agents, anhydride coupling agents, epoxy coupling agents, and silanol coupling agents.

In some embodiments, the acrylate coupling agent is selected from the group comprising of penta erythrytol tetra acrylate, pentaerythrityl triacrylate, di-trimethylol-propane tetraacrylate, PEG-trimethylol-propane triacrylate, and mixtures thereof.

In some embodiments, the thiol coupling agents can be pentaerythrityl tetramercaptopropionate; mercaptopropyltrimethoxysilane; trimethylolpropane tris-mercapto-propionate. In some embodiments, the anhydride coupling agent is polymaleic anhydride. In some embodiments, the epoxy coupling agents can be 4-methylen-2,6-epoxydecane; 3-methyl-1-phenyl-3-hexene 1,5-epoxide. In some embodiments, the silanol coupling agent is glycidoxypropyl trimethoxysilane.

According to some embodiments, the pigment flakes are charged at a polarity opposite a polarity of the preliminarily cured hair masking film.

According to some embodiments, the method further comprises, subsequent to at least partially condensation curing of pigmented film, applying a clear protective coating, the protective coating including an amino-silicone elastomer, a cross-linking agent, an emulsifier and an optional catalyst emulsified in an aqueous carrier.

According to some embodiments, the fully cured film is wash resistant, wash resistance meaning that the hair can be washed at least 20 times with water and retain an Optical Density (OD) value of at least 80% of an original OD value as determined following full curing. Wash resistance of hair coated with a fully cured film can also be referred to as "cured wash resistance".

According to some embodiments, the at least partially cured film is wash resistant, wash resistance meaning that the hair can be washed at least 10 times with a cationic shampoo and retain an Optical Density (OD) value of at least 80% of an original OD value as determined following said at least partial curing.

Wash is performed by completely immersing the hair fibers in the washing liquid, rinsing liquid, or water, as desired. The fibers are generously massaged with the liquid for about one minute and are dried.

According to some embodiments, the method further comprises, subsequent to at least partial curing of one or more films as applied in one or more steps, removing the films from the individual hairs by applying a silicone decuring agent in an amount and for a time period sufficient to at least partially decure the films, the application of the decuring agent for a sufficient time being followed by rinsing away the decured silicone. The removal of the films including at least one colored film can be performed at any desired time point after coloration (*e.g.*, within days, within weeks or within months from application).

For instance, conventional permanent coloring methods usually require specific coloration to be reapplied within a few weeks from an initial coloration, coloring then only the region of the newly grown hair near the hair roots. As the present method allows, in some embodiments, for a rapid and non-damaging removal of a coloring film according to the invention, the hair could be advantageously decolored (and if desired recolored) in its entirety, providing for an even coloring of the hair fibers from roots to tips.

According to some embodiments, the silicone decuring agent is selected from the group including fluoride salts (including but not limited to tetra butyl ammonium fluoride (TBAF) and RonaCare® Olaflur), organic sulfonic acids (including but not limited to dodecyl benzene sulfonic acid (DBSA)) and an organic or inorganic base and salts thereof (including but not limited to tetra butyl ammonium hydroxide (TBAH), tetra butyl ammonium bromide (TBAB), tetra butyl ammonium chloride (TBAC), potassium hydroxide (KOH) and potassium tert-butoxide ($K(CH_3)_3CO$)).

In some embodiments, the fully cured film has a thickness above fiber surface of at least 100 nm, at least 500 nm, or at least 1 µm, said thickness not exceeding 5 micrometer, being no greater than 4 µm, no greater than 3 µm, or no greater than 2 µm.

According to an aspect of some embodiments disclosed herein, there is provided a kit for coloring or cosmetically treating an external surface of keratinous fibers, in one embodiment mammalian hair optionally attached to the mammalian subject, the kit comprising:

(a) a first compartment containing a pigmented formulation including:

  (i) at least one reactive condensation-curable film-forming amino-silicone pre-polymer;

  (ii) at least one dispersed plurality of sub-micronic organic or inorganic pigment particles;

  (iii) at least one dispersant; and optionally

  (iv) at least one silicone oil miscible with the film-forming amino-silicone pre-polymer;

(b) a second compartment containing water and an emulsifier to form an emulsion when mixed with the content of the first compartment;

(c) a third compartment, said third compartment containing at least one cross-linking agent and optionally at least one silicone oil miscible with the at least one cross-linking agent;

(d) a compartment containing water and at least one emulsifier to form an emulsion when mixed with the content of the third compartment, wherein the compartment of (d) is a fourth compartment or a second compartment.

In some embodiments wherein the kit comprises more than one type of reactive condensation-curable film-forming amino-silicone pre-polymers, and in the event the pre-polymers may at least partially react with one another, the pre-polymers can be supplied in separate compartments. For instance, if the pre-polymers consist of condensation-curable oligomers or polymers that may react with amino-silicone monomers acting in such instance as cross-linking agents, the different pre-polymers can be separated and, by way of example, the amino-silicone monomers can be supplied in the third above-mentioned compartment or in a further additional compartment.

According to some embodiments, the kit further comprises at least one curing auxiliary compartment, the at least one curing auxiliary compartment containing at least one curing accelerator or catalyst in water and optionally at least one silicone oil miscible with the curing accelerator or catalyst, and an additional compartment containing water and at least one emulsifier to form an emulsion when mixed with the content of the curing auxiliary compartment, the additional compartment optionally being the second compartment or the fourth compartment.

According to some embodiments, the kit further comprises a rinsing compartment, the rinsing compartment containing a rinsing formulation or a rinsing agent dispersible or soluble in water.

The methods, compositions and kits according to the present teachings advantageously color the keratinous fibers, such as mammalian hair, by providing a coating of pigment on the outer surface of the fiber, with minimal or no penetration of the pigment into the interior of the fiber, such as the hair shaft, thus reducing adverse effects and health concerns typically associated with penetration of conventional chemical compounds, which may lead to hair breakage or brittleness.

The methods, compositions and kits disclosed herein, in at least some embodiments, may provide coloring which is permanent *i.e.* wash resistant, using conventional, over-the-counter shampoos, after at least 30 washes, at least 50 washes, or even after at least 100 washes, as determined by optical density measurements using yak hair or human hair (*e.g.*, Chinese or European hair). A coloring is shampoo-resistant if the OD measured after shampooing is not below 80% of the baseline OD as measured following coloring, before any shampooing. In some embodiments, the resistance to shampooing is achieved with cationic shampoos. In some embodiments, the cationic shampoo has a high charge density. In some embodiments, cationic shampoos comprise cationic guar gum, optionally having charge density of from about 0.8 to about 7 meq/g and a molecular weight (MW) of from about 5,000 to about 10 million Daltons. When used in connection with polymers (including pre-polymers) which may be supplied as populations of mildly diverging molecules (*e.g.*, having a slightly different number of repeating units, such as siloxane units for some silicone prepolymers), the term molecular weight relates to the weighted or weight average MW, unless indicated otherwise by the supplier. The weight average MW can be measured by gel permeation chromatography.

In some embodiments, the coloring is reversible (also referred to as decoloring) by use of a solution for removal of the coloring composition (also referred to as a removal solution or decuring solution), comprising a silicone decuring agent, for example, (a) a fluoride salt such as TBAF (tetra butyl ammonium fluoride) and RonaCare® Olaflur; or (b) an organic acid such as DBSA (dodecyl benzene sulfonic acid); or (c) an organic or inorganic base (and salts thereof) such as TBAH (tetra butyl ammonium hydroxide), TBAB (tetra butyl ammonium bromide), TBAC (tetra butyl ammonium chloride), potassium hydroxide (KOH) and potassium tert-butoxide ($K(CH_3)_3CO$)). In some embodiments, TBAB or TBAC are used in combination with an inorganic base, and in particular embodiments the additional base can be KOH, NaOH, LiOH, $Mg(OH)_2$, or $Ca(OH)_2$. In one embodiment, the decuring agent can be formed by combining an organic base (*e.g.*, hydroxyethyl cetyldimonium phosphate, such as commercialized by BASF under tradename Luviquat® Mono CP AT1) and an inorganic base (*e.g.*, magnesium hydroxide).

Additional fluoride salts which can serve as decuring agents include, but are not limited to, ammonium fluoride, octadecenyl-ammonium fluoride, 3-(N-hexadecyl-N-2-hydroxy-ethylammonio) propylbis (2-hydroxyethyl) ammonium difluoride, ammonium monofluoro-phosphate, calcium fluoride, calcium monofluorophosphate, magnesium fluoride, potassium monofluorophosphate, sodium fluoride, sodium monofluorophosphate, N,N',N'-Tris(polyoxyethylene)-N-hexadecyl-propylenediamine dihydrofluoride, and nicomethanol hydrofluoride. Such decoloring is believed to be triggered by the decuring of the at least partially cured film formed by the amino-silicone elastomer on the surface of the keratinous fibers. Without wishing to be bound by any particular theory, the decuring is believed to loosen the bonds formed between the amino-silicone units constituting the cured film and/or its attachment to the fibers. In some embodiments, the decoloring of the fibers colored according to the present teachings is achieved by applying a decuring solution including a silicone decuring agent in an amount sufficient to at least partially decure the cured pigmented film so as to detach it from the fibers by subsequent rinsing.

When the silicone decuring agent is a fluoride salt, a suitable amount can be expressed in terms of fluoride content per total weight of the decuring solution. In such embodiments, a fluoride content of the agent is in an amount of at least 0.01wt.% and of at most 1wt.%, per weight of the silicone decuring solution.

Alternatively, and in particular when the silicone decuring agent is an organic acid or an organic or inorganic base, the agent can be suitably present in an amount of at least 0.1wt.%

and of at most 15wt.%, per total weight of the silicone decuring solution, or in the range of 0.5-10wt.% or in the range of 0.5-5wt.%.

In some embodiments, silicone decuring agents can be combined with one another or with other decuring promoting agents. By way of example, a fluoride salt can be present in the decuring solution in combination with a base (optionally an organic base including an amine group which can by itself serve as decuring agent). Such combinations of decuring agents may result in additive or synergistic effects further facilitating or accelerating the removal of the cured pigmented film from the keratinous fibers.

The decoloring or decuring solution is applied for a time period sufficient to at least partially decure the cured film, the application of the decuring agent for a sufficient time being followed by rinsing away the decured silicone with an aqueous rinse. The amount of time that may suffice to decure enough of the film so as to permit its removal may depend, among other things, on the concentration of the decuring agent, the viscosity of the decuring solution, the temperature of the decuring process, the type of the keratinous fibers, the thickness of the cured film, the relative humidity, and any such factors readily appreciated by the skilled person.

In some embodiments, the decuring solution is applied at a temperature in the range of at least ambient temperature of at least 18°C to at most 40°C, at most 38°C, at most 36°C, at most 34°C, or at most 32°C. In the experimental section herein, ambient temperature, unless otherwise indicated, generally refers to about 23°C. Ambient relative humidity (RH), unless controlled, hence otherwise indicated, is between about 60%RH and about 80%RH. Ambient pressure is typically of about 1 atmosphere.

In some embodiments, the decuring solution is applied for a time period between 1 minute and 30 minutes, 2 minutes and 20 minutes or 5 minutes and 10 minutes.

In some embodiments, the decuring solution is prepared by dispersing or dissolving the decuring agent(s) in a solvent which can be (a) an aqueous solvent which may optionally further comprise one or more water-miscible co-solvents and/or one or more dispersants; or (b) an organic solvent optionally comprising one or more dispersants.

In some embodiments, the organic solvent or the water-miscible co-solvent is selected from the group consisting of primary, secondary and tertiary C_1-C_6 alcohols, including isopropanol, cyclohexanol, and tert-butyl alcohol; saturated C_6-C_{12} hydrocarbon, including dodecane; MIBK, MPE, NOP, propionitrile, THF, toluene, and xylene. When the removal solution comprises 50wt.% or more of water, in addition to the aforesaid solvents or mixtures thereof, the composition is said to be an aqueous removal solution, as opposed to an organic removal solution in a contrary situation (< 50wt.% of water, including devoid of water). In embodiments wherein the decuring agent(s) are dispersed or dissolved in a mixture of water and organic solvent(s), the weight per weight ratio of the water to the organic solvent(s) is typically in the range of 1:9 to 9:1. It is to be noted that while the addition of water may increase compliance, it may also prolong the duration of the removal process.

Suitably the viscosity of the silicone decuring solution is sufficient for the solution to coat the fibers and remain thereon for a duration of time enabling the partial decuring, hence the subsequent film removal and decoloring of the fibers. In some embodiments, this viscosity is achieved by further adding to the decuring agent in its solvent, a thickening agent in an amount sufficient to provide said viscosity.

Following the application of the decoloring solution, the fibers are thoroughly washed with an aqueous rinsing agent, the last rinsing being optionally followed by shampooing of the fibers with a shampoo.

In some embodiments, no bleaching is needed during the coloring process.

The compositions disclosed herein, in at least some embodiments, may be used in a single-step coloring process, in contrast to known hair coloring compositions, which typically requires a two-step oxidation process

In some embodiments, subsequent coloration requires coloration only of the hair roots.

The compositions disclosed herein, in at least some embodiments, show improved resistance to discoloration by external agents and factors, as compared to known coloring agents. In some embodiments, the cured pigmented films can resist fading when exposed to light (*e.g.*, maintaining original color for longer periods of time when exposed to sun radiation), and the compositions are said in such cases to have or provide good lightfastness. In some embodiments, the cured pigmented films can resist bleaching, and the compositions are said in such cases to have or provide good chemical resistance, bleach being a relatively harsh agent deemed predictive of resistivity to milder chemical exposures, such as encountered for example in polluted environments or at a swimming pool.

The compositions disclosed herein, in at least some embodiments, provide improved aesthetic properties of keratinous fibers, such as improved appearance, increased volume, softness, smoothness and shine.

The term “reactive amino-functional silicone” (also referred to herein as “reactive condensation-curable amino-functional silicone pre-polymer” and such variants, in accordance with the present disclosure is an organosilicon pre-polymer which contains at least two hydrolysable reactive groups like alkoxy groups and at least one carbon bonded amine group in its molecule, said alkoxy radicals each independently having 1-4 carbon atoms.

The term “reactive group” is understood to mean any group capable of forming a covalent bond with another polymeric backbone or with a cross linker at least by way of condensation curing. Examples of reactive groups on a reactive condensation-curable amino-silicone are:

- C_1-C_4 alkoxy group, such as methoxy, ethoxy, propoxy, isopropoxy, or methoxyethoxy groups; or
- Hydroxyl group, such as silanol functional; or
- Acyloxy groups, such as acetoxy group; or
- Oxime groups, such as methylethylketoxime.

The amino functional group can be:

- Primary amine (I) groups, such as aminoalkyl groups,
- Secondary amine (II) groups, such as aminoethylaminopropyl group,

which can be located in the amino-silicone pre-polymer chain at terminal position or as side chain (pendant); or

- Tertiary (III) amino group, such as in N,N-dialkylaminopropyl group, which are typically located in branched amino-silicone polymer chain.

The amino-silicone pre-polymer can have one or more amine reactive groups, and be accordingly referred to as a monamino, diamino, triamino, tetramino and so on, amino-silicone.

As mentioned, the amino groups are further capable of reacting though curing processes other than condensation curing.

Additionally, the functional amines can be used as catalysts to promote condensation curing of alkoxy groups as found, for example, in amine/alkoxy functional silicones.

Cross-linking agents suitable for the polymerization of such condensation-curable pre-polymers may comprise similar reactive groups, and be for instance condensation-curable amino-silicone monomers. Cross-linking agents may display only amino functional groups, or additional reactive groups, such as aliphatic carbon moieties, vinyl, allyl, mercapto, epoxy, acrylate or methacrylate functional groups.

Cross-linking may be catalyzed using additional organic amines species or amino functional silicone for better compatibility with the reactive amino functional silicone pre-polymer.

Curing accelerators suitable for the cross-linking of these condensation-curable oligomers or polymers include carbodiimides (R-N=C=N-R') catalysts, such as diisopryl-carbodiimide and preferably multifunctional polycarbodiimides, such as commercially available under the trade name of Carbodilite from Nisshinbo Chemical Inc., Japan.

Curing accelerators can typically be present in the curable composition, in relatively low amount not exceeding 5% by total weight of the composition, or in less than 2wt.%, less than 1wt.% or less than 0.5wt.%.

Cross-linking may alternatively and additionally be further favored by adding to the composition a solid inorganic filler selected and adapted to facilitate and/or accelerate the curing of the condensation-curable film-forming amino-silicone pre-polymers. Such a film reinforcing filler can also be referred to as a reactive filler. Advantageously, the reactive reinforcement filler is a hydrophobic 3D network former contributing to the increase in cohesivity of the amino-silicone film. Suitable reactive fillers can be selected from hydrophobic fumed silica, the surface of which being at least partially covered by siloxane groups or other groups having a hydrophobic nature, such groups typically reacting with silanol functional units on the silica. Hence, in such cases, the hydrophobic fumed silica can be referred to as a silanol blocked silica, the surface treatment of the fumed silica blocking the silanol functionalities being achieved by one or more of HDMS, poly siloxane, cyclic poly siloxane, silazane, amino silane and silicone oils. The blocking treatment needs not to be complete, some residual silanol groups being permissible and even desirable for ensuring or facilitating at least partial curing. Hydrophobic fumed silica, when present, is typically disposed in the oil phase of the oil-in-water emulsion of condensation-curable silicone.

The term "non-reactive group" is understood to mean any group that is not capable of forming a covalent bond with another polymer backbone or with a cross linker. Examples of non-reactive groups are saturated C_1-C_4 alkyls, such as a methyl group.

BRIEF DESCRIPTION OF THE DRAWINGS

Some embodiments of the invention are described herein with reference to the accompanying figures. The description, together with the figures, makes apparent to a person having ordinary skill in the art how some embodiments of the invention may be practiced.

The figures are for the purpose of illustrative discussion and no attempt is made to show structural details of an embodiment in more detail than is necessary for a fundamental understanding of the invention. For the sake of clarity, some objects depicted in the figures are not to scale.

In the Figures:

FIG. 1A is a schematic illustration of a single keratinous fiber in presence of some of the dispersed components constituting a coloring formulation (pigments being omitted);

FIG. 1B is a schematic illustration representing how some of the components of FIG. 1A can migrate towards the fiber and arrange thereupon;

FIG. 1C schematically shows how the components may coalesce to form a continuous film on the external surface of the fiber;

FIG. 1D schematically illustrates the structure of mammalian hair at enlarged scale;

FIG. 2A is a graph showing the percentage of baseline OD value as a function of the number of shampooing and drying treatments to which a hair tuft is subjected for samples A, B, C, F and G;

FIG. 2B is a graph showing the percentage of baseline OD value as a function of the number of shampooing and drying treatments to which a hair tuft is subjected for samples AA, AD, AE, AF, AG and AJ;

FIGs. 3A to 3F are confocal laser scanning microscope images of Chinese black human hair coated with a composition J according to the principles of the present invention following 0 (A-C) and 30 (D-F) shampooing and drying treatments, panels A and D showing x20 magnified views, panels B and E showing x50 magnified views and panels C and F showing x100 magnified views;

FIG. 4A is a schematic illustration of the external surface of a native hair fiber displaying hair scales;

FIG. 4B is a schematic illustration of the external surface of a hair fiber coated with sub-micronic pigments or with pigment flakes according to the present teachings; and

FIGs. 4C to 4F are confocal laser scanning microscope images at x100 magnification of (C) native uncoated yak hair, (D) yak hair coated with a coloring composition according to one embodiment of the invention (sub-micronic Hostaperm Blue 15:3), (E) yak hair treated as in panel D subjected to a decoloring solution including TBAF, and (F) yak hair treated as in panel D subjected to a decoloring solution including DBSA.

DETAILED DESCRIPTION

The present disclosure relates to compositions for coloring or cosmetically treating keratinous fibers, including mammalian hair such as human or animal hair, and more particularly to compositions comprising a reactive condensation-curable amino-silicone pre-polymer and an insoluble pigment, the composition being in an aqueous medium. Methods of using the same and kits enabling such coloring are also described. The present invention encompasses the coloring of mammalian fibers when attached to a living subject and when isolated therefrom, for instance for the cosmetic treatment of wigs, or any other keratinous fibers detached from their subject of origin.

In some embodiments, the pigments for the compositions, kits and methods according to the present teachings, whether sub-micronic organic pigments, sub-micronic inorganic pigments, metallic-looking pigments and the like, as detailed herein, are not only insoluble in water or organic solvents, but additionally insoluble in the reactive condensation-curable amino-silicone pre-polymer and/or the resulting elastomer.

According to some embodiments, there is provided a method of coloring an external surface of keratinous fibers (*e.g.*, mammalian hair), the fibers in one embodiment attached to a body of a mammalian subject (*e.g.*, a human subject), the method comprising:

(a) applying, on the external surface of individual fibers (*e.g.*, individual hairs of the mammalian hair), a formulation comprising:

  (i) water;

  (ii) a reactive condensation-curable film-forming amino-silicone pre-polymer that, subsequent to condensation curing, forms an elastomer;

  (iii) a plurality of sub-micronic organic or inorganic pigment particles;

(iv) a dispersant for dispersing the sub-micronic pigment particles in the formulation; and optionally,

(v) a cross-linking agent adapted to cure said at least one pre-polymer;

(b) effecting partial condensation curing of said at least one pre-polymer at a temperature of up to 45°C, to form a pigmented, at least partially cured film on the external surface of the individual fibers; and

(c) after enabling said partial condensation curing to ensue, washing the fibers with a rinsing liquid to leave said pigmented, at least partially cured film on the external surface of the individual fibers.

Methods for preparing formulations suitable for implementing the present methods and kits comprising the same are also disclosed.

According to some other embodiments, there is provided a kit for treating an external surface of keratinous fibers (*e.g.*, mammalian hair optionally attached to a mammalian subject), the kit comprising:

(a) a first compartment containing a pigmented formulation including:

(i) a reactive condensation-curable film-forming amino-silicone pre-polymer;

(ii) a dispersed plurality of sub-micronic organic or inorganic pigment particles;

(iii) a dispersant; and optionally

(iv) a silicone oil miscible with said film-forming amino-silicone pre-polymer;

(b) a second compartment containing water and an emulsifier to form an emulsion when mixed with the content of the first compartment;

(c) a third compartment, said third compartment containing a cross-linking agent and optionally a silicone oil miscible with said cross-linking agent;

(d) a compartment containing water and an emulsifier to form an emulsion when mixed with the content of the third compartment, wherein the compartment of (d) is a fourth compartment or said second compartment.

In some embodiment, the kit may further comprise one or more of the following:

i) an applicator for applying any of the formulations according to the present teachings or combinations thereof to the external surface of the keratinous fibers;

ii) a thermometer for monitoring a temperature of any of said formulations or combinations thereof;

iii) a timer for monitoring a duration of application of any of said formulations or combinations thereof to the external surface of the keratinous fibers;

iv) a cationic shampoo for use, if desired, at least until the reactive condensation-curable amino-silicone elastomer of the pigmented formulation fully cures onto the keratinous fibers;

v) a leaflet guiding a user of the kit on the use of each formulation, including combinations thereof when applicable.

Without wishing to be bound by any particular theory, it is believed that FIGs. 1A-1C schematically illustrate the principles underlying a portion of one aspect of the method of the invention. FIG. 1A shows a schematic illustration of a single keratinous fiber **10** in the presence of some of the dispersed components constituting a coloring or coating formulation (*e.g.*, oil-in-water emulsion) as herein disclosed. The reactive condensation-curable amino-functional silicone pre-polymer (or micelles or emulsion droplets containing the same) **12** is represented by circles. The cross-linking agents capable of cross-linking the curable amino-silicone elastomer (or micelles or emulsion droplets containing the cross-linking agent) **14** are represented by triangles. The optional cross-linking accelerator or catalyst, as well as the optional 3D network former (*e.g.*, fumed silica), collectively referred to as curing facilitators (or micelles or emulsion droplets containing such curing facilitators) **16** are represented by stars. For clarity, the dispersant and pigment particles are not shown. For simplicity, all illustrated materials are displayed on a single side of the fiber. FIG. 1A is deemed to represent the situation upon initial exposure of the fibers to the condensation-curable amino-silicone formulation. In some embodiments, the keratinous fiber **10** is mammalian hair and its outer surface is negatively charged as shown in the figure. In some embodiments, the reactive condensation-curable amino-functional silicone pre-polymer **12** is positively charged when dispersed in a carrier. In some embodiments, the cross-linking agent **14** (*e.g.*, some non-amino materials) and/or the cross-linking facilitator **16** are each negatively charged when dispersed in a carrier.

FIG. 1B is a schematic macroscopic illustration representing how, with time, some of the components of FIG. 1A can migrate towards the fiber and arrange themselves thereupon. Based at first on electrostatic interactions, the amino-silicone elastomer, micelles or emulsion droplets thereof (being in one embodiment positively charged) form a layer **12’** on the surface of fiber **10** (being in the same embodiment conversely negatively charged). Similarly, the cross-linking agents, micelles or emulsion droplets thereof (being in the exemplified embodiment negatively charged, but not necessarily so as a rule) will form a layer **14’** on the surface of layer **12'** (being in the same embodiment conversely positively charged). For clarity, the optional curing facilitators shown as **16** in FIG. 1A, which would "intercalate" in layer **14'**, are omitted from FIG. 1B.

FIG. 1C schematically shows how, given further time, the components previously partially represented by **12**, **14** and **16**, coalesce, merge and/or react to form a continuous film **20** on the external surface of the fiber, so as to form an amino-silicone coated fiber. Such a preliminary wetting of the fibers by the coloring compositions, according to the present teachings, is believed to be a pre-requisite for the entire coloring method. This step, at its beginning, may be herein referred to as "preliminary curing". With time, the amino-silicone elastomers of the film will cross-link with one another, the process proceeding towards full curing through a progressive phase of partial-curing. While not shown in the figure, it is believed that the film **20** formed according to the above described exemplary embodiment would be positively charged. A polymer is believed to be fully cured when, for instance, its glass transition temperature no longer changes over time, in other words has reached a substantially stable value, suggesting that no further cross-linking is taking place. Alternatively and additionally, an amino-silicone polymer would be fully cured, when the number of siloxane bonds it can form in the curable fluid and under the curing conditions applicable, does not substantially change over time. The number of siloxane bonds in a cured amino-silicone polymer can be assessed by routine analytical methods, such as by Fourier transform infrared (FTIR) spectroscopy.

As explained, the relative polarity of the fiber substrate to be coated or colored (*e.g.*, a keratinous fiber, whether native, pre-treated, for instance by bleaching, or coated according to present teachings) and of the overall charge of the coloring or masking compositions due to treat the substrate (including the active constituents of these compositions) is believed to facilitate the initial wetting of the substrate by the compositions. Hence, in some embodiments, when a subsequent coating is desired, the subsequent composition can have a polarity opposite to the polarity of the coated substrate. Thus in the present illustration, if a negatively charged hair fiber is first coated with a pigmented amino-silicone film forming composition resulting in a positively charged film, the now positively charged substrate can be subsequently coated with an overall negatively charged subsequent composition. However, as opposite polarities are not essential, in alternative embodiments, subsequent coatings, if desired, can have similar polarity (positive or negative), the overall charge being similar or different.

It can be readily understood that the relative charge of the surface being coated and of the droplets or particles coating it form a gradient which decreases as the migration of the charged polymer-forming materials to the fiber proceeds. For illustrative example, assuming a negatively charged human hair and positively charged droplets of amino-silicone pre-polymers, at first there is a large gradient driving the positive droplets to the negative hair. As the hair gets coated with the positive droplets, its charge increases and therefore the gradient driving the surrounding droplets towards the fiber decreases until it is too small to drive any additional positively charged droplet to the hair. Without wishing to be bound by the above theory, it is believed that the process of the present method is self-terminating.

FIG. 1D is a schematic, magnified illustration representing a surface of a mammalian hair fiber **10** as provided in FIG. 1A. The exterior of the hair filament or fiber is made up of cuticle cells. These cells have multiple layers, the outward-most of which is the cell membrane complex **50**. The cell membrane complex includes a dense protein matrix **30** attached to the outer surface **25** of the A-layer of the cuticle, and a lipid layer **40** having fatty acid chains attached at a first end (typically, but not exclusively, the fatty acid end) to protein matrix **30**, and, at the opposite, free end, extending away from protein matrix **30**. These fatty acid chains contribute to the hydrophobicity (and to the lubricity) of the hair.

The height of cell membrane complex **50** may be less than 10 nm, typically about 5-7 nm. The inventors have observed that penetration through cell membrane complex **50**, towards or to outer surface **25** of the A-layer of the cuticle, may be highly impeded for viscous materials, sterically-hindered materials or negatively-charged droplets, particularly in view of the narrow openings (*circa* 2 nm) between adjacent free ends of the fatty acid chains of cell membrane complex **50**. The inventors believe that the various advantages of utilizing viscous polymeric materials notwithstanding, such materials may be significantly less suitable for achieving permanent hair coloring, with respect to their less viscous, monomeric and/or oligomeric counterparts.

Again, without wishing to be limited by theory, the inventors believe that for the pre-polymeric amino-silicone composition (*e.g.*, liquid emulsion) according to the present teachings to appreciably contact the hydrophobic upper surface **42** of the fatty acid chains **40**, the amino-silicone droplets need to be sufficiently hydrophobic. Moreover, this hydrophobicity aids in displacing the air disposed on the surface of the fatty acid chains **40**, which is also required to enable penetration there-between.

The wetting process may be driven by charge interactions between the positively-charged amine moieties of the amino-silicone and various negatively-charged counterparts on the hair surface. Such drive can also be assessed by the gap in surface energy of the wetting liquid and the wetted surface. Amino-silicones having a surface energy of no more than the surface energy of the keratinous substrate are deemed advantageous. For instance, untreated, undamaged human hair typically has a surface energy of 24-28 milliNewton/meter (mN/m; also referred to as dyn/cm), while treated hairs are in the range of 38-47 mN/m.

Consequently, the Amine Number, or more generally, the charge density of the amino-silicone pre-polymer appears to be of particular importance. The Amine Number of an amino-silicone pre-polymer is generally supplied by the manufacturer, but can be independently determined by standard methods, as described for example in ASTM D 2074-07. It can be provided in terms of the amount of milliliters of 0.1N HCl needed to neutralize 10 g of the material under study.

This charge relationship, coupled with the requisite viscosity, surface tension and lack of steric hindrance of the amino-silicone pre-polymer, enables “pinning” of the pre-polymer within, or deeply within, the cell membrane complex **50**. Such pinning may be grossly insufficient in terms of permanence, but allows at least partial curing of the pre-polymer (*e.g.*, formation of a 3D network of siloxane cross-linking bonds in and around the protruding elements of the cell membrane complex **50**).

According to some embodiments, the reactive condensation-curable amino-functional silicone pre-polymer has an average molecular weight in the range of from about 100 to about 100,000. Typically, a monomer has a MW in the range of from about 100 to about 600, an oligomer has an average MW in the range of from about 200 to about 2,000, and a polymer has an average MW of at least about 2,000, and in some embodiments, of at most 50,000.

According to some embodiments, the reactive condensation-curable amino-functional silicone pre-polymer forms, when in emulsion, emulsion droplets having an average size (D_V50) in the range of 200 nm to 1 μm, or from 0.5 μm to 5 μm or from 1 μm to 10 μm.

According to some embodiments, the reactive condensation-curable amino-functional silicone pre-polymer is present at a concentration in the range of from about 0.01 to 20% by weight of the total weight of the composition, such as from about 0.05 to 10% by weight of the total weight of the composition.

According to some embodiments, the sub-micronic pigment particles comprise an organic pigment, for example an organic pigment selected from the group consisting of perylene pigments; phthalocyanine pigments; quinacridone pigments; and imidazolone pigments.

According to some embodiments, the sub-micronic pigment particles comprises an inorganic pigment, for example an inorganic pigment selected from the group consisting of titanium dioxide, cadmium sulfoselenide, iron oxide, bismuth vanadate, cobalt titanate, sodium aluminosulfosilicate, mixed Fe-Mg-Ti oxides, manganese ferrite, and metallic or alloy pigments.

In some embodiments, the sub-micronic organic or inorganic pigments (or combinations thereof) serve as color imparting agents. The sub-micronic pigments may also be referred to as light absorbing pigments or simply as absorbing pigments.

According to some embodiments, the sub-micronic pigment is an organic or inorganic pigment selected from the group consisting of the following EU-approved colors for cosmetic use: CI 10006, CI 10020, CI 10316, CI 11680, CI 11710, CI 11725, CI 11920, CI 12010, CI 12085, CI 12120, CI 12370, CI 12420, CI 12480, CI 12490, CI 12700, CI 13015, CI 14270, CI 14700, CI 14720, CI 14815, CI 15510, CI 15525, CI 15580, CI 15620, CI 15630, CI 15800, CI 15850, CI 15865, CI 15880, CI 15980, CI 15985, CI 16035, CI 16185, CI 16230, CI 16255, CI 16290, CI 17200, CI 18050, CI 18130, CI 18690, CI 18736, CI 18820, CI 18965, CI 19140, CI 20040, CI 20470, CI 21100, CI 21108, CI 21230, CI 24790, CI 26100, CI 27755, CI 28440, CI 40215, CI 40800, CI 40820, CI 40825, CI 40850, CI 42045, CI 42051, CI 42053, CI 42080, CI 42090, CI 42100, CI 42170, CI 42510, CI 42520, CI 42735, CI 44045, CI 44090, CI 45100, CI 45190, CI 45220, CI 45350, CI 45370, CI 45380, CI 45396, CI 45405, CI 45410, CI 45430, CI 47000, CI 47005, CI 50325, CI 50420, CI 51319, CI 58000, CI 59040, CI 60724, CI 60725, CI 60730, CI 61565, CI 61570, CI 61585, CI 62045, CI 69800, CI 69825, CI 71105, CI 73000, CI 73015, CI 73360, CI 73385, CI 73900, CI 73915, CI 74100, CI 74160, CI 74180, CI 74260, CI 75100, CI 75120, CI 75125, CI 75130, CI 75135, CI 75170, CI 75300, CI 75470, CI 75810, CI 77000, CI 77007, CI 77266, CI 77267, CI 77268:1, CI 77891, CI 77947, lactoflavin, caramel, capsanthin, capsorubin, beetroot red, anthocynanins, bromothymol blue, bromocresol green, and acid red 195.

According to some embodiments, the sub-micronic pigment is selected from the group consisting of the following US-certified organic colors for cosmetic use:

D&C Black No. 2, D&C Black No. 3, FD&C Blue No. 1, D&C Blue No. 4, D&C Brown No. 1, FD&C Green No. 3, D&C Green No. 5, D&C Green No. 6, D&C Green No. 8, D&C Orange No. 4, D&C Orange No. 5, D&C Orange No. 10, D&C Orange No. 11, FD&C Red No. 4, D&C Red No. 6, D&C Red No. 7, D&C Red No. 17, D&C Red No. 21, D&C Red No. 22, D&C Red No. 27, D&C Red No. 28, D&C Red No. 30, D&C Red No. 31, D&C Red No. 33, D&C Red No. 34, D&C Red No. 36, FD&C Red No. 40, Ext. D&C Violet No. 2, FD&C Yellow No. 5, FD&C Yellow No. 6, D&C Yellow No. 7, Ext. D&C Yellow No. 7, D&C Yellow No. 8, D&C Yellow No. 10 and D&C Yellow No. 11.

In some embodiments, to be detailed in the following sections, inorganic pigments can be used in compositions, kits or methods according to the present teachings in a size range greater than sub-micronic range. Such inorganic pigments are either made of metals, alloys or oxides thereof, or formed as multilayer pigments based on substrates (such as mica, silica, borosilicate, plastic or even metals) coated with the same afore-mentioned metallic materials. Multilayer pigments having for instance a mica core or a silica core are also referred to as mica coated flakes or silica coated flakes, the coat (*e.g.*, sometimes applied by chemical vapor deposition (CVD) or physical vapor deposition (PVD)) providing the look. These pigments typically provide a metallic appearance, and are thus collectively termed metallic pigments or metallic-looking pigments irrespective of chemical type.

While some of the above-mentioned metallic pigments may provide for a broad range of light reflection, others may be more specific, reflecting a narrow range of wavelengths or even a single wavelength (*e.g.*, interference pigments). Such narrowly reflective pigments include by way of example mica pigments coated with a thin layer of metals, alloys or oxides thereof. As used herein, the term “reflective pigment” encompasses any metallic pigment able to reflect at least one wavelength. In some embodiments, the reflective pigment is further tinted to provide a coloring effect in addition to a light reflective effect.

In some embodiments, the reflective pigment is tinted with a dye selected from the group consisting of an azo dye (such as Color Index (C.I.) Reactive Yellow 4); an anthraquinone dye (such as C.I. Reactive Blue 19); and a phthalocyanine dye (such as C.I. Direct Blue 86).

In some embodiments, the metallic pigment is selected from the group consisting of aluminum, copper, zinc, iron, titanium, gold, or silver and alloys of these metals, such as brass, bronze or steel alloys. In some embodiments, the metallic pigment is selected from the group consisting of bismuth oxychloride, mica and silica coated with titanium dioxide, silicon dioxide, iron oxide, chromium oxide, zinc oxide, aluminum oxide, and tin dioxide. In some embodiments, the metallic pigment is further coated with dyes or sub-micronic pigments to additionally provide or enhance a coloring effect, such as, for example, aluminum pigment coated with phthalocyanine blue or Cinquasia® red. In some embodiments, there are provided multi-layer pigments based on synthetic substrates such as alumina, silica, calcium sodium borosilicate or calcium aluminium borosilicate, and aluminium.

In addition to having, in some embodiments, at least one dimension above one micrometer, the metallic pigments have advantageously a flake-like or platelet shape.

In some embodiments, the pigments of the present compositions provide a special visual effect, instead of or in addition to a coloring effect and/or a metallic appearance. Special effects include, by way of non-limiting example, a fluorescent effect, a glittering effect, a pearlescent effect and a phosphorescent effect. These effects may be visible under regular illumination or may require (or be further increased) by special lighting conditions. For instance, fluorescent pigments may become visible or may provide a fluorescent effect when subjected to ultraviolet (UV) light. At the other end of the spectrum, up-converting pigments are luminescent materials which are able to convert near infrared (NIR) light to visible (VIS) light. Additional colorants providing for less typical coloring further include, by way of non-limiting example, thermo-chromic pigments or dyes, allowing the compositions comprising them to change color as a result of a change in temperature, and pH dependent pigments, whose color is modified by pH.

Depending on their morphology, particles (*e.g.*, sub-micronic (absorbing) pigments, metallic (reflective) pigments, and the like) may be characterized by their length, width, thickness, diameter, or any such representative measurement of their X-, Y- and Z-dimensions. Typically such sizes are provided as average of the population of particles and are provide by the manufacturer of such materials. These sizes can be determined by any technique known in the art, such as microscopy and Dynamic Light Scattering (DLS). In DLS techniques, the particles are approximated to spheres of equivalent behavior and the size can be provided in terms of hydrodynamic diameter. DLS also allows assessing the size distribution of a population. The same applies to liquid droplets and may assist for instance in the characterization of emulsion droplets, all typically having a globular shape. As used herein, particles having a size of, for instance, 1 μm or less, have at least one dimension equal to or smaller than 1 μm, and possibly two or even three, depending on shape. When concerned with emulsion droplets having, by way of example, a size of 5 µm or less, the droplets are understood to have an average diameter equal to or smaller than 5 µm.

Though not essential, the particles or emulsion droplets of any particular kind may preferably be uniformly shaped and/or within a symmetrical distribution relative to a median value of the population and/or within a relatively narrow size distribution for this particular kind. In the following, and unless otherwise clear from context, the term "particle" refers both to solid particles (*e.g.*, pigments and the like) and to liquid droplets (*e.g.*, emulsion droplets, micelles and the like).

A particle size distribution (PSD) is said to be relatively narrow if at least one of the two following conditions applies:

A) the difference between the hydrodynamic diameter of 90% of the particles and the hydrodynamic diameter of 10% of the particles is equal to or less than 150 nm, or equal to or less than 100 nm, or equal to or less than 50 nm, which can be mathematically expressed by: $(D90 - D10) \leq 150$ nm and so on; and/or

B) the ratio between a) the difference between the hydrodynamic diameter of 90% of the particles and the hydrodynamic diameter of 10% of the particles; and b) the hydrodynamic diameter of 50% of the particles, is no more than 2.0, or no more than 1.5, or no more than 1.0, which can be mathematically expressed by: $(D90 - D10)/D50 \leq 2.0$ and so on.

D10, D50 and D90 can be assessed by number of particles in the population, in which case they may be provided as D_N10, D_N50 and D_N90, or by volume of particles, in which case they may be provided as D_V10, D_V50 and D_V90. The foregoing measurements can be obtained by DLS techniques when the samples to be studied are suitably fluid or by microscopy when the particles under study are in dry form. As used herein, D50, which can also be termed the "average measured particle size" or simply the "average particle size" may refer, depending on the measuring method most suited to the particles being considered and their media, either to D_V50 (by DLS and the like) or to the volume average size of particles found in a field of view of a microscope adapted to analyze in the scale of the particles. D90 accordingly relate to measurements applying to 90% of the population under study, thus also termed the "predominant measured particle size" or simply the "predominant particle size" which can for instance be assessed by DLS techniques as D_V90.

As mentioned above, such relatively uniform distribution may not be necessary for certain applications. For instance, having a relatively heterogeneously sized population of sub-micronic pigments or of metallic pigments particles may allow, in a coating formed thereby, relatively smaller particles to reside in interstices formed by relatively larger particles providing in combination a relatively uniform coating.

The particles may be characterized by an aspect ratio, *i.e.*, a dimensionless ratio between the smallest dimension of the particle and the longest dimension or equivalent diameter in the largest plane orthogonal to the smallest dimension, as relevant to their shape. The equivalent diameter (Deq) is defined by the arithmetical average between the longest and shortest dimensions of that largest orthogonal plane. Particles having an almost spherical shape, and emulsion droplets amongst them, are characterized by an aspect ratio of approximately 1:1, whereas rod-like particles can have higher aspect ratios and flake-like particles can even have an aspect ratio of up to 1:100, or even more.

Such characteristic dimensions are generally provided by the suppliers of such particles and can be assessed on a number of representative particles by methods known in the art, such as microscopy, including, in particular, by light microscope for particles of several microns or down to estimated dimensions of about 200 nm, by scanning electron microscope SEM for smaller particles having dimensions of less than 200 nm (SEM being in particular suitable for the planar dimensions) and/or by focused ion beam FIB (preferably for the thickness and length (long) dimensions of sub-micronic particles, also referred to herein as nanoparticles or nanosized particles). While selecting a representative particle, or a group of representative particles, that may accurately characterize the population (*e.g.*, by diameter, longest dimension, thickness, aspect ratio and like characterizing measures of the particles), it will be appreciated that a more statistical approach may be desired. When using microscopy for particle size characterization, a field of view of the image-capturing instrument (*e.g.*, light microscope, SEM, FIB-SEM *etc.*) is analyzed in its entirety. Typically, the magnification is adjusted such that at least 5 particles, at least 10 particles, at least 20 particles, or at least 50 particles are disposed within a single field of view. Naturally, the field of view should be a representative field of view as assessed by one skilled in the art of microscopic analysis. The average value characterizing such a group of particles in such a field of view is obtained by volume averaging. In such case, $D_V50 = \Sigma[(Deq(m))^3/m]^{1/3}$, wherein m represents the number of particles in the field of view and the summation is performed over all m particles. As mentioned, when such methods are the technique of choice for the scale of the particles to be studied or in view of their media, such measurements can be referred to as D50.

According to some embodiments, the sub-micronic pigment (*i.e.* the color imparting pigment) comprises particles having a size predominantly not exceeding 250 nm. In some embodiments, the predominant size of the pigment particles is assessed by the volume of the particles, also termed D_{V90}, and is equal or less than 225 nm, or less than 200 nm, or less than 175 nm, or less than 150 nm, or less than 125 nm, or less than 100 nm. In particular embodiments, the measured organic pigment particle size is alternatively or additionally measured as the average particle size (D_V50) and is equal to or less than 100 nm, or less than 90 nm, or less than 80 nm, or less than 70 nm, or less than 60 nm, or less than 50 nm, or less than 40 nm. In some embodiments, the average particle size D_V50 of the organic pigments is of at least 10 nm, or at least 20 nm, or at least 30 nm.

According to some embodiments, the composition or kit disclosed herein further comprises a cross-linker, for example, an organosilicon compound able to react through all non-amino reactive groups of the reactive silicone, and a cross-linking agent comprising a mercapto group, an epoxy group or an acrylate group, all able to react through amino reactive groups of the reactive silicone.

Generally, cross-linking agents comprise at least three reactive groups for the formation of the network of oligomers and polymers resulting in the elastomeric network.

The organosilicon cross-linking agent must have hydrolysable groups (Y).

After hydrolysis, the silanol groups obtained can undergo condensation reaction with the reactive amino-silicone pre-polymer to give siloxane bonds.

The organosilicon cross linker can contain:

- tetrafunctional hydrolysable groups and consist for example of silane having a Q units ($SiO_{4/2}$), such as SiY_4
- or trifunctional hydrolysable groups and consist of silane or siloxane oligomers having T units of the formula $R^aSiO_{3/2}$, like R^aSiY_3
- or difunctional hydrolysable groups and consist of silane or siloxane oligomers having D units of the formula $R^b_2SiO_{2/2}$, like $R^b_2SiY_2$

where the hydrolysable group (Y) can be selected from

- Alkoxy (*e.g.*, methoxy, ethoxy, propoxy, isopropoxy, methoxyethoxy and the like)
- Oxime (*e.g.*, methylethylketoxime)

- Acyloxy (*e.g.*, acetoxy)

where the R^a and R^b substituents are selected from

- C_1-C_4 Alkyl groups,
- Alkenyl groups (vinyl, allyl, *etc.*),
- Aminoalkyl groups (monoamino, such as aminopropyl $NH_2(CH_2)_3$: diamino, such as aminoethylaminopropyl $NH_2(CH_2)_2NH(CH_2)_3$; or triamino)
- Epoxy group (*e.g.*, glycidoxypropyl)
- Acrylate group (*e.g.*, methacryloxypropyl)
- Mercapto group (*e.g.*, mercaptopropyl)

According to some embodiments, the cross-linking agent can be a branched polyorganosiloxane comprising Q units, T units and D units or a linear polyorganosiloxane, *i.e.*, having D units.

According to some embodiments, the cross-linker can be an ethylsilicate, such as tetraethylsilicate (CAS No 78-10-4), poly(diethoxysiloxane) oligomers, such as Evonik Dynasylan® 40 with a silicon dioxide content of approximately 40-42% upon complete hydrolysis, Colcoat® Ethylsilicate 48 with a silicon dioxide content of approximately 48% upon complete hydrolysis (CAS No. 11099-06-2), and poly(dimethoxysiloxane) (CAS No. 25498-02-6).

According to some embodiments, the cross-linker can be aminopropyltriethoxysilane (CAS No. 919-30-2), bis(triethoxysilylpropyl)amine (CAS No. 13497-18-2), or mixtures thereof.

According to some embodiments, the pigment is further coated with a chemical coat which does not interfere with the visual effect of the underlying pigment. Such a chemical coat can provide protection to the pigment, such as providing anti-oxidant properties, or any other desired property, by way of example, dispersibility, stability, ability to adhere to the fibers, charge and like characteristics that improves pigment activity and intended effect. For instance, the chemical coat can be a fatty acid, such as oleic acid, stearic acid, an adhesion promoting polymer coat, such as an acrylic polymer, a silane polymer or an amino-silane polymer, and such chemical coats known in the art of pigments.

In other embodiments, the chemical coat provides a visual effect, for instance when the pigment a flake-like shaped metallic pigment (*e.g.* mica or glass flakes, having an average greatest dimension in the range of 2 to 20 μm), the coating may be a metal oxide, such as, for example, titanium dioxide or ferric oxide.

According to some embodiments, the emulsion comprises an oil-in-water emulsion.

According to some embodiments, the aqueous carrier comprises at least 60% water by weight of the liquid carrier, or at least 65wt.%, or at least 70wt.%, or at least 75wt.%, or at least 80wt.%, or at least 85wt.%, or at least 90wt.%, or at least 95wt.% water. In cases in which the amount of pigments and/or their density is high, while the liquid carrier will predominantly comprise water, the water may constitute only 30% by weight of the total composition.

According to some embodiments, a pH of the composition is in the range of from about 4 to about 11.

According to some embodiments, a viscosity of the composition is in the range of from about 1 to about 100,000 mPa•s at 25°C, such as from about 10 to about 12,500 mPa•s at 25°C.

According to some embodiments, the composition or kit further comprises an additive selected from the group consisting of dispersant, pH modifying agents, preservatives, bactericide, fungicide, viscosity modifiers, thickeners and perfumes.

According to some embodiments, the composition is in the form selected from the group consisting of a paste, a gel, a lotion, and a cream.

According to some embodiments, the keratinous fibers are mammalian hair. In some embodiments, the hair is human hair or animal hair, the hair being selected from body hair, facial hair (including for example moustaches, beards, eyelashes and eyebrows) or head hair. In further embodiments, the hair is attached to a body or scalp of a human or an animal subject. Human hair can be of any human race (*e.g.*, European, Asian, African, *etc.*) and any type, such as straight, wavy, curly, or kinky, whether naturally or artificially so. Human hair not attached to a subject can be found in wigs, hair extensions, eyelash extensions, and like products.

EXAMPLES

Example 1: Coloring of light-colored keratinous fibers

Materials

Hair

Yak white body hair; Chinese black human hair; European black human hair (all supplied by Kerling International Haarfabrik GmbH, as tufts of about 2.5 g of hair having a length of approximately 7 cm)

Organic pigments

Heliogen® Green K8730 (BASF, Germany)
Cromophtal® Yellow 3RT (BASF, Germany)
Irgazin® Magenta 2012 (BASF, Germany)

Dispersant

2-ethylhexanoic acid (Sigma-Aldrich, USA)

Reactive Condensation-Curable Amino-silicone pre-polymers

Amino-silicone ATM 1322 (Amine Number 80); (Gelest® Inc., USA)

Amino-silicone GP-34 (Amine Number 3.3, MW ~33,596); Amino-silicone GP-145 (Amine Number 11, MW ~18,052); Amino-silicone GP-397 (Amine Number 116, MW ~3,754); Amino-silicone GP-657 (Amine Number 54, MW ~3,700); and Amino-silicone GP-846 (Amine Number 110); (all of Genesee Polymers Corp., USA).

Amino-silicone KF-857 (Amine Number 127); Amino-silicone KF-862 (Amine Number 53); (all of Shin-Etsu Polymer Co. Ltd., Japan).

Amino-silicone Rhodorsil 21642 (Amine Number 20); (Bluestar Silicones International, France).

Amino-silicone SF 1706 (Amine Number 47); Amino-silicone TSF 4703 (Amine Number 62); Amino-silicone TSF 4707 (Amine Number 15); Amino-silicone TSF 4708 (Amine Number 38); (all of Momentive Performance Materials Inc., USA).

Xiameter® OFX 8630 (Amine Number 25); Xiameter® OFX 8822 (Amine Number 45); (all of Dow Corning, USA).

Diluents

Hexamethyldisiloxane 98% (Acros Organics, USA)

Ethanol (Gadot, Israel)

Aluminum pigment

Vacuum metalized passivated aluminum flake pigments (AQ-4172 PA, Silberline, USA)

Cross-linker

3-Glycidyloxypropyl trimethoxysilane (Evonik® Industries, Germany)

Emulsifier

Tween® 80 (Sigma Aldrich, USA)

Cure accelerator

Carbodilite Emulsion E-05 (40% multifunctional polycarbodiimide in anionic emulsion)

Carbodilite V02-B (100% multifunctional polycarbodiimide)

Shampoo

Shea Natural Keratin Shampoo (Saryna Key, Israel)

Equipment

Attritor® HD01 (Union Process, USA)

T25 Ultra Turrax digital (IKA, Germany)

Digital Orbital Shaker TOU 50 (MRC Lab, Israel)

Heraeus oven, UT 12 (Thermo Scientific, USA)

Sonicator Q700 (Qsonica LLC, USA)

Zetasizer Nano S light scattering device (Malvern Instruments Ltd., UK)

Water bath WBL-200 (MRC, UK)

528 Spectro-Densitometer (X-Rite Inc., USA)

Methods

Preparation of slurry comprising sub-micronic particles of pigment

4 kg of stainless steel 5 mm beads were added to 100 gr of organic pigment and 100 gr of 2-ethylhexanoic acid. Organic pigments initial size was as provided by respective suppliers, generally all in the tens of micrometers range. The slurry was then bead-milled for 1 hour, at 400 RPM, 55°C using an Attritor® HD01 with a double jacket tank-refrigerated circulated water bath WBL-200 to produce a milled slurry comprising sub-micronic particles of the pigment. The slurry was separated from the beads by gravitation.

Size analysis

100 mg of the milled slurry were diluted in 10 g 2-ethylhexanoic acid at ambient temperature (*circa* 23°C). The diluted slurry was re-suspended in 2-ethylhexanoic acid using a Sonicator Q700 at 500W amplitude for 7 sec.

1 g of the sonicated suspension was then placed in a plastic cuvette and allowed to equilibrate for 60 seconds at ambient temperature. Particle size was measured using a dynamic light scattering (DLS) device, Zetasizer Nano S, with 10 measurements of 10 seconds each. The average particle diameter size by volume D_V50, was found to be approximately 150 nm for all size-reduced organic pigments.

Additional slurries of sub-micronic pigments were similarly prepared by replacing the dispersant 2-ethylhexanoic acid by BYK LPX 21879, an amino-silicone dispersant known as a wetting and dispersing additive for unipolar systems. Unless otherwise indicated, the weight per weight (w/w) ratio of pigment to dispersant in the milling stage was of 1:1. In this method, the pigment : dispersant mix was supplemented with 200 g of a volatile solvent, such as hexamethyldisiloxane. Pigments, size reduced in presence of this alternative dispersant, were similarly milled down to average sizes of about 150 nm, as assessed by D_V50. The volatile solvent was evaporated before further use of the sub-micronic pigments.

Preparation of compositions for coloring keratinous fibers

Coloring compositions A to E were prepared, comprising components as detailed in Table 1.

Component	Function	Composition (weights in grams)				
		A	B	C	D	E
Heliogen® Green K8730	Green organic pigment	1.25	–	–	1.25	1.25
Cromophtal® Yellow 3RT	Yellow organic pigment	–	1.25	–		
Irgazin® Magenta 2012	Red organic pigment	–	–	1.25		
2-ethylhexanoic acid	Dispersant	1.25	1.25	1.25	1.25	1.25
Amino-silicone GP-397	Reactive terminal amino functional silicone polymer	10	10	10		
Amino-silicone GP-657	Reactive terminal amino functional silicone polymer				10	
Amino-silicone KF-862	Reactive side chain amino functional silicone polymer					10
Hexamethyldisiloxane 98%	Diluent	87.5	87.5	87.5	87.5	87.5

Table 1

All compositions of Table 1 were prepared as follows:

80 g of reactive amino-silicone were added to 25 g of milled slurry comprising sub-micronic particles of organic pigment (green, yellow or red), prepared as described above. The mixture was then sonicated using Qsonica Sonicator Q700 at 500W amplitude for 1 min. 12.5 g of the mixture were diluted with 87.5 gr hexamethyldisiloxane. It is to be noted that the present samples, while being technically coloring compositions, are intentionally devoid of cross-linking agents and optional accelerating agents or catalysts as claimed for practical coloring, in order to obtain a preliminary assessment of the basic adherence of the amino-silicone elastomers to keratinous fibers.

Coating of keratinous fibers

Coated samples A to E were prepared by immersing tufts of untreated yak hair (2.5 grams per tuft), in one of compositions A to E, respectively, for about 1 minute at ambient temperature. As yak hair has a very light straw-like shade, the coloring samples due to result in darker shades were applied to the fibers without any pre-treatment (*e.g.*, no bleaching).

The samples were subsequently rinsed thoroughly in tap water at ambient temperature and then transferred to a Heraeus oven, UT 12, for 7 days at 60°C and 100% relative humidity, to fully cure the condensation-curable reactive polyamino-silicone (*e.g.*, by self cross linking) in the absence of agents otherwise favoring or accelerating such curing, as cross-linking agents and optional catalysts.

For comparative purposes, samples F and G were prepared, comprising yak hair tufts coated with commercial black and brown hair dyes, respectively, both providing for a coloring effect deemed permanent. Yak hair tufts (2.5 grams each) were first bleached with a commercial bleaching kit (Elgon De Color, comprising bleach powder and 6% Joya oxygen cream, at a ratio of 4:3 weight percentage bleach powder : oxygen cream) for 30 minutes and then thoroughly rinsed with tap water. In the present case, bleaching was performed not to remove the original hair color but to facilitate the penetration of the dyes through the hair surface.

Following rinsing, sample F was prepared by immersing a bleached tuft in Elegon Moda & Styling color cream, black 1 for 45 minutes and sample G was prepared by immersing a bleached tuft in Kosswell professional Equium color cream, dark blonde 6, for 45 minutes. Samples F and G were subsequently thoroughly rinsed in tap water.

Color-fade measurements

The extent of coloring of samples A to G was measured in terms of optical density (OD) using a 528 Spectro-Densitometer (X-Rite, Inc.) within a spectral range of 400-700 nm. The value obtained following the coloring process (and when applicable the full curing of the condensation-curable amino-silicone elastomer) was taken to be the baseline OD for each sample.

The measured OD at baseline (0 shampoo) varied depending on the color imparting sub-micronic pigment or commercially available permanent dyes, and was of about 1.5, 1.1, 1.3, 1.8, 1.2, 1.7 and 1.6, for samples A-G, respectively. For comparison, the OD of yak hair samples without any coloring treatment or coated under similar conditions with a composition comprising 10% amino-silicone GP-397 diluted in hexamethyldisiloxane without any pigment were also measured and found to both have an average value of approximately 0.36 supporting the transparency of the cured amino-silicone on the coated hair.

Color-fade was studied by measuring the OD of each of the samples following various numbers of standard shampooing treatments, using Shea Natural Keratin Shampoo and drying with a Philips Compact Hair Dryer. The shampooing and drying treatment was repeated up to 130 times, and the OD measured after 1, 2, 4, 10, and then after every 10 treatments.

Unless otherwise stated, each measurement was performed in triplicate and the results reported below represent the mean value obtained.

Results are presented in FIG. 2A, showing OD as a function of the number of shampooing and drying treatments, expressed as percentage of baseline OD. For convenience, computer generated trendlines were added for each series.

Results

The reduction in the extent of coloring of the hair samples under study became detectable to the naked eye (*i.e.* visibly detectable) when the measured OD decreased below about 80% of the baseline OD value.

As seen in FIG. 2A, samples A, B and C appeared to be resistant to color-fade for up to at least about 110, 70 and 90 shampooing and drying treatments, respectively (*i.e.* OD remained above 80% of the baseline OD value for the respective number of treatments). As wash resistance of at least 30 shampooing is often considered as threshold for the lasting effect of coloration, it can be concluded that samples A, B and C as herein disclosed are suitable for permanent coloring of keratinous fibers even in the absence of cross-linking agents / catalysts. Addition of such agents is expected to accelerate the initial curing on the keratinous fibers, rapidly providing for non-sticky hairs. Such addition of cross-linking agents is necessary when coloring human or animal hair attached to respective subjects to promote a dry feeling to the touch, enhancing compliance, but not essential if coloring fibers that can be incubated for prolonged period of times at relatively elevated temperatures. Similarly, an optional accelerating agent or catalyst can be further added to promote such rapid initial partial-curing. It is believed that such additions do not significantly affect the color-fade resistance of full coloring compositions comprising them in addition to the condensation-curable amino-silicone and the sub-micronic pigments.

Comparative samples F and G, prepared using commercially available permanent dyes (penetrating the hair shaft and believed to react therein), also exhibited significant resistance to shampooing, both maintaining OD within range of undistinguishable color change for at least 150 treatments. Samples D and E, not shown on the graph, displayed a coloring resistance to about 8-10 and 5-6 shampooing cycles, respectively, qualifying them as semi-permanent coloring compositions. It is to be noted that a commercially available coloring composition sold as a temporary coloring formulation achieved a color-fade resistance of only about 2-3 shampooing, further supporting the significance of the result achieved by the compositions of the present disclosure.

Example 2: Aqueous compositions for coloring keratinous fibers

Preparation of compositions

Samples AA to AN were prepared comprising components as detailed in Table 2 and as described below, wherein the condensation-curable silicone was selected from the list shown in the following table in which some parameters concerning these elastomers are presented.

Sample	**Silicone**	**Amine No.***	**Amine Position (Polymer type**)**	**Amine Type**	**Reactive Group**	**Viscosity (mPa•s)**	**Shampoo Resist**
AA	ATM 1322	101	Pendant (LP)	I, II	Methoxy	250	≥ 65
AB	GP-34	3.3	Terminal (LP)	I	Methoxy	3500	≥ 20
AC	GP-145	11	Terminal (LP)	I	Ethoxy	1900	≈ 18
AD	GP-397	116	Terminal (LP)	I, II	Methoxy	130	≥ 110
AE	GP-657	54	Terminal (LP)	I	Methoxy	120	≥ 100
AF	GP-846	110	N/A (BP)	I, II	Methoxy	30	≥ 55
AG	KF-857	127	Pendant (LP)	I	Methoxy	65	≥ 130
AH	Bluesil 21642	15	Pendant (LP)	I, II	Methoxy	1400	≥ 10
AI	SF 1706	47	Pendant (BP)	I, II	Methoxy	30	≈ 20
AJ	TSF 4703	62	Pendant (LP)	I, II	Methoxy	1000	≥ 50
AK	TSF 4707	15	Pendant (LP)	I, II	Methoxy	7000	≥ 20
AL	TSF 4708	38	Pendant (LP)	I, II	Methoxy	1000	≥ 10
AM	Xiameter® OFX 8630	25	Pendant (LP)	I	Ethoxy	3500	≥ 30
AN	Xiameter® OFX 8822	45	Pendant (LP)	I	Methoxy	1500	≈ 20

* Amine Number refers to milliliters of 0.1N HCl needed to neutralize 10 g of polymer

** LP = Linear polymer; BP = Branched polymer

Table 2

All compositions of Table 2 were prepared as follows:

8 g of reactive amino-silicone were added to 2 g of milled slurry comprising sub-particles of Cromophtal® Yellow 3RT with BYK LPX 21879 as dispersant, prepared as described above, and mixed on a Teflon® surface using a painting trowel. The mixture was then homogenized using IKA Ultra Turrax T25 at 25,000 rpm for 30 seconds, to obtain a colored paste. 0.2 g of the colored paste were diluted with 60 g of water with 0.1wt.% Tween® 80. The diluted mixture was then sonicated using Qsonica Sonicator Q700 for 10 seconds at 80% amplitude to obtain a colored emulsion.

Coating of keratinous fibers

Coated samples were prepared by immersing tufts of untreated white yak hair (2.5 g per tuft) in one of compositions AA to AN, respectively, for 45 seconds at ambient temperature, with gentle stirring. The samples were subsequently rinsed thoroughly in tap water at about 40°C, then dried for 30 seconds with a Philips compact hair dryer.

Results

The measured OD at baseline (0 shampoo) varied depending on the amino-silicone elected and was generally between about 1.1 and about 1.4, demonstrating satisfactory baseline coloring. It should be noted that such coloring was rapidly obtained, the process till drying being completed within minutes of application of the condensation-curable amino-silicone coating composition. Such rapidity is in clear contrast with conventional wet coloring methods.

Color-fade was studied as previously described, by measuring after every 5 cycles the OD of each of the samples following various numbers of standard shampooing and drying treatments, which were performed up to 130 times.

Results were analyzed and the change in OD as a function of the number of shampooing and drying treatments, expressed as percentage of baseline OD, was calculated for each sample. The patterns of selected samples are shown in FIG. 2B, which for convenience includes computer generated linear trendlines for each series. The number of shampoos each sample could withstand before undergoing a visible change in color (as confirmed by a measured OD smaller than 80% of baseline OD) is reported in the above table.

As seen in FIG. 2B showing the color resistance over the first 50 cycles, samples AA, AD, AE, AF, AG and AJ appeared to be resistant to color-fade for up to at least 45 shampooing and drying treatments. As shown in Table 2, samples AD, AE and AG are expected to resist even more than 100 shampooing. As wash resistance of at least 30 shampooing is often considered as threshold for the lasting effect of coloration, it can be concluded that samples AA, AD, AE, AF, AG, AJ and AM as herein disclosed are suitable for permanent coloring of keratinous fibers even in absence of cross-linking agents / catalysts. Similarly, as wash resistance in the range of about 10-30 shampooing is qualifying coloration as demi-permanent, it can be concluded that the condensation-curable amino-silicones as used in samples AB, AC, AH, AI, AK, AL and AN are suitable for the preparation of demi-permanent coloring compositions, capable of coloring keratinous fibers.

As seen from Table 2, based on the present reactive condensation-curable amino-silicone elastomers, two trends seem to emerge. First, while satisfactory coloring can be obtained with elastomers having an Amine Number as low as about 3 (see sample AB resisting 20 or more shampooing cycles), it can be generally observed that elastomers having higher Amine Numbers provide for an increase in resistance to shampooing (see for instance sample AG resisting more than 100 cycles).

A second trend concerns the viscosity of the elastomers. While coloring has been obtained with reactive condensation-curable amino-silicone elastomers having a wide range of pre-curing viscosities (from 30 to 7000 mPa•s), generally the elastomers having a relatively lower viscosity tended to provide a higher resistance to shampoo-induced color fading.

To analyze the above findings, a ratio termed AN/Visc. was defined in which the Amine Number (AN) of the elastomer was divided by its initial viscosity (Visc.), the resulting value being multiplied by 1000. Results of this analysis, values being rounded up, are presented in the following table in which the elastomers are presented in two series, first those being linear (LP), then the branched polymers (BP). In each series, the reactive condensation-curable amino-silicone elastomers are ranked by decreasing value of AN/Visc. ratio.

Sample	**Silicone**	**Amine No.***	**Viscosity (mPa•s)**	**AN/Visc.**	**Shampoo Resist**
AG	KF-857 (LP)	127	65	1954	≥ 130
AD	GP-397 (LP)	116	130	892	≥ 110
AE	GP-657 (LP)	54	120	450	≥ 100
AA	ATM 1322 (LP)	101	250	404	≥ 65
AJ	TSF 4703 (LP)	62	1000	62	≥ 50
AL	TSF 4708 (LP)	38	1000	38	≥ 10
AN	Xiameter® OFX 8822 (LP)	45	1500	30	≈ 20

Sample	Silicone	Amine No.*	Viscosity (mPa•s)	AN/Visc.	Shampoo Resist
AH	Rhodorsil 21642 (LP)	15	1400	11	≥ 10
AM	Xiameter® OFX 8630 (LP)	25	3500	7	≥ 30
AC	GP-145 (LP)	11	1900	6	≈ 18
AK	TSF 4707 (LP)	15	7000	2	≥ 20
AB	GP-34 (LP)	3.3	3500	1	≥ 20
AF	GP-846 (BP)	110	30	3667	≥ 55
AI	SF 1706 (BP)	47	30	1567	≈ 20

Table 3

As can be seen from Table 3, reactive condensation-curable amino-silicone elastomers having a linear structure seem to provide more shampoo resistance than branched counterparts having similar AN/Visc. ratios. However, it should be noted that the number of branched elastomers tested is not sufficiently large to be necessarily representative of the whole class of such polymers.

Similarly, though information on the average MW of the condensation-curable amino-silicones is scarce, it seems that samples prepared from pre-polymers having a relatively lower MW provided for greater shampoo resistance than pre-polymers having a relatively higher MW (hence higher viscosity). See for instance samples, AD and AE prepared from reactive condensation-curable amino-silicones having a MW of about 3,700, which successfully resisted at least 100 shampooing cycles, as compared to samples AB and AC, made of pre-polymers having respective MW of about 33,600 and 18,000, which only withstood approximately twenty shampooing.

Considering now the linear condensation-curable amino-silicone elastomers, it seems that elastomers having an AN/Visc. ratio of up to about 40 can provide semi-permanent coloring (or less if so desired). Elastomers having a higher ratio can provide for permanent coloring (see, for instance, samples AG, AD, AE, AA and AJ). It should be noted that the addition of curing agents (lacking in present example wherein condensation is mainly triggered by humidity) to complete the preparation of the intended coloring compositions is expected to further improve wash resistance (increasing the number of cycles where the OD is not less than 80% of baseline values).

Example 3: Emulsions comprising cross-linkers for coloring keratinous fibers

Materials

Function	**Material Name**	**Supplier**	**CAS No.**
Reactive Amino-silicone Amine Number 110	GP-397	Genesee	68083-19-2
Reactive Amino-silicone Amine Number 127	KF-857	Shin Etsu	
Bis 3-aminopropyl tetramethyldisiloxane Amine Number ~800	GP-967	Genesee	2469-55-8
Cross-linker AminoAlkyl silane	Dynasylan® SIVO 210	Evonik	919-30-2 13497-18-2
Organically modified Polysiloxane	LP X 21879	BYK	
Decamethylcyclopentasiloxane	SID 2650 - D5	Gelest	541-02-6
PolyCarbodiimide	Carbodilite Emulsion E-05	Nisshinbo	
PolyCarbodiimide	V-02B	Nisshinbo	
Ethylsilicate oligomer	Dynasylan® 40	Evonik	
Ethylsilicate oligomer	Ethylsilicate 48	Colcoat	11099-06-2
Surfactant Polyalkylenoxide Castor oil based siloxane	Silube® CO-J208	Siltech	
Surfactant	Tween® 80	Sigma-Aldrich	9005-65-6

Preparation of compositions

Samples BA to BE were prepared as described below.

Sample BA: 8 g of reactive amino-silicone (GP-397) were mixed with 8 g of cross-linker (Dynasylan® SIVO 210, itself containing a mixture of three condensation-curable amino-silicone monomers). The mixture was added to 2 g milled slurry comprising sub-micronic particles of Cromophtal® yellow 3RT with BYK LPX 21879 (at a 1:1 w/w ratio), prepared as described above, and mixed on a Teflon® surface using a painting trowel. The mixture was then homogenized using IKA Ultra Turrax T25 at 25,000 rpm for 30 seconds, to obtain a colored paste. 0.18 g of the colored paste were diluted with 60 g of water. The diluted mixture was then sonicated using Qsonica Sonicator Q700 for 10 seconds at 80% amplitude to obtain a final coloring emulsion.

It is to be noted that Dynasylan® SIVO 210 (having an estimated Amine Number of 370) contains, according to its suppliers, a blend of three monomers: 3-aminopropyl-triethoxysilane (CAS No. 919-30-2, generally present at 25% or more) having an Amine Number of 450, bis(triethoxy-silylpropyl) amine (CAS No. 13497-18-2, generally present at more than 20%) having an Amine Number of 235 and 1-(3-(triethoxysilyl)propyl)-2,2-diethoxi-1-aza-2-silacyclopentane (CAS No. 1184179-50-7, generally present in the range of 1-5%) having an Amine Number of 263. These materials are individually available respectively as Dynasylan® AMEO from Evonik, SIB1824.5 and SIT8187.2 from Gelest and their respective effect can be separately assessed by replacing Dynasylan® SIVO 210 by any one of its constituents.

Sample BB: 6 g of reactive amino-silicone (GP-397) were mixed with 2 g of cross-linker (Dynasylan® SIVO 210) and 2 g of decamethyl cyclopentasiloxane. The mixture was added to 2 g milled slurry comprising sub-micronic particles of Cromophtal® yellow 3RT with BYK LPX 21879 (at a 1:1 w/w ratio), prepared as described above, and mixed on a Teflon® surface using a painting trowel. The mixture was then homogenized as described above, to obtain a colored paste. 0.12 g of the colored paste was diluted with 60 g of water containing 0.06 g Tween® 80. The diluted mixture was shaken manually for a few seconds to obtain a homogenous emulsion. 0.1 g of Carbodilite Emulsion E-05 (cure accelerator) was added, with shaking for 10-15 seconds, to obtain a final coloring emulsion.

Sample BC: 6 g reactive amino-silicone (GP-397) were mixed with 2 g of cross-linker (Dynasylan® SIVO 210) and 2 g of decamethyl cyclopentasiloxane. The mixture was added to 2 g milled slurry comprising sub-micronic particles of Cromophtal® yellow 3RT with BYK LPX 21879 (at a 1:1 w/w ratio), prepared as described above, and mixed on a Teflon® surface using a painting trowel. The mixture was then homogenized as described above, to obtain a colored paste. 0.12 g of the colored paste were diluted with 60 g of water containing 0.06 g Tween® 80. The diluted mixture was shaken manually for a few seconds to obtain a homogenous emulsion. 0.1 g of Carbodilite Emulsion E-05 (cure accelerator) were added, with shaking for 10-15 seconds, to obtain a colored emulsion (emulsion I). In a separate container, 0.02 g of GP-967 cure accelerator were mixed with 6 g of water and shaken until a homogeneous emulsion (emulsion II) was obtained. 6.02 g of emulsion II were added to 60.19 g of emulsion I with shaking for 13-15 seconds, to obtain the final coloring emulsion. In a kit, emulsion I and emulsion II can be provided in separate compartments.

Sample BD: As for sample BB, but with reactive amino-silicone GP-397 (Genesee) replaced by KF-857 (Shin Etsu).

Sample BE: 7 g of reactive amino-silicone (GP-397) were mixed with 3 g milled slurry comprising sub-micronic particles of Cromophtal® yellow 3RT with BYK LPX 21879 (at a 1:2 w/w ratio), prepared as described above, and mixed on a Teflon® surface using a painting trowel. The mixture was then homogenized as described above, to obtain a colored paste. 0.2 g of the colored paste were diluted with 60 g of water. The diluted mixture was then sonicated using Qsonica Sonicator Q700 for 10 seconds at 80% amplitude to obtain a cross-linkable colored emulsion (emulsion I).

In a separate container, 0.1 g of Evonik® Industries ethyl polysilicate cross-linker Dynasylan® 40 were mixed with 6 g of water and 0.06 g of Silube® CO-J208 (a castor oil based siloxane, of Siltech Corporation, Canada, serving as emulsifier) and sonicated for 5 seconds at 30% amplitude to obtain cross-linker emulsion II.

6.02 g of emulsion II and 0.2 g of Carbodilite Emulsion E-05 were added to 60.2 g of emulsion I with shaking for 10-15 seconds, to obtain the final coloring emulsion. In a kit, cross-linkable emulsion I and cross-linking emulsion II can be provided in separate compartments.

Sample BF: 8 g of reactive amino-silicone (GP-397) were mixed with 2 g milled slurry comprising sub-micronic particles of Cromophtal® yellow 3RT with BYK LPX 21879 (at a 1:1 w/w ratio), prepared as described above, and mixed on a Teflon® surface using a painting trowel. The mixture was then homogenized as described above, to obtain a colored paste. 0.1 g of the colored paste were diluted with 60 g of water. The diluted mixture was then sonicated using Qsonica Sonicator Q700 for 10 seconds at 80% amplitude to obtain a cross-linkable colored emulsion (emulsion I).

In a separate container, 0.05 g of Evonik® Industries cross-linker Dynasylan® 40 and 0.05 g of Colcoat cross-linker Ethylsilicate 48 were mixed with 6 g of water and 0.06 g of Silube® CO-J208 (a castor oil based siloxane, of Siltech Corporation, Canada, serving as emulsifier) and sonicated for 5 seconds at 30% amplitude to obtain cross-linker emulsion II.

6.16 g of emulsion II and 0.2 g of “Carbodilite L” (Carbodilite L is a blend of 40g carbodilite V-02B, 3g BYK LPX 21879, 60g Water) were added to 60.1 g of emulsion I with shaking for 10-15 seconds, to obtain the final coloring emulsion. In a kit, cross-linkable emulsion I and cross-linking emulsion II can be provided in separate compartments.

Coating of keratinous fibers with amino-silicone emulsions

Coated samples were prepared by immersing tufts of untreated yak hair (2.5 g per tuft) in one of compositions BA to BF, respectively, for 45 seconds at ambient temperature, with gentle stirring. The samples were subsequently rinsed thoroughly in tap water at about 40°C, then dried for 30 seconds with a Philips compact hair dryer.

The resulting colored sample BA was observed to be glossy; sample BB was glossy, not sticky, and left no color residue on the fingertips after contact; sample BC and BD were glossy, not sticky, totally dry, and left no color residue on the fingertips after contact; sample BE was not sticky, and left no color residue on the fingertips after contact; sample BF was not sticky, totally dry and left no color residue on the fingertips after contact.

The colored sample was kept at ambient temperature for three weeks (sample BA) or one week (samples BB, BE); or for 3 days at 60°C (samples BC, BD), then color fade was studied as previously described, by measuring after every 5 cycles the OD of each of the samples following various numbers of standard shampooing and drying treatments, which were performed up to 100 times (sample BA) or 50 times (samples BB, BC, BD, BE).

Results were analyzed as above, expressed as percentage of baseline OD, which was calculated for each sample. The number of shampoos each sample could withstand before undergoing a visible change in color (as confirmed by a measured OD smaller than 80% of baseline OD) is reported below.

Results

An OD of at least 80% of was retained by sample BA for up to about 70 washes; for samples BB, BC, BE for at least 40 washes; for sample BD for at least 50 washes.

As the results obtained, for instance, with samples BB and BD indicated that condensation-curable amino-silicone pre-polymer GP-397 (Genesee) can be replaced by KF-857 (Shin Etsu), further experiments were conducted suggesting that GP-397 can additionally be replaced by GP-657 and GP-145 (also of Genesee) to prepare compositions having similar desired effects.

Example 4: Coloring of dark-colored keratinous fibers

Materials

Aryl modified polydimethylsiloxane (Siltech® E-2154, Siltech Corporation, Canada)

Reactive amino-functional polydimethylsiloxane (Wacker Finish WR 1100, Wacker Chemie AG, Germany)

Sodium dodecyl benzenesulfonate (Sigma-Aldrich Co. USA, Cat. No. 28,995-7)

Mica flakes (Pyrisma T30-20 Color Space Yellow, Merck, Germany)

Pentaerythritol tetraacylate (Sigma-Aldrich Co. USA, Cat. No. 408263)

Dynasylan® Hydrosil 2926 (Evonik® Industries AG, Germany)

Triethanolamine (Sigma-Aldrich Co. USA, Cat. No. 90279)

Isopropanol (Sigma-Aldrich Co. USA, Cat. No. W292912)

Aluminum silica coated pigments, Powdal 2900 (Schlenk, Germany)

Vacuum metallized passivated aluminum flake pigments AQ-4172 PA (Silberline, Germany)

Lithoflex® XA 40 01 Rich gold; Lithoflex® XA 40 02 Rich pale gold; and Lithoflex® XA 40 03 pale gold (Eckart, Germany)

Metallic flakes of Rich gold Bronze 12K and Aluminum 6150 (Manfong Fujian, China)

Equipment

Centrifuge: Z383 high speed, high capacity centrifuge (Labnet International Inc., USA)

Vortex: Vortex Genius 3 (IKA, Germany)

In previous examples, the hair color was modified from a lighter shade (*e.g.*, yak white body hair) to a darker shade. Therefore the coloring treatment could be directly applied to the keratinous fibers without requiring any pre-treatment aimed to first reduce or eliminate the original color. As mentioned, in conventional hair coloring such pre-treatment involves penetration of bleaching chemicals into the hair shaft, a method negatively renowned for the resulting damage to the hair and the associated health concerns.

In the following, an alternative method and composition are proposed for the pre-treatment of hair achieving a similar effect of masking or reducing the visibility of an original relatively dark shade. While this method can also be applied to light shaded keratinous fibers, it is not essential when the desired end coloring is darker than the original color.

Coating of dark keratinous fibers by aluminum flakes

Composition H was prepared, comprising passivated thin film aluminum flakes and a diluent, wherein the weight of components in grams is presented in Table 4:

Component	Function	Weight (g)
AQ-4172 PA 20% Aluminum pigment suspension in isopropanol	Aluminum pigment	5
(3-Glycidyloxypropyl) trimethoxysilane, GLYMO	Cross-linker	1
99.9% Ethanol ABS AR anhydrous solution	Diluent	94

Table 4

Composition H was prepared as follows: 1 g of (3-Glycidyloxypropyl)trimethoxysilane (GLYMO) was added to 5 g vacuum metallized passivated aluminum flake pigments AQ-4172 PA under vigorous stirring in ethanol. The excess GLYMO silane was then removed by 3 centrifugation cycles with ethanol, using Z383 high speed, high capacity centrifuge (Labnet International Inc., USA) at 5000 RPM for 10 minutes. This process resulted in the coating of aluminum flake pigment with GLYMO silane.

Coloring composition I was prepared by re-suspending the GLYMO silane coated aluminum flakes of coloring composition H in ethanol to obtain a 20% aluminum pigment dispersion in ethanol.

Coloring compositions J and K were prepared, wherein the weight of components in grams is presented in Table 5:

Component	Function	Composition	
		J	K
AQ-4172 PA 20% Aluminum pigment in isopropanol	Aluminum pigment	1.5	
Composition I: 20% Aluminum GLYMO coated pigment in ethanol	Aluminum pigment		1.5
Amino-silicone GP-397	Reactive terminal amino functional silicone polymer	0.5	0.5
98% hexamethyldisiloxane	Diluent	3	3

Table 5

Coated samples J and K were prepared by immersing tufts of untreated Chinese dark human hair (2.5 grams per tuft) in compositions J and K, respectively, as described above for coating of yak hair.

Magnified images of the Chinese natural hair tufts coated with aluminum pigments were recorded using an Olympus® LEXT OLS4100 confocal laser scanning microscope, following 0, 2, 4, 10, 20, 30, 40, 50, 60, 70, 80 and 90 standard shampooing treatments using Shea Natural Keratin Shampoo and drying with a Philips Compact Hair Dryer.

Aluminum flake pigments blended with amino-silicone were found to completely coat dark hair. Due to their thickness (~50nm-100nm) and average longest dimension in the range of 2-20 μm, the vacuum metalized aluminum pigment were found to conform well to the shape of a hair surface, as confirmed by microscope analysis.

Confocal laser scanning microscope images of Chinese human hair coated with composition J are shown in FIGs. 3A to 3F, where panels A-C display coated fibers prior to washing (0) and panels D-F similar fibers after 30 washing and drying treatments, at which time the reduction in the extent of coating became detectable to the naked eye. FIGs. 3A and 3D images were captured at x20 magnification, FIGs. 3B and 3E at x50 and FIGs. 3C and 3F at x100. While all hair coatings may include a small amount of uncoated spots each having small surfaces undetectable taken as a whole on the macroscopic level (see FIGs. 3A-3C), the amount of such clearings and their areas can increase with each shampoo until they reach a number and/or overall uncoated surface (see FIGs. 3D-3F) which becomes macroscopically detectable (*e.g.*, to the naked eye) and detrimental to the desired coloring effect.

While for clarity these pictures show the coated patterns of relatively large metallic flake pigments, similar phenomena can be observed with fibers coated with pigments of sub-micronic size. Such images clearly illustrate the good correlation between the visual assessment of the hair color and reduction thereof after any predetermined number of shampoos, the measured OD (a decrease below 80% being detectable by the naked eye) and the microscopic analysis of hair fibers underlying such observations.

Coating of dark hair with interference pigment

Curable polymer-based primer composition L, an aqueous silicone emulsion comprising alkoxy silane and aminoethyl aminopropyl groups, as shown in Table 6, was prepared as follows. 6 g of Siltech® E-2154 (aryl-modified polydimethylsiloxane emulsion (50% in water)), 2 g of Wacker Finish WR 1100 (reactive amino-functional polydimethylsiloxane) and

250 mg of 20% w/w sodium dodecyl benzenesulfonate were mixed for about 30 seconds using a vortex. 4 g of mica flakes were added followed by an additional period of 30 seconds of mixing by vortex to obtain a milky suspension.

Component	**Percentage of final composition (w/w)**
Aryl modified polydimethylsiloxane emulsion 50% in water	49
Reactive aminoethylaminopropyl functional polydimethylsiloxane	16
20wt.% sodium dodecyl benzenesulfonate in water	2
Mica flakes	33

Table 6

Curable polymer-based coating composition M, as shown in Table 7, was prepared by suspending interference pigments (mica flakes) in an aqueous silicone oligomer capable of forming covalent bonds with primer solution L as follows. 6 g of mica pigment were added to 6 g of 1% w/w pentaerythritol tetraacylate in acetone and the suspension mixed for about 30 seconds using a vortex then allowed to evaporate for about 30 minutes in a chemical hood at ambient temperature to obtain a dry powder. 8 g Dynasylan® Hydrosil 2926 and 150 mg triethanolamine were then added to the dry powder and mixed for about 30 seconds by vortex.

Component	**Percentage of final composition (w/w)**
Mica flakes	43
Dynasylan® Hydrosil 2926	56
Triethanolamine	1

Table 7

Untreated tufts of European natural black hair were immersed in composition L for about 2 minutes at ambient temperature. The samples were subsequently rinsed thoroughly in tap water preheated to a temperature in the range of 35-40°C. The wet tufts were immersed for about 3 minutes in composition M, then removed from the composition and dried with a Philips compact hairdryer. Unless otherwise stated, each composition was applied to at least three tufts of hair.

Coating of dark hair with metal pigment

Curable polymer-based primer composition N, an aqueous silicone emulsion comprising alkoxy silane and aminoethyl aminopropyl groups, as shown in Table 8, was prepared as follows: 6 g of Siltech® E-2154 (aryl-modified polydimethylsiloxane emulsion (50% in water)), 2 g of Wacker Finish WR 1100 (reactive amino-functional polydimethylsiloxane) and 250 mg of 20wt.% sodium dodecyl benzenesulfonate in water were mixed for about 30 seconds using a vortex.

Component	**Percentage of final composition (w/w)**
Aryl modified polydimethylsiloxane emulsion 50% in water	75
Reactive aminoethylaminopropyl functional polydimethylsiloxane	25

Table 8

Curable polymer-based coating composition O, as shown in Table 9, was prepared by suspending metal flakes in an aqueous silicone oligomer capable of forming covalent bonds with primer solution N, was prepared as follows: 0.7 g Bronze Rich gold 12K, 8 g Dynasylan® Hydrosil 2926 and 150 mg NaOH 1N were mixed with 0.5 g isopropanol and mixed for about 30 seconds by vortex.

Component	**Percentage of final composition (w/w)**
Rich gold bronze	7.5
Isopropanol	5
Dynasylan® Hydrosil 2926	86
NaOH 1 N	1.5

Table 9

Untreated tufts of European natural black hair were immersed in composition N for about 2 minutes at ambient temperature. The samples were subsequently rinsed thoroughly in tap water preheated to a temperature in the range of 35-40°C. The wet tufts were immersed for about 3 minutes in composition O, then removed from the composition and dried with a Philips compact hairdryer. Unless otherwise stated, each composition was applied to at least three tufts of hair.

Interference pigments were found to add a layer having a thickness of about 0.5 µm to each hair fiber, while metal flakes added a layer having a thickness of up to 0.1 µm. Such increases are considered acceptable, and possibly even desirable. In view of their relatively greater thickness, the interference pigments behaved more rigidly than the relatively more flexible other "non-interference" metallic pigments. Hence, the ability of interference pigments to conform to the outer surface of fibers is expected to be relatively lower.

Example 5: Removal of cured coating compositions from keratinous fibers

Materials

Tetra butyl ammonium fluoride (TBAF) 75% (Sigma-Aldrich Co., USA, Cat. No. 361399)

N-Octyl pyrrolidone (NOP) (Sigma-Aldrich Co., USA, Cat. No. 332186)

4-Dodecyl benzene sulfonic acid (DBSA) (Sigma-Aldrich Co., USA, Cat. No. 44198)

Tetrabutylammonium hydroxide pentahydrate (TBAH) 95% (Sigma-Aldrich Co., USA, Cat. No. 87741)

Isopropanol (Sigma-Aldrich Co., USA, Cat. No. Cat. W292912)

Dodecane (Sigma-Aldrich Co., USA, Cat. No. D221104)

Hexamethyl disiloxane (HMDS) (Gelest Inc., USA)

Equipment

Heraeus oven, UT 12 (Thermo Scientific, USA)

Unimax 1010 Digital Orbital Shaker (Heidolph, Germany)

LEXT OLS4100 confocal laser scanning microscope (Olympus Corporation, Japan)

Compact hair dryer (Philips, The Netherlands)

Methods

Coating compositions

The following coating compositions were prepared using 1.3% w/w pigment, 1.3% w/w 2-ethylhexanoic acid, 10% w/w amino-silicone GP-397 and about 87% w/w HMDS:

Yellow coating, using yellow pigment P.Y. 83 (Cappelle Pigments NV, Belgium)

Green coating, using Heliogen® Green K8730 pigment (BASF, Germany)

Red coating, using Irgazin® Magenta 2012 pigment (BASF, Germany)

Blue coating, using Hostaperm Blue 15:3 (Clariant Int.)

Silver coating, using vacuum metallized passivated aluminum flake pigments AQ-4172 PA (Silberline Germany).

Coating protocol

Coated samples of yak hair A, B, C and J (using green, yellow, magenta and silver coloring compositions, respectively) were prepared as described above. In addition, tufts of yak hair which were further bleached prior to coating with yellow coloring composition were prepared.

The samples were subsequently rinsed thoroughly in tap water at ambient temperature and then transferred to a Heraeus oven, UT 12 for 7 days at 60°C and 95%RH, to cure the reactive polyaminosiloxane (*e.g.*, by cross linking).

Removal of coloring composition

Three types of coloring removal solutions were prepared by dissolving the active ingredient in an appropriate solvent:

A) Organic fluoride salt (tetrabutyl ammonium fluoride (TBAF)) as active agent, at a concentration of 0.25%, 0.5%, 1% or 2% (w/w) in dipolar aprotic solvent (N-octyl-pyrrolidone (NOP)),

B) Acidic active agent (dodecyl benzene sulfonic acid (DBSA)) at a concentration of 0.5%, 1%, 2% or 4% (w/w) in non-protic solvent (dodecane);

C) Basic active agent (tetrabutyl ammonium hydroxide (TBAH)) at a concentration of 1%, 2% or 4% (w/w) in protic solvent (isopropanol).

Coated samples were immersed in the coloring removal solutions of the example and maintained under slow orbital shaking (50 rpm) at ambient temperature. Samples were removed from coloring removal solutions after a period of time (immersion time) as specified in Table 8 below, and either not subjected to shampoo or subjected to a single standard shampooing treatment with Shea Natural Keratin Shampoo, as specified in Table 8. Samples were then dried with a Philips compact hair dryer at 60-80°C.

Evaluation of colorant removal was based on visual inspection and by use of Confocal Laser Scanning Microscope (Olympus® LEXT OLS4100).

Results

Results are presented in Tables 8 to 11 below and in FIGs. 4D to 4F. In the tables, ++ indicates complete removal of coloring composition, + indicates partial removal and – indicates no visible change, a single asterisk indicating that such findings result from visual observations with a naked eye and two asterisks indicating that such visual findings were confirmed by laser scanning microscopy).

Table 10 and FIGs. 4D and 4F present results obtained for unbleached samples colored by pigment Hostaperm Blue 15:3 after immersion in coloring removal solutions comprising TBAF or DBSA for different immersion times. FIG. 4C shows a fiber colored with same pigment before the removal procedures.

Active ingredient wt.%	**Solvent**	**No. of shampoos**	**Immersion time**	**Results**
TBAF 2%	NOP	0	5 mins	++**
TBAF 1%	NOP	0	5 mins	++**
TBAF 0.5%	NOP	0	30 mins	++**
TBAF 0.125%	NOP	1	30 mins	-**
DBSA 4%	Dodecane	1	10 mins	++**
DBSA 2%	Dodecane	1	10 mins	++**
DBSA 1%	Dodecane	1	20 mins	+*
DBSA 0.5%	Dodecane	1	20 mins	-**

Table 10

As shown in Table 10, complete removal of coloring composition was achieved with an immersion time of 5 minutes in coloring removal solutions comprising at least 1wt.% TBAF solution, while 30 minutes immersion time was required for complete removal in solutions comprising 0.5wt.% TBAF. No observable visible changes were detected with solutions comprising only 0.125wt.% TBAF, even after 30 minutes immersion time and even with the mechanical rubbing a shampoo would additionally supply to facilitate the removal.

For coloring removal solutions comprising DBSA, complete removal of coloring composition was achieved with an immersion time of 10 minutes in solutions comprising at least 2wt.% DBSA. A coloring removal solution comprising 1wt.% DBSA provided partial removal even after 20 minutes immersion time followed by a shampoo. No observable visible changes were detected with solutions comprising 0.5wt.% DBSA, even after 20 minutes immersion time followed by a shampoo.

Table 11 presents results obtained for samples which were bleached prior to coloring with pigment yellow (P.Y. 83) after immersion in coloring removal solutions comprising TBAF, DBSA or TBAH for different immersion times.

Active ingredient wt.%	**Solvent**	**No. of shampoos**	**Immersion time**	**Results**
TBAF 2%	NOP	0	5 mins	++**
TBAF 1%	NOP	0	5 mins	++**
TBAF 0.5%	NOP	1	10 mins	+*
TBAF 0.25%	NOP	1	10 mins	+*
TBAF 0.125%	NOP	1	30 mins	-**
DBSA 4%	Dodecane	1	10 mins	++**
DBSA 2%	Dodecane	1	10 mins	++**
DBSA 1%	Dodecane	1	20 mins	+*
DBSA 0.5%	Dodecane	1	20 mins	-**
TBAH 4%	Isopropanol	1	20 mins	++**
TBAH 4%	Isopropanol	1	10 mins	+*
TBAH 2%	Isopropanol	1	20 mins	+*
TBAH 2%	Isopropanol	1	10 mins	-**
TBAH 1%	Isopropanol	1	20 mins	-**

Table 11

As shown in Table 11, results obtained with yak hair which was bleached prior to coloring were similar to those obtained with unbleached, colored yak hair. Complete removal of color was achieved with an immersion time of 5 minutes in coloring removal solutions comprising at least 1wt.% TBAF. No observable visible changes were detected with solutions comprising 0.125wt.% TBAF, even after 30 minutes immersion time.

For coloring removal solutions comprising DBSA, complete removal of coloring composition was achieved with an immersion time of 10 minutes in solutions comprising at least 2wt.% DBSA. No observable visible changes were detected with solutions comprising 0.5wt.% DBSA, even after 20 minutes immersion time.

For solutions comprising TBAH, complete removal of coloring composition was achieved with an immersion time of 20 minutes with solutions comprising 4wt.% TBAH.

Tables 12 and 13 present results obtained for samples colored with green, red and silver pigments, following treatment with coloring composition removal solution, wherein the samples were removed from coloring removal solution after 20 minutes (Table 12) and after 5 minutes (Table 13).

Active ingredient wt.%	**Removal solvent**	**Sample**		
		Green (A)	Red (C)	Silver (J)
2% TBAF	NOP	++	++	++
1% TBAF	NOP	++	++	++
0.5% TBAF	NOP	++	++	++
4% DBSA	Dodecane	++	++	++
2% DBSA	Dodecane	+	++	+

Table 12

Active ingredient wt.%	**Removal solvent**	**Sample**		
		Green (A)	Red (C)	Silver (J)
2% TBAF	NOP	++	++	++
1% TBAF	NOP	+	++	++
4% DBSA	Dodecane	++	++	++
2% DBSA	Dodecane	+	+	++

Table 13

As shown in Table 12, after 20 minutes in coloring composition removal solution, complete removal of coloring composition was seen from all samples tested with each of the solutions of TBAF used. Complete removal of coloring composition was also seen from all samples tested with 4% DBSA solution and from sample C with 2% DBSA. Partial removal of coloring composition was seen from samples A and J with 2% DBSA solution.

As shown in Table 13, after 5 minutes in 2% TBAF solution, complete removal of coloring composition was seen from all samples tested. After 5 minutes in 1% TBAF solution, complete removal of coloring composition was seen from samples C and J, and partial removal was seen from sample A. After 5 minutes in 4% DBSA solution, complete removal of coloring composition was seen from all samples tested. After 5 minutes in 2% DBSA solution, complete removal of coloring composition was seen from sample J and partial removal from samples A and C.

FIG. 4 shows x100 magnification confocal laser scanning images of (C) uncoated yak hair, (D) yak hair coated with a coloring composition (sub-micronic Hostaperm Blue 15:3), (E) the hair as shown in (D) followed by treatment with a coloring removal solution comprising TBAF or (F) with a coloring removal solution comprising DBSA.

FIG. 4A is a schematic illustration of the external surface of a native hair fiber displaying hair scales; such as appearing in the uncoated sample shown in FIG. 4C and in the decolored samples shown in FIGs. 4E and 4F.

FIG. 4B is a schematic illustration of the external surface of a hair fiber coated with sub-micronic pigments or with pigment flakes; such as appearing in the colored pigment coated sample shown in FIG. 4D.

As seen in FIGs. 4D-4F virtually no scale lifting or crumbling of the cuticle scale edges was observed as compared to the uncoated hair. Clean cuticle edges were seen after complete removal of the pigment.

Similar decoloring experiments were successfully performed using an alternative fluoride salt, namely RonaCare® Olaflur by Merck KGaA, and the following combinations of decuring agents or resulting in a decuring agent: (TBAB+KOH), (TBAC+KOH) and (Luviquat® Mono CP AT1+$Mg(OH)_2$). Luviquat® Mono CP AT1 is an organic phosphate salt purchased from BASF Care Solutions which was shown to form a suitable decuring agent in combination with inorganic base magnesium hydroxide.

The following solvents were also tested and found suitable: methyl isobutyl ketone (MIBK), methyl phenyl ester (MPE), Propionitrile, Tert-butyl alcohol, tetrahydrofuran (THF), Toluene and Xylene. Detailed results are not shown, but a successful decoloring with these additional decuring agents and/or solvents and mixtures thereof means that the colored coat was removed within less than 30 minutes (typically within 5-10 min) with concentrations of decuring agents of less than 15wt.%, generally between 1 wt.% and 10 wt.%.

Furthermore, representative decoloring solutions were supplemented with thickening agents to form creamy preparations that were as efficient as their respective “unthickened” controls. The thickening agents tested in the present study included glyceryl tristearate, an hydroxypropyl methylcellulose (Benecel™ K200M by Ashland), a fluoropolymer (Zonyl® MP1300 by DuPont), a modified polypropylene wax (Micropro 600VF by Micro Powders) and a micronized polyethylene (Micropoly® 220L by Micro Powders). All successfully yielded thickened formulations at concentrations in the range of 0.5wt.% (for Benecel™ K200M) up to 40wt.% (for Micropoly® 220L) by weight of the decoloring cream.

<u>Example 6: Effect of cationic shampoos following coloring of keratinous fibers</u>

Cationic shampoo consisting of 3% (w/w) aqueous solution of cationic guar was prepared by adding 30 g cationic guar (N-Hance BF 17, Ashland Inc., USA) to 970 g water, with stirring using a magnetic stirrer for 1 hour until the guar was fully dissolved. The pH of the solution was measured and found to be 5.0.

Samples of yak white body hair were colored with composition AD as defined in Table 2, Example 2, above.

The initial OD (0 shampoos) following application of the coloring composition was measured after 1 hour at ambient temperature, as described above.

Sample hair tufts were wetted with water and a few drops of shampoo applied. The hair tuft was massaged gently 4 times with the shampoo. The hair tufts were subsequently rinsed thoroughly in tap water at about 40°C, then dried for 30 seconds with a Philips compact hair dryer. The process was repeated, and the OD measured after every 5 shampoos, for 15 shampoos. Results are presented in Table 14.

No. of Shampoos	OD	% variation
0	1.116	0.0
5	1.110	0.5
10	1.100	1.4
15	1.100	1.4
20	1.106	0.9

Table 14

As shown in Table 14, almost no variation in optical density was seen after 20 washes with a cationic shampoo. For comparison, washing with an anionic shampoo or non-ionic shampoo during the same initial period of time following coloring, while the amino-silicone has not yet fully cure, proved deleterious to the stability of the coat on fibers. Namely, the OD monitored after washing with such non-cationic shampoos dramatically decreased after only a few washes (*i.e.* the OD dropped below 80% of baseline in no more than 3 washes).

A commercially available shampoo (TRESemmé Perfectly (un)Done cationic shampoo) was found to provide similar results and was used in additional experiments where rinsing with a cationic shampoo was desired.

Example 7: Differential Scanning Calorimetry (DSC) study

Coloring composition

8 g of reactive amino-silicone (GP-397, Genesee) were added to 2 g of milled slurry comprising sub-micronic pigment particles of Cromophtal® Yellow 3RT with BYK LPX 21879 as dispersant, prepared as described above, and mixed on a Teflon® surface using a painting trowel. The mixture was then homogenized using IKA Ultra Turrax T25 at 25,000 RPM for 30 seconds, to obtain a colored paste. 0.2 g of the colored paste were diluted with 60 g of distilled water. The diluted mixture was then sonicated using Qsonica Sonicator Q700 for 10 seconds at 80% amplitude to obtain a colored emulsion.

Coating of keratinous fibers

Coated sample was prepared by immersing tufts of untreated Chinese black hair (2.5 g per tuft), for 45 seconds at ambient temperature, with gentle stirring. The sample was subsequently rinsed thoroughly in tap water at about 40°C, then dried for 30 seconds with a Philips compact hair dryer.

Three days after the coloring, the hair was cut into small pieces (about 2 mm long) using regular scissors. For each measurement, about 10 mg of hair pieces were placed in a 100 µl aluminum DSC crucible. Distilled water was added to fill the crucible using a pipette. The crucible was sealed and allowed to stand for 12 hours at room temperature.

The ON moisture equilibrated samples were placed in a Differential Scanning Calorimeter DSC Q200 (TA Instruments, USA) and DSC measurements were carried out. Specifically, the samples were first heated to and maintained at 80°C for 5 minutes to allow thermal equilibration. Then, while data acquisition and storage were activated, the samples were heated to 300°C at a rate of 20°C/min.

The stored data was then used to obtain a DSC curve for the sample. The DSC curve of each sample was compared to a reference DSC curve obtained in the same way for uncolored Chinese black hair from the same hair batch. An additional sample was first colored as described, then decolored as above-detailed with 2% TBAF. All samples displayed similar patterns in the DSC curve. Therefore, it may be concluded that the coloring process as described herein, as well as the coloring removal one, maintains integrity of the hair. For comparison, hair colored by a conventional oxidative chemistry resulted in a significant shift in the DSC pattern, as compared to the uncolored reference.

Example 8: Elemental analysis of coated hair

Analysis of hair samples coated by the present method using scanning electron microscope (SEM) Energy-dispersive X-ray spectroscopy (EDS) revealed in addition to carbon, oxygen and nitrogen, an appreciable percentage of silicone atom (typically >10% by weight of all elements) attributed to the amino-silicone elastomer coating the hair fibers and attached thereto. Analysis was performed on a Crossbeam 340 ZEISS/Gemini SEM microscope under the following experimental conditions: energy 5KV; Apertures 120; working distance 5mm. The results reported below are average of at least 4 repeats.

A first control of native / uncoated European hair revealed, as expected, an absence of silicone signal with baseline value of 0.2%. A sample of the same hair colored according to the present teachings indicated the presence of about 18% of silicone. These results demonstrate that the presence of a silicone film on hair coated according to the present teachings can be detected by SEM-EDS.

The person skilled in the art of chemical analysis can readily appreciate that additional techniques may allow similar detection of features characterizing the polymers of the coating compositions. Mass spectrometry techniques, in particular soft ionization technique such as matrix-assisted laser desorption time-of flight mass spectrometry (MALDI-ToF-MS) may additionally provide unique information related to polymer end-groups and branching structure, as well as establishing the molecular mass distribution of the studied materials.

Example 9: Coloring with combinations of emulsions

In previous examples, coloring of hair samples was performed using a single composition of condensation-curable amino-silicone pre-polymers comprising pigment particles of a unique shade. In the present study, such coloring emulsions are considered and used as the “primary colors” (*e.g.*, yellow, red, blue, black) of a color palette. In other words, two or more pigmented emulsions of amino-silicone pre-polymers, each providing for a different primary color are combined so as to provide a wider range of coloring options.

The condensation-curable amino-silicone emulsions were prepared as described for sample BC of Example 3, with three different sub-micronized pigments: Hostaperm® Blue B2G and Hansa Yellow 10G, both by Clariant, and Paliotol® Yellow D 1155, by BASF. The combinations of the formulations, each comprising a distinct pigment, so prepared are presented in Table 15. The combinations are described in weight percent of each pigmented emulsion per the total weight of the combination.

Combination No.	Hostaperm® Blue B2G	Hansa Yellow 10G	Paliotol® Yellow D1155
1	50wt.%	50wt.%	0wt.%
2	75wt.%	25wt.%	0wt.%
3	25wt.%	75wt.%	0wt.%
4	50wt.%	0wt.%	50wt.%
5	75wt.%	0wt.%	25wt.%

Table 15

All combinations of the individual emulsions, prepared as detailed in Example 3, resulted in coloring compositions having different greenish shades. Yak hair tufts were dipped in each of the greeny emulsions for 45 seconds while gently stirring. The hair sample were then washed with tap water at about 37°C and dried with a hair dryer, yielding a variety of green colored hair.

These results support the suitability of the present compositions to serve in hair coloring methods wherein the end-color can be personally customized for each subject, in a manner comparable to the multitude of end-colors in a digitally printed ink image which results from a limited number of initial colors.

Example 10: Repeated coatings

In previous examples, coloring of hair samples was performed using a single application of one or more compositions of condensation-curable amino-silicone pre-polymers, each comprising pigment particles of one or more colors. Such experiments resulted in the formation of a single amino-silicone film upon the coated hair. In the present study, similar coloring steps are repeated, the emulsions of the first and second repeat each providing for a separate amino-silicone film. While the pigments used during a repeat coloring can provide for the same color (*e.g.*, so as to modify its intensity), different colors were used in the present example for each repeat, so as to facilitate the demonstration.

Yak hair was coated with a first condensation-curable amino-silicone emulsion prepared substantially as described for sample BA of Example 3. This first emulsion was prepared using a colored paste comprising 50wt.% GP-397, ~16.7wt.% Dynasylan® SIVO-210, ~16.7wt.% decamethyl cyclopentasiloxane (D5), ~8.3wt.% Paliotol® Yellow 1155 (BASF) and ~8.3wt.% BYK LPX 21879, the paste being emulsified prior to coloring in distilled water including Tween® 80 and Carbodilite Emulsion E-05, as previously detailed.

The hair sample was dipped in the yellow color emulsion for 45 seconds while gently stirring. The sample was then washed with tap water at ambient temperature and dried with a hair dryer, yielding yellow colored hair. The colored hair sample was assessed using a spectrophotometer (X-Rite 939, of X-Rite Inc., USA) able to translate a color into three variables plotted along the three axis of a standardized color space known as CIE L*a*b*. The illumination used was D65 and the standard observer was set at 10°. The L*a*b* values of the dried yellow colored hair were found to be: 77.00, -6.60, and 60.47, respectively.

A second emulsion was similarly prepared wherein Paliotol® Yellow 1155 (BASF) was replaced by PV Fast Orange H2GLS (Clariant). The dry hair sample, already colored in yellow by the first emulsion, was dipped in the orange color emulsion for 45 seconds while gently stirring. The sample was then washed with tap water at ambient temperature and dried with a hair dryer, yielding orange colored hair. The L*a*b* values of the dried now orange colored hair were found to be: 63.03, 31.88, and 62.87, respectively.

These results support the suitability of the present method to apply more than one film of amino-silicone on the hair fiber. This can be used to modulate the intensity of a shade of a first coat and/or to change the final color. This may prove advantageous if the subject coloring his/her hair wishes more flexibility with respect to the desired end-color, being able to modulate the “intermediate” results obtained from a first coating by a second coating. Moreover, it may permit selectively coating different portions of a multitude of hair fiber with different colors.

Example 11: Removal of repeated coatings

In the present example, the removal protocol was applied on hair fibers previously coated in two coloring steps, each step having resulted in a distinct amino-silicone film providing for a different color.

Yak hair was repeatedly coated, first with a condensation-curable amino-silicone emulsion comprising a yellow pigment and secondly with a similar coat comprising an orange pigment, as described in Example 10. Three types of coloring removal solutions were prepared by dissolving representative decuring agents in exemplary solvents, to yield the following:

A) 2wt.% TBAF in N-octyl-pyrrolidone (NOP), representing a fluoride salt in a dipolar aprotic solvent;

B) 4wt.% DBSA in dodecane, representing an acidic decuring agent in a non-protic solvent; and

C) 4wt.% TBAH in Tert-butyl alcohol, representing a basic decuring agent in a protic solvent.

The colored hair tufts were placed in a mixing bowl and covered with about 5 ml of the coloring removal solutions. The tufts were thoroughly brushed with the aid of a dye brush with the removal solution to ensure their complete coverage thereby. Samples were taken out of the coloring removal solutions after 5 minutes rinsed thoroughly with tap water at about 35-40^{0}C. The samples were subjected to a single standard shampooing treatment with Shea natural keratin shampoo (Gilam Cosmetics Ltd., Israel) and dried for approximately 30 seconds with a hair dryer. The efficacy of the removal of the double-coat was assessed by visual inspection of the dried hair tufts. All tested removal solutions were found efficacious within 5 minutes, suggesting that the removal solutions as herein disclosed as not particularly limited to single film coated fibers.

Example 12: Coloring form

While in previous examples, the coloring or coating compositions, also simply referred to as the amino-silicone emulsions, generally displayed prior to curing a relatively low viscosity comparable to water, the present study demonstrates the ability to prepare similar compositions, but at an elevated viscosity. Such gel-like formulations are believed to have a longer contacting time with the hair to be coated than their non-thickened counterparts.

An amino-silicone blend was prepared by mixing condensation-curable amino-silicone monomers of Dynasylan® Sivo 210 (73wt.%) with amino-silicone oils (GP-967 and GP-965, respectively at 20wt.% and 7wt.% of the total blend). 0.2 g of this first blend were added to 60 ml of aqueous forms. In a first reference sample, the amino-silicone blend (ASB) was added to plain distilled water. In additional samples, the water carrier was first supplemented with thickening agents, the ASB being subsequently added to an aqueous carrier having a gel form. A first thickened aqueous carrier was prepared by adding 0.5wt.% Polyquaternium 7 (PQ-7) and 0.1wt.% Polyquaternium 10 (PQ-10), per weight of distilled water. The Polyquaternium nomenclature is as assigned by the Cosmetic, Toiletry and Fragrance Association (CTFA) to most cationic conditioning polymers. PQ-7 is a poly(acrylamide-co-diallyl-dimethylammonium chloride) copolymer and PQ-10 is a quaternized hydroxyethyl cellulose, both supplied by Dow. A second thickened aqueous carrier was prepared by further adding 0.1wt.% Benecel™ K200 (an hydroxypropyl methylcellulose supplied by Ashland) to previous 0.5wt.% PQ-7 and 0.1wt.% PQ-10. All three samples were manually shaken to obtain three types of amino-silicone emulsions, derived from the same initial blend of materials. The viscosity of the reference sample (ASB in water) and of the thickened samples was measured at 25°C using a HAAKE™ MARS™ III Rheometer with Spindle - C60 at a shear rate of 30 sec^{-1}. While the reference sample had a viscosity of about 0.89 mPa•sec, the thickened counterparts respectively displayed a viscosity of about 20.1 mPa•sec (PQ-7 + PQ-10) and of viscosity of about 56.7 mPa•sec (PQ-7 + PQ-10 + Benecel™ K200M). While for the sake of feasibility testing, the coating compositions were prepared without any coloring agent, it is expected that similar thickening can be obtained in presence of a pigment.

Example 13: Bleach Resistance

It was already demonstrated that hair samples colored according to the present disclosure are resistant to a high number of shampooing cycles, to an extent allowing classifying coloring methods according to some embodiments of the invention as permanent coloring. While shampooing can be considered as a chemical treatment of the hair fibers, it is typically intended to be a gentle one, not significantly damaging the hair, if at all. In the present study colored hair samples were subjected to a harsher chemical treatment, commonly used in the field and feared for the severe damages it causes, namely hair bleaching.

Hair tufts colored with a pigment-embedded amino-silicone emulsion as described herein were tested as follows. First, yak hair tufts were colored with an emulsion prepared substantially as described for sample BC of Example 3, the pigment now being Heliogen Blue D 7079 (BASF). The hair samples were dipped in the blue color emulsion while gently stirring for 45 seconds at ambient temperature. Following the coloration, the hair was washed with tap water and dried as previously detailed. Hair samples were allowed to fully cure before being subjected to the bleaching test.

Reference samples were prepared by coloring yak hair of a same source with a commercially available blue hair coloring product (Midnight Blue, La Riche, UK). The coloring of the reference samples was performed according to manufacturer's instructions, the semi-permanent color being brushed onto the hair and allowed to properly cover the hair fibers for 30 minutes. Following the reference coloration, the hair was washed with tap water and dried as previously detailed.

A bleaching composition was prepared by mixing in a coloring bowl: 20 g of hydrogen peroxide cream (L'Oréal Oxidant Cream (9%)) with 4 ml of a solution of ammonium hydroxide (at 25wt.% concentration). Mixing was conducted with a coloring brush until a homogenous viscous cream was obtained. The bleaching cream was then applied on the hair samples colored according to the invention or using commercially available reference product. Bleaching was allowed to proceed for 30 minutes at room temperature. The bleaching cream was then washed off from the hair samples, which were abundantly rinsed with tap water and dried with a hair dryer.

The OD of the various hair samples before and after bleaching was measured with a spectrophotometer using a cyan filter. The baseline OD for the reference colored by a commercial product was of 1.304, while the baseline OD for the hair samples colored according to the present teachings was of 1.650. The post-bleaching OD of the reference was of 1.048, whereas the post-bleaching OD of the inventive samples was of 1.696. These results first illustrate the strong coloring effect that can be achieved using the present method and compositions, the baseline OD of the inventive sample being about 27% higher than the OD of the commercial reference. Secondly, while the commercial product fails to maintain baseline value following bleaching, the OD of the bleached reference corresponding to about 80% of the unbleached reference, the OD of the hair samples coated with the inventive coloring compositions remained unaffected by this process.

As no visible changes in color are detected in the samples prepared by the present methods, when subjected to bleaching, the coatings formed with the present compositions are deemed suitable to protect the hair from harsh chemical treatment. It is therefore expected that such amino-silicone films can also afford protection of the hair fibers against milder chemical exposure (*e.g.*, low concentrations of disinfecting agents found in swimming pools *etc.*).

Example 14: Hair styling

Hair coated according to the present teachings can undergo further hair styling. Some hair styling processes may constitute a physical stress (*i.e.* heat and strokes of hair ironing), while others are considered to subject the hair to a chemical stress. Hair tufts colored with a pigment-embedded amino-silicone emulsion comprising Paliotol® Yellow D 1155, by BASF, prepared as described in Example 9, were tested as follows.

Hair Ironing

Following the coloration, the hair was washed with a cationic shampoo, rinsed, combed and dried as previously detailed. The dried colored hair tufts were then ironed at 140°C for 10 strokes, using a BaByliss Pro™ ironing machine by BaByliss® Sarl, France. The resulting samples of ironed hair were found to have a straightened appearance, supporting the suitability for hair colored according to the present teachings to undergo further hair styling.

Permanent Curling

Hair samples colored, washed with a cationic shampoo, rinsed, combed and dried as previously detailed, were rolled over a 10 cm diameter roll to imitate professional hair perming rolls. The tip of the hair fibers was adhered to the rod to maintain the curled position of the fibers during the perming procedure which was carried out with a commercially available set (such as, Dulcia Advanced formula enriched with Ionène G, by L'Oréal SA, France). Ten drops of first step Dulcia G 0 perming composition were applied on the rolled hair, so as to fully cover all hair fibers. After 8 minutes of perming, the hair samples (still rolled on the rod) were abundantly rinsed with tap water. Then, 10 ml of second step neutralizing solution, Dulcia Neutraliser, were poured on the still rolled hair samples. Neutralization was allowed to proceed for 10 minutes. The hair samples were then removed from the supporting rod and massaged by hand for about 1 minute. Hair samples were then rinsed with water, shampooed once with Shea natural keratin shampoo and dried.

The permed hair samples displayed a stable curling / waving of the fibers supporting the suitability for hair colored according to the present teachings to undergo further hair styling as conventionally performed.

Example 15: Hair appearance

Hair coated according to the present teachings were generally soft to the touch, displayed a shiny healthy appearance, as well in some instances as a volume improvement, as assessed by trained observers. The volume improvement was assessed against an uncoated reference and is believed to be due to the mild increase in hair diameter as a result of the thin amino-silicone film formed thereon. A film having a thickness of about 0.3-1.0 μm increases the diameter of the fiber by about 0.6-2.0 μm. Assuming an hair fiber having a diameter of about 50-100 μm, such coats provide for a diameter increase of approximately 0.5-5%.

In addition to satisfactory or even improved appearance, the hair samples coated according to the present disclosure were combable (the coating/coloring resulting in smooth individual fibers) and found to behave in this respect in a manner comparable to uncoated controls. Such findings (even made in control compositions devoid of coloring pigments) are notable, since conventional coloring methods generally tend to reduce the natural shine of the hair and/or are likely to weaken the hair fibers. In order to quantify such observations, hair samples coated/colored according to the present teachings can be subjected to the following assessment.

The coated hair samples are mounted and combed on a cylinder to align hair fibers. Shine can be monitored using a Samba hair system, Bossa Nova Technologies, USA, the measurements being collected using a polarized incident light for the identification between specular and diffused light on the cylinder mount on which samples are disposed. The shine parameter is the first reflection that carries the same polarization of the incident light. For each hair sample, including an uncoated control of the same hair type, gloss measurements are taken in at least three different areas of the tuft and averaged. Results are provided in Arbitrary Units (AU) of shine. For reference, changes in 1 AU or less are generally not detectable to the naked eye, while changes in 2 AU or less are considered tolerable for most colors. Advantageously the shine of hair fibers coated according to the present teachings will be stable as long as the coating is not removed from the fibers. The available qualitative results suggest that the present coloring method does not harm the hair fibers, and may even improve their volume.

Example 16: Hair robustness

While conventional coloring methods, especially when a permanent effect is sought, generally damage the hair fiber and are likely to weaken it, reducing its mechanical resilience, hair samples coated according to the present teachings are believed to be at least as resistant as uncoated counterparts. The robustness of the hair was assessed as follows.

The hair samples were coated as described for sample BC of Example 3. Uncoated hair served as control. For each sample, individual hair fibers were tested in an LR X Plus test machine of Ametek Lloyd Instruments to assess the force applied at break point, the fiber being subjected to a load of 20 Newton at a load speed of 1 mm/min. The diameter of each tested fiber was measured using a handheld micrometer. The Force at Break Point (in N) was normalized to the diameter (in mm), and the results of 6 fibers were averaged. The normalized force at breakpoint of native uncoated hair fibers was found to be on average 14.78 with a standard deviation of 2.57. The normalized force at breakpoint of hair fibers coated according to the present teachings was found to be on average 14.20 with a standard deviation of 3.35.

As can be seen from these results, coated and uncoated samples displayed similar behavior as far as resistance to tension and breakpoint force is concerned. This supports that the compositions according to the present teachings do not impair the mechanical properties of the hair, a damage frequently observed when coloration is performed by conventional dye methodology.

Example 17: Amino-silicone compositions including a reactive filler

While in previous examples the cross linkers of the condensation-curable amino-silicone pre-polymers were typically miscible therewith and sometimes even amino-silicone reactants (*e.g.*, amino-silane monomers), in the present study alternative compositions were prepared in which the cross-linkers (*i.e.*, the three-dimensional (3D) network former) of the amino-silicone film included hydrophobic fumed silica, typically surface after treated. The surface treatment of the amorphous fumed silica, when known, consisted of one or more of silicone oils, poly siloxanes, hexamethyl disilazane (HMDS, as available for example under CAS No. 68909-20-6) and amino silanes. The particles of reactive fumed silica were provided either in dry form or in dispersions, the below amounts referring to the solid contents of the materials. The particles tested differed in their surface treatment and/or in their size (as estimated by their specific surface area). The particles tested had a specific surface area (as assessed by BET and reported by their respective manufacturers) between about 25 m^2/g and about 245 m^2/g. All fillers were selected to have a refractive index identical or similar (±10%) to the refractive index of the amino-silicone matrix. Even in powder form the fumed silica may be provided with a residual water content of up to 2.5wt.%.

In a vial, were mixed for about 5 seconds using a Vortex Genie 2 mixer (from Scientific Industries Inc., USA) the following series of formulations:

First series

0.012 g of condensation-curable amino-silicone polymer, GP-397 (having an Amine Number of 116 and a MW ~3,754 g/mol) supplied by Genesee Polymers Corp., USA.

0.048 g of amino-functional silane cross-linker, Dynasylan® SIVO 210 including a combination of three condensation-curable monomers each having MW between about 221 g/mol and about 425 g/mol, supplied by Evonik Industries AG, Germany.

0.02 g of an hydrophobic fumed silica (30wt.% of the combined weight of the afore-listed amino-silicone pre-polymers) selected from Aerosil® R 8200, Aerosil® NA 50 H, Aerosil® R

812 S, and Aerosil® NA 50 Y, supplied by Evonik Resource Efficiency GmbH, NanoBYK 3650 and NanoBYK 3652, supplied by BYK USA Inc.

Second series

0.04 g of condensation-curable amino-silicone polymer, KF-857 (having an Amine Number of 127), supplied by Shin Etsu.

0.16 g of amino-functional silane cross-linker, Dynasylan® SIVO 210 (Evonik) or of (1-(3-triethoxysilyl)propyl)-2,2-diethoxy-1-aza-2-silacyclopentane (such as commercialized by Gelest as SIT8187.2).

0.006 g of silicone oil being a slow cure amine/alkoxy end-blocked silicone, GP-145 (having an Amine Number of 11 and a MW of 18,000) by Genesee.

0.021 g, 0.031 g, 0.041 g or 0.062 g of Aerosil® R 8200 (corresponding to 10 wt.%, 15 wt.%, 20wt.% or 30wt.% of the combined weight of the above-provided amino-silicone reactants).

Third series

In a third series, a colored sample was prepared by adding 5wt.% of Carbon Black nano-powder (Colour Black FW 182, Orion Engineered Carbons, CAS No. 1333-86-4) pre-milled with BYK LPX 21879 at a 1:1 weight ratio, to a blend of the second series including 0.04 g of KF-857, 0.16 g of Dynasylan® SIVO 210, 0.006 g of GP-145 and 0.031 g of Aerosil® R 8200.

The resulting curable amino-silicone blends (colored or uncolored ASBs) were further sonicated for 15 seconds at 30% of maximal amplitude of a Q700 sonicator (QSonica LLC, USA) until they formed a clear solution.

In a separate vessel, a 0.1wt.% emulsifier dispersion was prepared by adding 0.06 g of polyoxyethylene (20) sorbitan monooleate surfactant (Tween® 80, CAS No. 9005-65-6, supplied by Sigma-Aldrich Co., USA) to 59.94 g of deionized water. The mix was manually shaken until a clear and homogeneous surfactant solution was obtained.

Unless otherwise stated, each Amino-Silicone Emulsion (ASE) was prepared by adding the total weight of each ASB clear blend into 60 g of the 0.1wt.% surfactant solution and by sonicating the mixture for 15 seconds at 50% of maximal amplitude of a Q700 sonicator, until a homogeneous emulsion was obtained. The average size (Dv50) of the resulting emulsion droplets was measured using a laser diffraction particle size analyzer (Mastersizer AWA 2003 from Malvern Instruments Ltd., United Kingdom) and was found to be sub-micronic for all tested emulsions.

Hair samples were dipped in the various ASEs prepared with each of the afore-described hydrophobic fumed silica and rinsed as previously detailed. All samples provided for the formation of amino-silicone films which coated the hair fibers at least as well as their counterpart compositions devoid of fumed silica. Among the hydrophobic fumed silica samples tested, Aerosil® R 8200, surface treated with HMDS, was found particularly suitable.

The addition of a reactive filler, such as exemplified by the above-mentioned hydrophobic fumed silica, is expected to accelerate the curing of the amino-silicone film following its application on the hair fibers. In the event such materials are used as in the condensation-curable amino-silicones of the present coating compositions, then in a kit such reactive fillers will be preferably supplied in a compartment separate from the reactive amino-silicone pre-polymers.

Example 18: Pre-treatment of coating materials

While in previous examples, the amino-silicone pre-polymers used for the preparation of the condensation-curable amino-silicone coating compositions were preferably inherently water-insoluble (enabling the formation of an emulsion), the present study demonstrated that water-soluble pre-polymers (their solubility optionally resulting from hydrolysis), can also be used. However, the resulting relatively weak coloration prompted the Inventors to prefer first rendering such relatively soluble materials less soluble or insoluble ahead of emulsification and application.

The “desolubilization” or “insolubilization” step was performed by mixing 20wt.% of a water soluble aminopropyltriethoxysilane (APTES; CAS No. 919-30-2) (Dynasylan® AMEO from Evonik), with 70wt.% of a water insoluble non-amine functionalized silane, methyltrimethoxysilane (MTMS; CAS No. 1185-55-3, purchased from Sigma Aldrich) and 10wt.% distilled water, the constituents being added to a vial in the listed order. After a brief stirring by Vortex, the mixture was left to react in the open vial for two hours at ambient temperature. During such time, MTMS is expected to react with APTES forming condensation bonds therewith, so as to render APTES less water soluble. Following the reaction, the blend including the at least “desolubilized” material is mixed with hexamethyldisoxane (M2) in a w/w ratio of 2:1, and the two are stirred for about 5 sec at ambient temperature. 0.2 g of the resulting product (forming an ASB) was added to 60 g of distilled water and manually shaken for about 10 seconds. The resulting ASE was used to coat hair fibers as previously described. Briefly, hair tufts were dipped in this ASE, washed with tap water to remove excess, then dried using a hair dryer. The method provided coating of the fibers.

__Example 19: Preparation of amino-silicone emulsions lacking reactive amino-silicone polymers__

While in previous examples, the amino-silicone emulsions included an amino-silicone condensation-curable polymer, optionally in combination with condensation-curable amino-silicone monomers or oligomers, in the present example the amino-silicone film is achieved in absence of amino-silicone reactive polymers.

Exemplary formulations are provided in Table 16 where the amounts of the compounds are provided in grams. As the purpose of the present study was to establish suitability of various types of condensation-curable amino-silicone pre-polymers for the preparation of compositions able to coat hair fibers, the following compositions were devoid of pigment particles. Similar compositions including pigments were previously detailed.

In the table, M2 stands for hexamethyldisiloxane, a silicone oil having a MW of 162.38 and a RI of ~ 1.377 provided under CAS No. 107-46-0 by Gelest, and DMDES stands for diethoxydimethyl silane (a slow curing condensation-curable monomer having two silanol forming groups per molecule, a MW of 148.28 and an RI of ~ 1.381) provided under CAS No. 78-62-6 by Sigma-Aldrich.

Compound	**ASE (NP) 1**	**ASE (NP) 2**	**ASE (NP) 3**	**ASE (NP) 4**	**ASE (NP) 5**	**ASE (NP) 6**
Dynasylan® SIVO 210	2.0	1.8	1.6	1.6		
Dynasylan® 1146					2.0	
Dynasylan® AMEO						1.0
Gelest SIO6629.1		0.2				
Gelest DMS-S12				0.4		
DMDES			0.4			
M2	8.0	8.0	8.0	8.0	8.0	
Deionized Water	10.0	10.0	10.0	10.0	10.0	10.0*

* The deionized water included 50wt.% water acidified to pH 4 with acetic acid.

Table 16

In a vial, were mixed for about 5 seconds using a Vortex Genie 2 mixer (from Scientific Industries Inc., USA) all the materials listed for each ASE in the amounts reported in the table. The cross-linkable amino-silicone mixtures were then emulsified by sonication for 15 seconds at 50% of maximal amplitude of a Q700 sonicator, until a homogeneous emulsion was obtained in absence of added dedicated emulsifier. The average size (Dv50) of the resulting emulsion droplets was measured using a laser diffraction particle size analyzer (Mastersizer AWA 2003 from Malvern Instruments Ltd., United Kingdom) and was found to be sub-micronic.

As Dynasylan® SIVO 210 (having an estimated Amine Number of 370) contains, according to its supplier, a combination of reactive monomers individually commercially available as Dynasylan® AMEO from Evonik, SIB1824.5 and SIT8187.2 from Gelest, formulations similar to ASE(NP)1 wherein the 2 g of Dynasylan® SIVO 210 was replaced by 2 g of each of its constituent molecules were also prepared.

Dynasylan® 1146, used for the preparation of ASE(NP)5, is a condensation-curable oligomer having an Amine Number of 455 and more than three silanol-forming groups per molecule, purchased from Evonik. SIO6629.1, used for the preparation of ASE(NP)2, is a non-amino hydrophobic condensation-curable monomer having two silanol forming groups per molecule, a MW of ~359 and a RI of ~ 1.443, supplied by Gelest under CAS No. 70851-50-2. DMS-S12, used for the preparation of ASE(NP)4, is a non-amino hydrophobic condensation- curable oligomer having a MW in the range of ~400-700 and a RI of ~ 1.401, supplied by Gelest under CAS No. 70131-67-8.

Hair samples were dipped in the ASEs prepared with each of the afore-described condensation-curable pre-polymers, excluding amino-silicone reactive polymers, and rinsed as previously detailed. All samples provided for the formation of amino-silicone films which coated the hair fibers at least as well as the formulations of Example 1 additionally comprising an amino-silicone reactive polymer. However the resulting films generally displayed a more brittle behavior. The ASE(NP)2 formulation displayed the best behavior, providing for an acceptable feel to the touch. From the comparison of the results obtained with ASE(NP)1 formulation including Dynasylan® SIVO 210 and the comparative formulations each including one of the three molecules of the blend, it appeared that all constituents similarly provided a good adhesion to the hair fibers.

In the description and claims of the present disclosure, each of the verbs, “comprise” “include” and “have”, and conjugates thereof, are used to indicate that the object or objects of the verb are not necessarily a complete listing of members, components, elements, steps or parts of the subject or subjects of the verb.

As used herein, the singular form “a”, “an” and “the" include plural references and mean “at least one” or “one or more” unless the context clearly dictates otherwise.

Unless otherwise stated, the use of the expression “and/or” between the last two members of a list of options for selection indicates that a selection of one or more of the listed options is appropriate and may be made.

In the discussion, unless otherwise stated, adjectives such as “substantially” and “about” that modify a condition or relationship characteristic of a feature or features of an embodiment of the present technology, are to be understood to mean that the condition or characteristic is defined to within tolerances that are acceptable for operation of the embodiment for an application for which it is intended, or within variations expected from the measurement being performed and/or from the measuring instrument being used. Furthermore, unless otherwise stated, the terms used in this disclosure should be construed as having tolerances which may depart from the precise meaning of the relevant term but would enable the invention or the relevant portion thereof to operate and function as described, and as understood by a person skilled in the art.

When the term “about” precedes a numerical value, it is intended to indicate +/-10%, or +/-5%, or +/-1%, and in all instances is meant to include the precise value.

While this disclosure has been described in terms of certain embodiments and generally associated methods, alterations and permutations of the embodiments and methods will be apparent to those skilled in the art. The present disclosure is to be understood as not limited by the specific embodiments described herein.

CLAIMS

1. A method of coloring an external surface of mammalian hair, attached to a body of a mammalian subject, the method comprising:

(a) applying, on the external surface of individual hairs of the mammalian hair, a formulation comprising:

(i) water;

(ii) a reactive condensation-curable film-forming amino-silicone pre-polymer that, subsequent to condensation curing, forms an elastomer, wherein the reactive condensation-curable film-forming amino-silicone pre-polymer is an organosilicon pre-polymer which contains at least two hydrolysable reactive groups and at least one carbon bonded amine group;

(iii) a plurality of sub-micronic organic or inorganic pigment particles;

(iv) a dispersant for dispersing the sub-micronic pigment particles in the formulation; and optionally,

(v) a cross-linking agent adapted to cure said pre-polymer;

(b) effecting partial condensation curing of said pre-polymer at a temperature of up to 45°C, to form a pigmented, at least partially cured film on the external surface of the individual hairs; and

(c) after enabling said partial condensation curing to ensue, washing the hair with a rinsing liquid to leave said pigmented, at least partially cured film on the external surface of the individual hairs.

2. A method according to claim 1, the formulation further comprising a condensation-cure accelerator or catalyst adapted to cure said pre-polymer.

3. A method according to claim1 or claim 2, wherein the pigment particles are dispersed in the condensation-curable film-forming amino-silicone pre-polymer and/or in the water.

4. A method according to any one of claim1 to claim 3, the formulation further comprising a solid reactive inorganic filler, the reactive filler being adapted to facilitate curing of said condensation-curable film-forming amino-silicone pre-polymer, said reactive filler optionally being a hydrophobic fumed silica.

5. A method according to any one of claim 1 to claim 4, further comprising, subsequent to step (b), further curing said at least partially cured film for a period of at least 4 hours, at least 6 hours, at least 12 hours, or at least 24 hours at a temperature of at least 15°C and of at most 38°C, at most 36°C, at most 34°C, or at most 32°C, so as to obtain full curing of the film, said period optionally being at most 3 weeks, at most 2 weeks, at most 10 days, at most 7 days, at most 5 days, at most 3 days or at most 2 days.

6. A method according to claim 5, wherein said further curing for said period is effected solely by or substantially solely by humidity or ambient humidity.

7. A method according to claim 5 or claim 6, wherein said further curing is effected in the absence of any added non-cationic surfactant.

8. A method according to any one of claim 5 to claim 7, wherein shampooing of the hair during the period of the further curing is effected with a cationic shampoo.

9. A method according to any one of the preceding claims, further comprising combining at least first and second sub-formuations to produce said formulation, said first sub-formulation including said water, said pre-polymer, said plurality of sub-micronic pigment particles and said dispersant; and said second sub-formulation including said cross- linking agent, the combination of the at least two sub-formulations forming an oil-in-water emulsion.

10. A method according to claim 9, further comprising combining a third sub-formulation comprising a hydrophobic fumed silica in the oil phase of said oil-in-water emulsion.

11. A method according to claim 9 or claim 10, further comprising mixing together said at least first and second sub-formulations at most 4 hours, at most 2 hours, at most 60 minutes, at most 45 minutes, at most 30 minutes, at most 20 minutes, or at most 10 minutes prior to said applying.

12. A method according to claim 11, wherein the at least first and second sub-formulations are emulsified following said mixing.

13. A method according to any one of the preceding claims, wherein said pre-polymer is dispersed in the form of an oil-in-water emulsion.

14. A method according to any one of the preceding claims, wherein said formulation or sub-formulation, when appended to any one of claim 9 to claim 13, further comprises a non-ionic or an anionic emulsifier.

15. A method according to any one of the preceding claims, wherein said formulation is charged and has a positive surface zeta potential of at least 10 mV, at least 20 mV, at least 40 mV, or at least 60 mV; and of no more than 100 mV, or no more than 80 mV, said surface zeta potential being optionally measured at a pH of10.

16. A method according to any one of claim 9 to claim 15, wherein said first sub-formulation containing said pre-polymer is charged and has a positive surface zeta potential of at least 10 mV, at least 20 mV, at least 40 mV, or at least 60 mV; and at most 100 mV, or at most 80 mV, said surface zeta potential being optionally measured at a pH of10.

17. A method according to any one of claim 9 to claim 16, wherein said second sub-formulation including said cross-linking agent is charged and has a negative surface zeta potential whose negativity is at least -10 mV, at least -20 mV, at least -40 mV, or at least -60 mV; and whose negativity is at most -100 mV, or at most -80 mV, said surface zeta potential being optionally measured at a pH of10.

18. A method according to any one of the preceding claims, wherein the sub-micronic pigment particles have a DV90 of at most 250 nm, at most 150 nm, or at most 100 nm, and optionally, a DV50 of at most 150 nm, at most 100 nm, or at most 75 nm.

19. A method according to any one of the preceding claims, wherein said reactive condensation-curable amino-silicone pre-polymer satisfies at least one of the following structural properties:

a) said pre-polymer includes terminal amino-moieties;

b) said pre-polymer has a viscosity in the range of 50 – 10,000 mPa•s as measured at 25°C;

c) said pre-polymer has an Amine Number in the range of 3-200;

d) said pre-polymer has a ratio of Amine Number (AN) to viscosity (Visc.) in mPa•s, which when multiplied by 1000, is of at least 40, at least 100, at least 200, or at least 500, which can be mathematically expressed as $1000*(AN/Visc.) \geq 40$, and so on;

e) said pre-polymer is devoid of cyclic moieties;

f) said pre-polymer is hydrophobic;

g) said pre-polymer has a solubility in water at 25°C of less than 5% by weight, less than 2% by weight, or less than 1% by weight;

h) said pre-polymer is capable of wetting said hair;

i) said pre-polymer includes reactive groups selected from the group consisting of alkoxy-silane reactive groups, silanol reactive groups and combinations thereof;

j) said pre-polymer is a linear or a branched polymer, the polymer having a weight average molecular weight between 2,000 and 100,000;

k) said pre-polymer is a linear or a branched oligomer, the oligomer having a weight average molecular weight between 200 and 2,000; and

l) said pre-polymer is a monomer, having a molecular weight between 100 and 600.

20. A method according to any one of the preceding claims, wherein said formulation or sub-formulation, when appended to any one of claim 9 to claim 19, further comprises a cosmetically acceptable oil, miscible with said pre-polymer, and/or miscible with said cross-linking agent, and/or miscible with said condensation-cure accelerator or catalyst, the cosmetically acceptable oil including, but not limited to, a silicone oil.

21. A method according to any one of the preceding claims, wherein said formulation or sub-formulation, when appended to any one of claim 9 to claim 20, has a pH of at least 4.0, at least 5.5, at least 7, at least 8.5, at least 10.0; and of at most 11.0.

22. A method according to any one of the preceding claims, wherein the duration of time enabling the partial curing is between 5 seconds and 30 minutes, or between 1 minute and 15 minutes.

23. A method according to any one of the preceding claims, wherein said rinsing liquid is (i) water, or (ii) a cationic rinsing liquid, or (iii) a rinsing liquid devoid of non- cationic surfactants, degreasing agents and/or swelling agents, the degreasing and swelling agent respectively able to degrease and swell the at least partially cured pigmented film.

24. A method according to claim 8 or claim 23, wherein the cationic shampoo or the cationic rinsing liquid, respectively, includes a cosmetically-acceptable primary, secondary, tertiary, or quaternary ammonium compound or polymer.

25. A method according to claim 24, wherein the cationic shampoo or the cationic rinsing liquid includes a polyquaternium polycationic polymer having a quaternary ammonium function.

26. A method according to any one of the preceding claims, wherein the plurality of sub-micronic organic or inorganic pigment particles provide a first color, the method further comprising subsequent to step (c) leaving on the individual hairs an at least partially cured film pigmented with the first color, repeating steps (a) to (c) the sub-micronic organic or inorganic pigment particles of repeated step (b) providing a second color, said second color being same or different from said first color.

27. A method according to any one of the preceding claims, further comprising, prior to step (a), or prior to a first step (a) if repeated according to claim 26, applying a degreasing agent to effect degreasing of said external surface of said hair without effecting degreasing of an inner surface of said hair and/or without penetration of said degreasing agent within said hair and/or without bleaching said hair.

28. A method according to any one of the preceding claims, further comprising, prior to step (a), or prior to a first step (a) if repeated according to any one of claim 26 or claim 27, and optionally following a degreasing step, if performed, applying, on the external surface of the individual hairs, a film-forming hair masking binder formulation so as to produce a polymeric film on the hair.

29. A method according to claim 28, wherein the film-forming hair masking binder formulation further includes (i) a plurality of sub-micronic organic or inorganic pigment particles, and/or (ii) pigment particles, including pigment flakes, so as to produce a tinted binder polymeric film on the external surface of the individual hairs or on top of a previously laid-down film on the hair.

30. A method according to claim 28 or claim 29, wherein the film-forming hair masking binder formulation comprises a reactive condensation-curable amino-silicone elastomer, a cross-linking agent, an emulsifier and an optional catalyst emulsified in an aqueous carrier.

31. A method according to any one of claim 28 to claim 30, further comprising, after A) applying the film-forming hair masking binder formulation:

B) allowing the film-forming binder to preliminarily cure;

C) washing the hair with a rinsing liquid to leave a preliminarily cured polymeric film on the external surface of the individual hairs, the film being optionally tinted;

D) applying to the preliminarily cured film a flake dispersion including of a plurality of pigment flakes, a dispersant and an aqueous carrier;

E) washing the fibers with a rinsing liquid to leave a layer of metallic-looking pigment flakes on and adhering to the preliminarily cured film.

32. A method according to any one of claim 29 to claim 31, wherein the pigment flakes are metallic pigment flakes containing, coated with, consisting essentially of, or made of metals, alloys and oxides thereof, said flakes being selected from the group comprising aluminum flakes, brass flakes, bronze flakes, copper flakes, gold flakes, mica coated flakes, silica coated flakes and silver flakes.

33. A method according to any one of claim 29 to claim 32, wherein the pigment flakes are further coated with a coupling agent capable of covalently binding the reactive amino-silicone elastomer of the film-forming hair masking binder formulation.

34. A method according to claim 33, wherein the coupling agent is a cosmetically acceptable coupling agent selected from the group including acrylate coupling agents, thiol coupling agents, anhydride coupling agents, epoxy coupling agents, and silanol coupling agents.

35. The method according to any one of claim 29 to claim 34, wherein the pigment flakes are charged at a polarity opposite a polarity of the preliminarily cured hair masking film.

36. The method according to any one of the preceding claims, further comprising, subsequent to at least partially condensation curing of pigmented film, applying a clear protective coating, the protective coating including an amino-silicone elastomer, a cross-linking agent, an emulsifier and an optional catalyst emulsified in an aqueous carrier.

37. A method according to any one of the preceding claims, when appended to any one of claim 4 to claim 8, wherein the fully cured film is wash resistant, wash resistance meaning that the hair coated with the fully cured film can be washed at least 20 times with water and retain an Optical Density (OD) value of at least 80% of an original OD value as determined following full curing.

38. A method according to any one of the preceding claims, wherein the at least partially cured film is wash resistant, wash resistance meaning that the hair coated with the at least partially cured film can be washed at least 10 times with a cationic shampoo and retain an Optical Density (OD) value of at least 80% of an original OD value as determined following said at least partial curing.

39. A method according to any one of the preceding claims, the method further comprising, subsequent to said at least partial curing of one or more films as applied in one or more steps, removing said films from the individual hairs by applying a silicone decuring agent in an amount and for a time period sufficient to at least partially decure the films, the application of the decuring agent for a sufficient time being followed by rinsing away the decured silicone.

40. A method according to claim 38, wherein the silicone decuring agent is selected from the group including (a) fluoride salts (including but not limited to tetra butyl ammonium fluoride (TBAF)), (b) organic sulfonic acids (including but not limited to dodecyl benzene sulfonic acid (DBSA)) and (c) an organic or inorganic base and salts thereof (including but not limited to tetra butyl ammonium hydroxide (TBAH), tetra butyl ammonium bromide (TBAB), tetra butyl ammonium chloride (TBAC), potassium hydroxide (KOH) and potassium tert-butoxide (K(CH3)3CO)).

41. A method according to claim 39 or claim 40, wherein said silicone decuring agent is applied in a solvent optionally comprising one or more dispersants, the solvent being an aqueous solvent or an organic solvent, water, if present, not exceeding 90wt.% of the solvent.

42. A kit for coloring an external surface of mammalian hair, the kit comprising:

(a) a first compartment containing a pigmented formulation including:

  (i) a reactive condensation-curable film-forming amino-silicone pre-polymer;

  (ii) a dispersed plurality of sub-micronic organic or inorganic pigment particles;

  (iii) a dispersant; and optionally

  (iv) a silicone oil miscible with said film-forming amino-silicone pre-polymer;

(b) a second compartment containing water and an emulsifier to form an emulsion when mixed with the content of the first compartment;

(c) optionally, a third compartment, said third compartment containing a cross-linking agent and optionally a silicone oil miscible with said cross-linking agent;

(d) optionally, a compartment containing water and an emulsifier to form an emulsion when mixed with the content of the third compartment, wherein the compartment of (d) is a fourth compartment or said second compartment.

43. A kit according to claim 42, further comprising a curing auxiliary compartment, said curing auxiliary compartment containing a curing accelerator or catalyst in water and optionally a silicone oil miscible with said curing accelerator or catalyst, and an additional compartment containing water and an emulsifier to form an emulsion when mixed with the content of said curing auxiliary compartment, the additional compartment optionally being said second compartment or said fourth compartment.

44. A kit according to claim 42 or claim 43, further comprising a 3D network forming compartment, said compartment containing a hydrophobic fumed silica dispersible in an oil phase of the emulsion.

45. A kit according to any one of claim 42 to claim 44, further comprising a rinsing compartment, said rinsing compartment containing a rinsing formulation or a rinsing agent dispersible or soluble in water.